TREATMENT OF PRODUCED WATER USING GRAPHENE

by

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Dedication

I dedicate this research study to Almighty God, my creator and my source of faith and strength.

I also dedicate this work to my caring Mom and Dad, also to my sister Alice, thank you for your unconditional love and encouragement.

This work is also dedicated to my supervisors Dr. Taleb Ibrahim, Dr. Mustafa Khamis Dr. Yehya El Sayed and Mr. Ziad Sara.

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Abstract

Adsorption is a well-known method for high efficiency in treatment of water and wastewater at low costs. It is a promising method that can compete strongly with conventional purification methods. Carbon-based materials including graphene, graphene oxide, and other nanomaterials have been investigated widely because of their outstanding properties such as chemical permanence, low density and large scale production. Graphene has been extensively used in the treatment of wastewater. In this study, graphene was used as an adsorbent for the removal of emulsified oil from produced water. Experimental work was performed to determine the most suitable method for quantification of emulsified oil in produced water and results showed that the UV-Visible Spectroscopy is the optimum analytical tool in comparison with the Total Organic Carbon (TOC) and Fluorescence Spectrophotometer. In addition, the results showed that the Fluorescence Spectrophotometer is not an appropriate tool to quantify the emulsified oil. Several batch tests were performed on produced water to find the optimum separation conditions by graphene. It was found that these optimum conditions are: contact time = 60 minutes, initial pH = 10.00, graphene dosage =3.00 (g/L), salinity = 1500 ppm and temperature 25. 0℃ with maximum removal efficiency of 80.0%. Fitting of experimental data to different isotherms revealed that the adsorption of emulsified oil using graphene follows Freundlich isotherm with $k_f = 5.29\ \left(\mathrm{mg}^{(1-\frac{1}{\mathrm{n}})}\mathrm{L}^{(\frac{1}{\mathrm{n}})}/g\right)$ and $n = 1.66$, whereas the adsorption kinetic of emulsified oil is described by the pseudo-second–order kinetic model with a rate constant of $0.020\ (g/mg.min)$. Regeneration of graphene was achieved by using n-hexane solvent, and results indicated that the removal efficiency of emulsified oil using graphene decreased from 80.0 % to 75.0 % and from 75.0 % to 71.5 %, over two adsorption-regeneration cycles, respectively. Freundlich isotherm gave the maximum adsorption capacity of graphene of 100 (mg/g).

Search terms: *Produced Water, Adsorption, Graphene, UV-Visible Spectroscopy, Adsorption Isotherms, Kinetic Models, Regeneration.*

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Nomenclature

$BTEX$	Benzene, Toluene, Ethyl-benzene and Xylene
BOD	Biochemical Oxygen Demand
C_a	concentration of emulsified oil on graphene at equilibrium (ppm)
C_e	Concentration at equilibrium (ppm)
C_f	Final Concentration of emulsified oil (ppm)
C_o	Initial Concentration of emulsified oil (ppm)
COD	Chemical Oxygen Demand
EHS	Environmental Health and Safety regulations
$GC-FID$	Gas Chromatography-Flame Ionisation Detection
$GCMS$	Gas Chromatography-Mass Spectroscopy
IR	Infrared
K'	Apparent equilibrium constant
LOD	Limit of Detection
m_i	Initial mass of emulsified oil (g)
m_g	Mass of graphene (g)
m_f	Final Mass of emulsified oil (g)
$NORM$	Naturally Occurring Radioactive Material
q_e	Adsorption capacity at equilibrium (mg/g)
q_t	Adsorption capacity at any time (mg/g)
q_m	Maximum adsorption capacity (mg/g)
R^2	Regression coefficient
RO	Reverse Osmosis
SBR	Sequencing Batch Reactors
SW	Surfactant/deionized Water solution
TDS	Total Dissolved Salts
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons

Chapter 1: Introduction

1.1 Background and Research Objectives

Even with its numerous sources and supplies, water will become scarce with time due to poor management of water infrastructure, increase in human population, change of climate, and lack of economic and physical aids to protect this precious resource. As well, the paucity of fresh water worldwide is coupled with lack of accessibility to this water; 1.2 billion people suffer from this problem [1]. These dire conditions must be minimized, and to achieve this aim, some methodologies should be implemented to fulfill the demand for safe water and develop a less polluted environment. Surface, ground, sea and rain water are all considered sources of water, which can be utilized in many different areas including domestic, agricultural, and industrial uses. However, waste water generated by these uses is sometimes returned back to the environment after certain treatments. Nevertheless, not only these uses contribute to waste water generation over the world; there is another component considered also a waste stream, namely the produced water. It is one of the main waste streams produced in the oil and gas industries, and hence, water pollution due to the discharge of these wastes back to oceans and lakes without treatment or without meeting the minimum treatment required will continue to increase and cause an environmental concern [2]. Oil contamination can be hazardous to humankind and marine life as they are subjected to polluted water and soil. Adverse effects have been reported on people's contamination with oil and organic compounds. It is therefore necessary to treat discharged streams from the oil and gas companies in order to protect the local environment as well as living creatures [3].

Adsorption is a widely used method to remove oil and heavy metals from produced water. Activated carbon and natural adsorbents such as eggshells, banana peels, and bentonite were employed by other investigators. In this work, graphene of industrial grade will be used to remove emulsified oil from produced water. Batch adsorption experiments will be performed to determine the optimum parameters in terms of contact time, initial pH, temperature, and adsorbent dosage. In addition, the best adsorption isotherm model that describes the removal of emulsified oil from the produced water will be selected. Furthermore, a kinetic model will be chosen that

best fits the experimental data. In addition, regeneration of graphene will be examined.

The focal objective of this proposed work is to investigate the effectiveness of graphene in the removal of emulsified oil from produced water and to determine the optimum conditions for the treatment process.

1.2 Literature Review

1.2.1 Produced water. Produced water is the water generated when oil and gas are produced either from onshore (land drilling) or offshore wells (deep water/shallow water drilling). Early in USA, communities were located near salt springs which provided people with salt, however, these springs were polluted with petroleum. Since there was presence of unwanted amounts of oil and gas within the saline water, hard work was required by digging wells. In 1855, it was learnt that distillation of petroleum produces light oil, which was similar to coal oil and with a better value that whale oil. It was until 1938 that the existence of water in oil reservoirs was acknowledged. Research was heavily conducted to understand the origin of water in oil and gas reservoirs till it was known that this water can be identified with consideration of the reservoir and its chemical properties. By then, operators thought that the costs of handling water are expensive for an older field to be commercial, so they used to sell the property to other operators. The new operator explore ways to minimize the impact of this water in order to generate smaller oil stream productivity, then they become dispirited and sell it to another operator and this process goes on. However, with better skills and engineering, it was potential to produce oil at high water reductions. A glossary was designated for oil and gas terms to ease the handling of different existing water in reservoirs [4].

The formation water is the freshwater/seawater that has been confined for many years with oil and natural gas in a geologic reservoir, enclosed in a porous sedimentary rock format ion between layers of impervious rock within the earth's shell. This formation water will emerge when a hydrocarbon reservoir is accessed by a well, accompanied by oil, natural gas, and/or gas liquids. In addition, freshwater, brine, and chemicals are infused into this reservoir to improve the rate of the recovery. The combination of formation and injected water is called produced water, which may contribute 80 % of the wastes and residuals generated from the natural

gas production operation [5]. Moreover, another vital water term to be highlighted is the flow back water. It is the water that is a major component of the fluids injected into the oil well under the process of the fracturing operation using high pressure. However, some of this water will appear again on the surface after some weeks from accomplishing the fracturing job. This returned water will contain higher levels of chemicals, as well as Total Dissolved Solids (TDS) [6].

Produced water can be reused for hydrological purposes, agricultural, industrial, or even domestic uses. Also, it can be re-injected into the reservoir to enhance oil recovery. Another option is to discharge the produced water; however, any method chosen to manage the produced water will require a certain level of treatment before usage, and as result, it is important to find an optimum management method to treat, re-use, or dispose of the produced water [6]. Figure 1 demonstrates a typical reservoir where the oil and gas are usually extracted, resulting in a decreased pressure in the reservoir, and hence water injected in the water layer to enhance the oil recovery and sustain the hydraulic pressure [7].

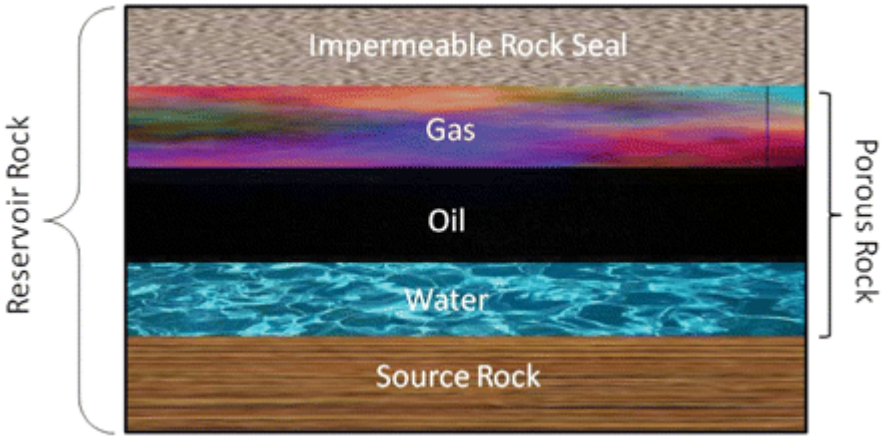

Figure 1: Typical oil reservoir [7]

1.2.2 Characteristics of produced water. Organic and inorganic materials are the main constituents of produced water, where its chemical and physical characteristics are determined by certain factors including geographic location of the oil reservoir, existence of the reservoirs, nature of hydrocarbons produced, operating conditions and the chemicals added. However, although the composition of the produced water can fluctuate according to different sources, most are analogous to the composition of oil/gas production.

The core compounds found in produced water are:

a) Dissolved and dispersed oil compounds.
b) Dissolved formation minerals.
c) Production chemical compounds.
d) Dissolved gases.
e) Production solids such as waxes, bacteria and scale products and corrosion products [2].

Regarding dissolved and dispersed oil compounds; they are mainly composed of hydrocarbons such as benzene, toluene, xylenes (BTEX), and polyaromatic hydrocarbons (PAH). Most of them are found dispersed in produced water due to immiscibility. However, the amount they are present in before the treatment depends on various factors including pH, salinity, TDS, the oil/water ratio, temperature, and oil composition. The soluble organic compounds such as formic and propionic acid exist in the produced water, and their existence is related to the type of oil, pH, pressure, and the temperature at which it presents, as the latter can change the relative carbon range within the produced water. In addition, aliphatic hydrocarbons and the most toxic, the aromatic hydrocarbons, are considered to be challenging to separate from produced water. Dispersed oil components in the produced water include the PAHs and some alkyl phenols which are less soluble in water, and factors such as the density of oil and the interfacial tension between water and oil can affect their concentrations. The oil presented in water is made of petroleum compounds which can be either hydrocarbons or heterocyclic compounds. The first corresponds to Total Petroleum Hydrocarbons (TPHs). These molecules have only carbon and hydrogen, whereas the latter contain heteroatoms including oxygen, sulfur, and nitrogen in addition to carbon and hydrogen. Hydrocarbons can be saturated, unsaturated and aromatics. The first can be divided into aliphatic and alicyclic. Alkanes and isoalkanes are the common names for the saturated compounds, where in the petroleum industry paraffins and isoparaffins are their industrial names. Acyclic compounds are those that have one or more ring such as cycloalkanes (or called cycle paraffins by the petroleum industry). The unsaturated hydrocarbons generated during the cracking processes, can be divided to alkenes and alkynes. Aromatics have a benzene ring structure [8]. These divisions are shown in Figure 2.

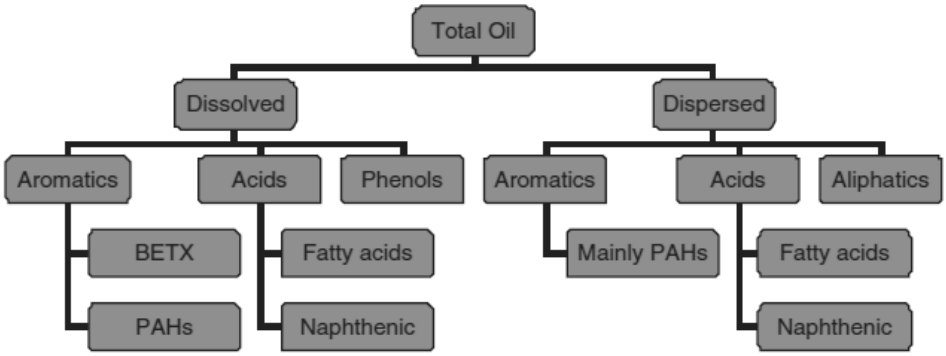

Figure 2: Total oil components in produced water [4]

The dissolved formation minerals consist mainly of heavy metals, cations, and anions as well as radioactive materials. Heavy metals include mercury, lead, silver, zinc, cadmium, copper and nickel. Their quantity in the produced water depends directly on the age of the oil well, besides the formation geology. The cations include Na^{+}, K^{+}, Mg^{2+}, Ca^{+} and Ba^{2+}, whereas the anions include SO_4^{2-}, HCO_3^{-}, Cl^{-} and CO_3^{2-}. Scale possibility, buffering capacity and salinity are the major issues altered due to the occurrence of these cations and anions in produced water. Produced water also contains radioactive materials such as ^{226}Radium and ^{228}Radium. These radioactive materials are Radium isotopes which are most abundant in the produced water, found along with precipitate of barium sulphate, that contribute to scale formation.

In addition, some chemicals are added during the production of oil and gas, which contribute to the composition of the production chemical compounds in the produced water. Such chemicals are emulsion breakers, corrosion inhibitors, water treatment chemicals, and biocides. Other polar and charged molecules present may include surfactants such as linear alkyl benzene sulfonate, 2-alkyl-1ethylamine-2-imizadolines, and alkyldimethyl-ammonium-ethyl ether. Many cationic and anionic surfactants such as alkyldimethylbenzylammonium and alkylbenzenesulfonate have been detected in produced water from the North Sea oilfields. However, the concentrations of such components are very low, around 0.1 ppm [2].

Other production compounds found in untreated produced water are the production solids such as waxes, bacteria, asphaltenes and corrosion products. The presence of anaerobic bacteria is usually detected in the produced water and is responsible for causing clogging and corrosion of equipment and pipelines. Carbon dioxide, oxygen, and hydrogen sulfide can be also found in produced water as

dissolved gases [2]. The chemical components along with their method of treatment, if available, are discussed in Section 2.2. Table 1 illustrates a summary of the major physical and chemical characteristics of produced water.

Table 1: Summary of the physical and chemical characteristics of produced water generated from oil-fields [2]

Parameter	Values	Metals	Values (mg/L)
Density (kg/m^3)	1014-1140	**Calcium**	13-25800
Surface Tension (dynes/cm)	43-78	**Sodium**	132-97000
TOC (mg/L)	0-1500	**Potassium**	24-4300
COD (mg/L)	1220	**Magnesium**	8-6000
TSS (mg/L)	1.2-1000	**Iron**	<0.1 – 100
pH	4.3-10	**Aluminum**	310-410
Total oil (Infrared (IR) detection, mg/L)	2-565	**Boron**	5-95
Volatile (BTX; mg/L)	0.39-35	**Barium**	1.3-650
Base/neutrals (mg/L)	<140	**Cadmium**	<0.005-0.2
(Total non-volatile oil and grease by GLC/MS base (ug/L))	275	**Chromium**	0.02-1.1
Chloride (mg/L)	80-200,000	**Copper**	<0.002-1.5
Bicrabonate (mg/L)	77-3990	**Lithium**	3-50
Sulfate (mg/L)	<2-1650	**Manganese**	<0.004-175
Ammoniacal nitrogen (mg/L)	10-300	**Lead**	0.002-8.8
Sulfite (mg/L)	10	**Strontium**	0.02-1000
Total polar compounds (organic acids and phenols) (mg/L) [8]	9.7-600	**Titanium**	<0.01-0.7
VFA's (volatile fatty acids, example: formic and acetic acids) (mg/L) [9]	2-4900	**Zinc**	0.01-35
		Arsenic	<0.005-0.3
		Mercury	<0.001-0.002
		Silver	<0.001-0.15
		Beryllium	<0.001-0.004

1.2.3 Technologies employed to treat produced water.

1.2.3.1 Dispersed oil and grease. This oil includes dispersed oil, free oil, and emulsified oil. Due to strict regulations for oil discharge in the produced water, the latter must be treated accordingly. Depending on the oil composition in the produced water before treatment and the target use of the treated water, the treatment choice is selected. The treatment technologies often include American Petroleum institute (API) gravity separator, gas flotation, induced gas flotation, hydrocyclones, centrifuges and macroporous polymer extraction [10]. The level required for removal is based on the imposed regulations [11]. Certain methods are employed to remove the dispersed oil and grease. These methods are described below:

1.2.3.1.1 Gravity separation. Equipment that separates the dispersed oil from produced water that are based on gravity include:

1. Skim Tanks
2. API separators
3. Plate coalescers
4. Skim piles

These pieces of equipment are usually cost-effective, but may require large storage space due to their high residence time. They can be used offshore or onshore for treatment [11]. A brief description of each is given below:

- Skim tanks: These tanks have a large residence time which is sufficient for gravity separation to happen. They also can be pressure vessels or atmospheric tanks [11].
- API separators: An API separator is an oil skimmer that could be horizontal and have a rectangular cross-section. They are used rarely offshore due to their large size [11]. American Petroleum Institute (API) is used for oil classification, where it represents the ratio of density of oil to the density of a reference substance (water). It is always calculated at 60 degrees Fahrenheit. The equation used to calculate API is shown below:

$$API = \frac{141.5}{specific\ gravity} - 131.5 \quad (1)$$

The classification of oil based on API is as follows: API > 31.1 is light oil, API between 22.3 and 31.1 is medium oil, API < 22.3 is heavy oil and API < 10.0 is very heavy [12].

- Plate coalescers: These could be in three different configurations:
    i. Parallel plate interceptors (PPI).
    ii. Corrugated plate interceptors (CPI).
    iii. Crossflow separators.

The basic principles of these plates are that they allow the oil droplets to rise upwards to the plate surface and form coalescers [11].

- Skim pile: This device is usually used offshore at which the flow through baffle plates results in inactive areas. This helps to minimize the distance for which an oil droplet will need to rise in order to be strained from the main flow [11].

1.2.3.1.2 *Gas flotation units.* Gas flotation units do not depend on gravity forces like the gravity separators, and, as well, are not a function of oil droplet size. These units use small diameter gas bubbles which are inserted into the oily water stream. These bubbles will get attached to the dispersed oil and hence will float on the water surface [11].

1.2.3.1.3 De-oiling hydrocyclones. Hydrocyclones are based on the fluid-pressure energy to generate rotational fluid motion. This rotational motion will lead to a relative movement of materials suspended in the fluid, and hence the separation of materials will occur. The centrifugal force will push the heavier material (water) outward, whereas the lighter material (oil) will be moved to the middle core of the cones. Then the water is withdrawn from the pointed end (Figure 3) [10,13]**.**

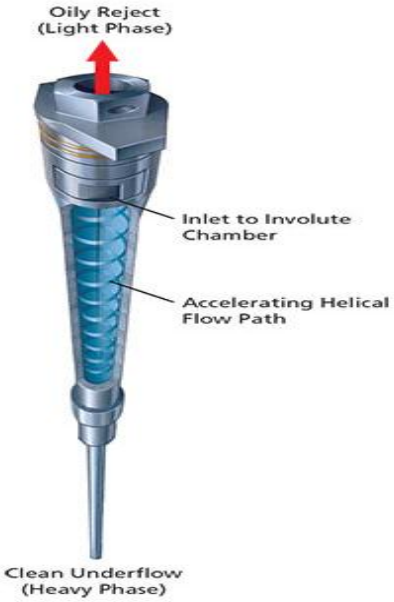

Figure 3: Schematic diagram of de-oiling hydrocyclone [13]

To enhance the oil removal efficiency, multiple cones are used in a hydrocyclone as shown in Figure 4 [10,11].

Figure 4: A vessel containing multiple hydrocyclones for de-oiling of produced water with maximum capacity – 120,000 barrels/day [10]

1.2.3.1.4 Centrifuge. Centrifuges have been known for their applications in removing very small oil droplets, or when the oil droplets do not coalesce [11].

1.2.3.1.5 Walnut shell filters. There is a particular type of media that uses walnut shells to remove dispersed hydrocarbons from produced water [11]. These utilize media-type filters to remove dispersed oil as well as small suspended solids from water.

1.2.3.2 Dissolved oil. Soluble organic compounds are present in produced water with high concentration. They can be removed by various methods, mainly adsorption. These methods are described below. Nonetheless, adsorption is widely used in packed columns filled with adsorbent, where the only limit would be the retention time required for high percent removal [10].

1.2.3.3 Physical treatments. Adsorption: An adsorption column is usually used, where it is packed with a certain adsorbent. Soluble hydrocarbons will bind to the surface of the adsorbent and eventually get engaged within the porous structure. Common adsorbents used include activated carbon, nutshell media, zeolites, modified organoclay, etc. where the surface area is a major factor in determining the adsorption performance of these adsorbents. The major concern of adsorption operation is the requirement of retention time which limits the throughput capacity. Activated carbon can remove soluble BTEX, whereas organoclay can

remove insoluble hydrocarbons which are part of TPHs [2,10]. Advantages include high efficiency and no corrosion of equipment as well as no scale decomposition. Disadvantages include high operating costs and disposal of spent material, as well as the possibility to foul the bed of material [11]. Zeolites have been used as one example of these adsorbents, where they are introduced as pellets in a fixed bed. On the other hand, Means et al. invented a column filled with resin which is capable of removing soluble organic compounds based on this adsorbent. Nevertheless, to regenerate the adsorbent, the used of solvents or acid backwash is proposed [2,14]. The performance of the adsorption process may be affected by factors such as temperature, pH, salinity, dispersed/suspended oil, dissolved organic chemicals, and heavy metals.

Table 2 presents the produced water characteristics before and after treatment using adsorption technology in which mixed adsorbents were used. These adsorbents include sodium bentonite modified orgonaclay and granular activated carbon. Inspection of this table reveals that the adsorption technique is highly effective in removing dissolved oil from produced water with quality that meets the environmental standards.

Table 2: Influent and effluent characteristics of produced water treated by packed columns adsorption system. The mixed adsorbents employed are sodium bentonite modified organoclay and granular activated carbon. Dissolved oil was measured using the EPA method 1664-A which is based on normal n-hexane extraction [10]

Contents	Before Treatment (ppm)	After treatment (ppm)
Total Petroleum Hydrocarbons (TPH)	148	1.1
Oil and Grease	151	1.2
Benzene	3.14	<0.5
Toluene	4.97	<0.5
Ethylbenzene	4.95	<0.5
Xylene	29.7	<1

• Evaporation: Evaporation is another method that can be used to remove oil components from saline produced water. It can be vertical tubes, falling film, or vapor compression evaporators. In this method, no chemical or physical treatment is

needed. Less maintenance is required for this method compared to the other methods used in treating produced water.

- Dissolved air precipitation: In this method, air is saturated in water in a packed column/separator at a pressure range 480-820 kPa. Upon releasing the pressure by a valve into the column, the air forms bubbles. The removal of dissolved octane, micro-dispersed decane and dissolved ethyl benzene by this method were found to be 95 %, 75 % and 40 %, respectively.
- C-TOUR: This is a patented method is based on liquid-liquid extraction in which the dissolved components existing in the produced water are removed by a water immiscible liquid. This method depends on the following factors:
    1. The condensate stream inserted into the produced water.
    2. The time of equilibrium between the water and condensate.
    3. The exclusion of the polluted condensate from the water.
    4. Recycling of the polluted condensate to the basic production flow streams.

Three field trials were conducted using this method, and the removal efficiency of dispersed oil was 70 %.

- Freeze-thaw/evaporation (FTE): This technique was used to treat produced water based on natural freezing and thawing/melting processes. Dissolved salts get accumulated, and at the same time, pure water is generated that can have various uses depending on the quality required for the intended use.
- Ionic liquids: This method utilizes ionic liquids to extract soluble organic matter from produced water. A study was done to extract polar organic compounds with ionic liquids and results demonstrated the affinity of ionic liquids to the organic compounds. However, this process might be challenging in terms of the solubility of these ionic liquids in the aqueous phase, besides being difficult to retain the solvent.
- Membrane treatment: The membrane treatment is a physical treatment based on separation of the molecules depending on the pore size of the membrane. This method is favored over chemical and biological treatments used in produced water because it does not require the use of chemicals. Also it does not need much space for installation. This method can utilize different pore sizes and, accordingly, they are categorized as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Microfiltration separates suspended particles, whereas ultrafiltration separates macromolecules. Moreover, Reverse Osmosis (RO) is separation of dissolved

particles as well as ionic constituents. These methods are becoming popular as they compete with other complicated treatments. They are suitable for water with high oil content, particles with small sizes, and flow rates which are greater than 150 (m^3/h), and, hence, they also work effectively for medium and large offshore platforms. One of the major drawbacks of this method is irreversible membrane fouling which renders this method expensive with high maintenance requirement.

1.2.3.3.1 *Oxidation processes.* Electrochemical process: A pilot-scale experiment was conducted using double anodes with active metal and graphite, and iron as a cathode. This configuration can oxidize hydrocarbons and dissolved organic compounds to carbon dioxide and water and other oxidation byproducts. It was reported that the Biochemical Oxygen Demand (BOD) as well as the Chemical Oxygen Demand (COD) were minimized by more than 90 % in 6 minutes using this method.

- Fenton process: Unlike the electrochemical method, this process is based on invasive redox reactions, in which the addition of iron and hydrogen peroxide reacts to produce the highly reactive hydroxyl radicles as shown in equations (2-3). These hydroxyl radicles will in turn, oxidize the contaminates into carbon dioxide and water and oxidation byproducts. These oxidation byproducts are then removed by flocculation, settlement and adsorption [15]. Applying this process in a lab-scale study had an impact on the COD and oil which were reduced significantly. The COD was reduced from 2634 (mg/L) to 100 (mg/L) and the oil from 93.1 (mg/L) to 5 (mg/L). The flocculent used in this lab-scale study is poly ferric sulfate, where it was left for 30 minutes to settle down. Other conditions were maintained as such: pH from 3-4, hydrogen peroxide was 30 %, mass ratio of 4% of Fe3+ to H2O, 120 minutes for oxidation, dose of activated carbon 4-5 (g/L) and 120 minutes for adsorption.

$$Fe^{2+} + H_2O_2 \quad \text{----->} \quad Fe^{3+} + .OH + OH \tag{2}$$

$$Fe^{3+} + H_2O_2 \quad \text{----->} \quad Fe^{2+} + .OOH + H^{+} \tag{3}$$

- Oxidation with ozone: The dissolved organic compounds in the produced water can be decomposed using ozone. This technique was first proposed by Morrow et al. [16]. Three days of exposure to ozone were sufficient to demolish the organics. The unsaturated and aromatic compounds are oxidized by ozone to produce carboxylic

acids and ketones. However, the oxidation of organic material is usually incomplete, as the TOC removal does not achieve more than 10-20 % [17].

• Photocatalytic treatment*:* Honda and Fujishima [18] have illustrated the use of this method to decompose water on TiO2 electrodes. In addition, this method is applicable for different contaminants. The organic treatment follows this process by the photocatalytic:

$$\text{Organic contaminant} + O_2 \xrightarrow{\textit{Semiconductor, hv}} CO_2 + H_2O + \text{mineral acids} \quad (4)$$

This method was tried in an open reactor at fixed pH followed by flocculation and settlement. The filtrate was removed, and then TiO_2 was used as a catalyst at high pressure conditions and ambient temperature. It was found that this method can minimize the toxicity of produced water.

• Biological Treatment: This method is based on oxidation by bacteria to digest organic compounds. These bacteria could function under aerobic or anaerobic conditions. In aerobic conditions, activated sludge is usually used, trickling filters, sequencing batch reactors (SBRs), or lagoons. A study was done using different aerobic bacteria in an activated sludge, where oil was skimmed off the surface then channeled to an aeration tank. It was found that 98 %-99% of the total petroleum hydrocarbons were removed. Various studies were also done using SBRs and trickling filters for produced water treatment. The efficiency of the process was known by measuring the COD and TOC removal.

1.2.3.4 Heavy metals. The concentrations of heavy metals present in produced water are function of the age of the wells and the formation geology. Usually heavy metals in produced water are in trace amounts and include cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc.

• Ion exchange: The most widely used technique in removing heavy metals is ion exchange. This is done by the use of resins. Ion exchange is defined as a chemical reaction which is reversible, and in which the charged ions in the produced water whether positive or negative are replaced by similarly charged ions in the resin. The resins used are either naturally occurring inorganic zeolites or organic resins produced synthetically [10].

• Chemical precipitation: In this method, coagulation and flocculation are utilized to remove suspended particles, especially heavy metals such as arsenic and mercury. Usually, produced water with a high amount of hardness, TDS, sulphides and oil particles can be purified to satisfy the quality required for its use as steam generator quality feed water. A study was conducted on produced water from oil and gas fields to test the efficiency of this method in treating hydrocarbons, arsenic, and mercury. Initial concentration of mercury, arsenic and TPHs are 36 ppb, 429 ppbw (parts by billion by weight), and 297 ppmw respectively [19]. Coagulant used was inorganic mixed metal polynuclear polymer (iron, magnesium and aluminium, (FMA)). The results showed that mercury in the effluent is less than 10 ppb, less than 250 ppb of arsenic, and around 40 ppm of TPHs.

• Sand filters: This method is used after a pre-treatment of waste stream is achieved. Pre-treatment includes pH monitoring for oxidation reaction to start, followed by an aeration tank where oxygen supply must be sufficient in the aeration unit. Then, a solid separating unit is used to settle precipitated solids. Enough retention time should be achieved in the solid separating unit. A sand filter is then employed to remove suspended solids. Results demonstrated that more than 90 % of the iron could be removed from the produced water [2].

1.2.3.5 Cations and anions. There are different cations and anions present in the produced water such as Na+, K+, Ca2+, Mg2+, Fe2+, Ba2+ and Cl-,HCO3-,CO_3^{2-},SO_4^{2-}- respectively. These have an impact on the chemistry of the produced water including the salinity, the scale possibility, and the buffering capacity. The existence of sodium and chloride ions may affect the salinity which might range from few ppm to 300,000 (mg/L). The common methods for removing cations and anions from produced water are electrodialysis and reverse osmosis [2].

1.2.3.6 Naturally occurring radioactive materials (NORM). Since naturally radioactive materials are soluble in presence of chloride ions, which exist in the formation water, the NORM get collected from the oil/gas formations. Radionuclides have low solubility in sulfate compounds, which results in a precipitate scale in the form of barium sulfate (equation 5).

$$Ba^{+} + Ra^{+} + SO_4^{-} \rightarrow Ba\,[Ra]SO_4 \quad (5)$$

This precipitate should be managed in a way to avoid any danger of radioactivity. A mobile treatment was made which comprises of separation of NORM solids with less than 30 pCi/g (Picocuries per gram, a measurement of radioactivity) radium and then dissolving it into aqueous solutions. The radionuclide is extracted from the scale by dissolving the radioactive material in one or more aqueous solvents in the hydrocyclone which will separate solids without NORM from the solution. The NORM solution is re-injected to the formation. Other forms of radioactive materials occur naturally in natural gas as Radon. Treating this gas employs packed bed adsorption of Radon with activated charcoal [10].

1.2.4 Integrated method for produced water treatment. In general, produced water with all its constituents undergoes the systematic treatments shown in Figure 5 followed by a desired technology from those described in Section 1.2.3.

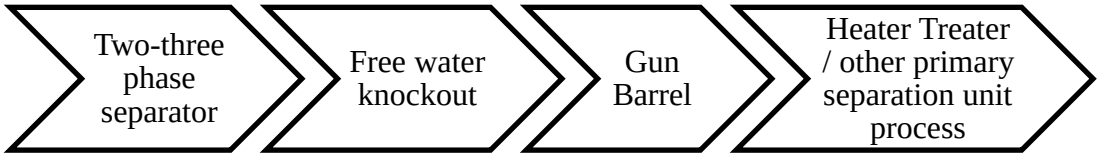

Figure 5: Pretreatment of produced water [19]

The two-three phase separators could separate liquid and oil, or liquid, oil and water. They can be onshore or offshore [20]. The free water knockout is a separator which could be horizontal or vertical that is used to eliminate any free water that may possibly lead to problems like formation of hydrates or corrosion. These are considered difficult to get rid of or break [21]. The gun barrel is a metal cylinder that expels gases at high velocity. The heater treater is used to break the emulsion in produced water, thus separating the oil from the water. Gas is removed before filtration and sedimentation, so that the liquid can separate without mixing with gas breaking out of the liquid [22]. However, the produced water at this stage will have dissolved hydrocarbons and other components which should be treated before being reused, injected, or disposed of. The quality of water to be reused or disposed of is based on regulations of the corresponding state, region, or nation [11]. A summary of the main methods employed in industries to treat produced water are presented in Table 3. Below is a review of the main objectives that operators need to achieve when treating produced water:

a) Remove dispersed oil and grease.
b) Remove dissolved organics.
c) Remove microorganisms, bacteria, and algae.
d) Remove suspended particles (turbidity) and sand.
e) Remove dissolved salts, nitrates, sulfates, and scaling agents.
f) Remove excess water hardness.
g) Adjust sodicity (sodium content) levels if water to be used for irrigation. This is done by addition of calcium or magnesium.
h) Remove NORMs.

1.2.5 Management of produced water. Produced water management practices:

- Water reduction: Water reduction is an essential option to minimize costs for operators, and it can be done by several ways including the following:
    1. Reduce the volume of water incoming the wells by adding mechanical blocking devices or water shut-off chemicals.
    2. Remote separation of water volume handled at the surface.
    3. Reduce the amount of water injected during the fracturing process by material substitution. For example, consider the use of nitrogen or carbon dioxide as an alternative to water [6].
- Recycle/Re-use: If water reduction is not a feasible option, then one should consider recycling or re-using produced water. Commonly, re-injection of produced water into a producing formation is employed in order to augment production. Almost all produced water is injected underground. The remainder is treated for reuse or discharged on the surface [23]. Several ways are used to recycle/re-use produced water including injection of water for future purposes, injection for hydrological uses such as subsidence control, agriculture uses (wetlands, livestock and irrigation), industrial uses (power plants, oil/gas industries) and others like firefighting, dust control, etc. [6]. Usually, if the water quality is acceptable for certain uses, then it would be considered beneficial, especially water with a low TDS (less than 10000 ppm) [24].
- Discharge management and quality: Disposal choices are more accessible for offshore facilities than onshore facilities. If not disposed, it can be injected for underground water recharge. Moreover, it can be evaporated, or disposed commercially offsite. All these techniques underline the importance of produced

water treatment, which is of great value, (both beneficial and cost effective,) if utilized properly [6]. National Pollutant Discharge Elimination System (NPDES) act is used to regulate the discharge of constituents present in produced water [6], where the oil and grease discharge limit is 29 (mg/L) weekly on average with a maximum of 42 (mg/L) daily [25]. For instance, in Dubai, the Environmental Health and Safety (EHS) regulations set the oil and grease maximum allowable discharge limit as 40 (mg/L) for offshore facilities and 10 (mg/L) for onshore facilities. Maximum allowable limits will vary according to the end use of the disposed stream as well as the end location [26].

Since this work is concerned with optimization of the oil removal from produced water by adsorption technique, the adsorption process as well as the adsorbent graphene is described below:

1.2.6 Adsorption. Adsorption is the process of substances holding onto solids, either from gaseous or liquid solutions. The process of adsorption entails the separation of a substance from one phase along with its accumulation at the surface of another. The material which gets adsorbed is the adsorbate, whereas the surface at which the material gets adsorbed is the adsorbent. Physical adsorption, as the name suggests, is the adsorption which happens by van der Waals forces and electrostatic forces between the adsorbate molecules and those of the adsorbent surface. Therefore, it is crucial to understand the surface properties of adsorbents including surface area and polarity. Chemical adsorption is the type of adsorption where the molecule holds to the surface by a chemical bond, unlike physical adsorption [27].

- Applications of adsorption: Adsorption is used in many applications and in various fields. It exists in natural, physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal which captures impurities, or in adsorption refrigerators used as thermal energy to increase pressures, and many others [27]. Some applications of adsorption which are well known include [28] the following:

1. Silica gel adsorbent used in adsorbing moisture.
2. Ion exchange method used for softening water.
3. Charcoal powder used to remove any colored impurities from sugar.
4. Soaps and detergents (cleaning) whose action is based on adsorption.
5. In heterogeneous catalysis.

6. Graphene and nanomaterials.

Table 3: Summary of methods employed for treating produced water

Physical Treatments	**Adsorption**
	Nanomaterials
	Zeolites
	Biosorbents
	Bentonite
	Activated carbon
	Sand filters
	Evaporation
	Freeze/thaw evaporation
	Cyclones
	Dissolved Air Precipitation
	Electrodialysis
	C-TOUR
	Membrane Treatment
	Reverse Osmosis
	Ultrafiltration
	Microfiltration
	Nanofiltration
Chemical Treatments	Chemical Precipitation
	Electrochemical Process
	Photocatalytic treatment
	Fenton Process
	Oxidation with Ozone
Biological Treatments	Activated Sludge
	Lagoons
	Trickling filters
	Sequencing Batch Reactors (SBRs)
	Chemostate Reactors

Some of the most effective adsorbents are graphene and nanomaterials. The chemical and physical properties of these nanomaterials are described below:

1.2.7 Graphene and Nanomaterials. Graphene is a single atomic layer of graphite where the hybridized carbons are hexagonally bonded in sp2 form. It is a newly developed material in the carbon family, and it is the major building block for all graphitic materials. Graphene possesses special characteristics including high mobility, high thermal conductivity, and admirable electronic and mechanical properties (Table 4). The history of graphene started in early 1950's where layers of graphite with several complexes in the middle of these layers were termed as graphene [29]. Then , it was isolated in 2004 by Andre Geim along with his colleague Kostya Novoselov [30]. It is a very promising nanomaterial in many fields such as electronics, energy storage, quantum dots, and sensors, and it is expected to boost the significance of nanotechnology [31].

Table 4: Charactersitics of graphene [32]

Theoretical specific surface area	2630 ($\frac{m^2}{g}$)
High intrinsic mobility	200,000 ($\frac{cm^2}{v.s}$)
High Young's modulus	1 (TPa)
Thermal conductivity	5000 ($\frac{W}{m\,K}$)
Optical transmittance	97.7 %

1.2.8 Graphene synthesis.

1.2.8.1 From graphite. Since graphene is a subunit of graphite, then the simplest way to produce graphene is to extract it from graphite. Graphite can occur in two forms: natural and synthetic. The natural form has single crystalline domains with the in-plane dimensions more than 1 mm; however, since the out-plane are much less than 1 mm, this makes it difficult to work with, Therefore, highly ordered prolytic graphite (HOPG) is used to make graphene. HOPG is made by thermal decomposition of hydrocarbons which yields graphite crystals with thicker consistency that the natural ones [33].

1.2.8.2 Mechanical cleavage. This method employs the use of scotch tape to physically cleave the parts of graphite into flakes and atomic flat surfaces. This method can be repeated so as to achieve the desired thinness of graphite. The flakes of graphite that stay on the tape can then be pressed with a substrate such as silicon oxide to generate graphene [33].

1.2.8.3 Liquid-phase mechanical exfoliation. Carbon-nanotubes have been known to be insoluble in any known solvent. Hence, they are usually mixed with a surfactant and sonicated. This allows the hydrophobic part of the nanotubes to adhere to the hydrophobic part of the surfactant, similarly for the hydrophilic part. This method is used to exfoliate graphene sheets from bulk graphite [33].

1.2.9 Applications of graphene. Graphene applications have been widely and thoroughly investigated since its discovery, aiming to utilize its superior properties to explore in various fields. Currently, graphene is being used to treat wastewater for heavy metals, toxic chemicals, dyes, and organic compounds. This evolution of using graphene as an adsorbent is feasible, efficient, and cost effective; therefore, it stimulates research to develop further uses of graphene. Since water shortage is increasing, as well as the demand for clean, safe water; the use of graphene in adsorption could be the next step in conventional waste water treatments. Chowdhury and Balasubramanian [34] tested graphene in removing dyes, organic compounds, and toxic elements from waste water, and results have proved that graphene is flexible, simple, and has a high adsorption capacity, which makes it a perfect candidate to remove such targets from wastewater. However, the use of graphene to remove emulsified oil has not been yet studied, and since this work

illustrates the performance of graphene in removing emulsified oil from produced water, this is considered one more advancement in the uses of graphene to protect surroundings from toxic materials, and guarantee that safe water will be returned to water resources, regardless of its initial state [34]. Furthermore, since graphene is an excellent conductor of electricity, is strong, and has a large surface area, it can be used for improving bioelectric sensory devices, measuring various health levels such as glucose, hemoglobin, and cholesterol, with continuous monitoring. In addition, graphene is now being thought of as the strong element, which can compete with steel in its stiffness, and being much lighter than steel, there is a way to replace steel by graphene in aircrafts. Presently, graphene is being analyzed as to its suitability for being the main component of super-capacitors that can surpass batteries' short lives and store a greater amount of energy as well [35].

1.2.10 Literature survey for treatment of produced by adsorption.

1.2.10.1 Adsorbents and adsorbates used in produced water. Adsorption is widely used to remove the oil present in produced water, and activated carbon is an adsorbent that is commonly used in the removal of a wide variety of organic compounds one of which is oil. It has been found to be technically feasible. The adsorption process using activated carbon is recommended by the United States Environmental Protection Agency (USEPA) as one of the best available technologies for treating organic compounds, but it still may be expensive, especially for developing countries.

Okiel et al. [36] conducted a study to remove emulsified oil from produced water using three different adsorbents, namely powdered activated carbon, deposited carbon, and bentonite. The oil-water emulsion samples were allowed to stabilize and then were divided into 200 mL portions where different doses of the adsorbents were added. Contact time was varied, after which the samples were filtered and extracted using 1,1,2-trichloro-1,2,2-trifluoroethane solvent. Then the extracted oil was diluted and tested by infrared spectroscopy. Results showed that adsorbents were able to remove oil, where the oil recovery ranged from 20 to 90 %. This recovery depended on the amount of adsorbents used, their weight, and the contact time. Deposited carbon had the highest adsorption capacity compared to powdered activated carbon and bentonite, and the contact time was found to be 2 hours. In

addition, it was concluded that as the concentration of oil increases, the oil removal % decreases.

On the other hand, to study the adsorption isotherms, samples with an initial concentration of oil 1000 mg/L were used to which adsorbents were added at dosages ranging from 0.1 to 1.5 g per 200 mL, for 2 hours. The Freundlich isotherm describes the data of adsorbed oil better than the Langmuir isotherm because it has a higher correlation coefficient. However, the main claim of this study is that bentonite and deposited carbon can outweigh the standard activated carbon due to lower cost and higher oil removal [36].

Another study was done showed that eggshells have the ability to adsorb oil providing almost 100 % oil removal by using just 1.8 g/L of the eggshell. The eggshells were crushed, washed, and dried -- after which they were added to samples of produced water. Different dosages of eggshells were used to find the optimum dosage, which was found to be 1.8 g to remove 194 mg of oil, i.e. 100 % of oil. Nonetheless, the adsorption was found to follow pseudo second order kinetics, whereas the Temkin-Pyzhev isotherm was the most favorable isotherm that has the highest correlation coefficient [37]. Other studies were also done by using natural adsorbents such as banana peels. The latter was chosen based on its low cost, abundance, and flexibility. It was presented that banana peels can contribute to a 100 % oil removal by just using 50 mg/L of the adsorbent. The contact time is 35 minutes. The kinetics were described by pseudo second order kinetics, and the Langmuir isotherm favors the adsorption process [38]. Furthermore, another study was done for the adsorption process using activated carbon as well as bentonite clay. The emulsion was prepared by adding a surfactant, namely Triton X-100 with water, after which diesel oil was added and shaken for a certain amount of time to ensure stability of emulsion. Different samples were prepared, acidified by sulfuric acid, and then extracted using 1,1,2-trichloro-1,2,2-trifluoroethane solvent. The organic layer was eluted through a column containing aluminum oxide and dried using sodium sulfate, after which measured by infrared spectroscopy. It was shown that the above adsorbents were effective in removing petroleum hydrocarbons from an oil-water emulsion. The adsorption of hydrocarbon was influenced by the pH and the initial concentration of oil. The contact time was 3 hours for bentonite and 4 hours for activated carbon. The data was best fit by Freundlich isotherm.

On the other hand, graphene has been tested to adsorb metal ions and organic contaminants from waste water, and it presented a high performance in adsorption. In addition, compared to zeolites, clay minerals, and carbon materials, graphene has a higher adsorption capacity and a better recycling ability for removal of heavy metal ions [39]. Graphene nanosheets were used to remove Pb(II), Co(II) and Fe(II). The study showed graphene as an excellent candidate for–the treatment of wastewater from industries of smelting, mining, etc. The uptake of graphene is a strong function of pH as well as the initial concentration of metal ions [34]. Gupta et al. [40] claim that graphene and graphene oxide can overcome other adsorbents such as activated carbon in removing dyes, pesticides, and heavy metal ions [40]. Graphene and graphene based materials were studied as adsorbents for different pollutants present in water such as Methyl blue, Endosulfan, Saphranin T, Tetracycline and others, and it was found that the maximum adsorption capacity of these pollutants in mg/g was relatively high [41].

The adsorption efficiency and the adsorption kinetics are the most important processes that are considered to quantify the adsorption process. Several models were introduced in order to analyze the thermodynamics and kinetics of adsorption. These are models are described below:

1.2.10.2 Adsorption isotherms. Different models were employed in the literature to quantify the efficiency of adsorption by given adsorbents. These models are called isotherms. Each isotherm is described below:

1.2.10.2.1 Langmuir isotherm. In the Langmuir adsorption model, it is assumed that the utmost adsorption is related to a saturated monolayer of solute molecules on the surface of the adsorbent, and there are no cross interactions between the adsorbed materials [42].

The Langmuir Model is described by:

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \tag{6}$$

Rearranging Equation 6 will give the linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{7}$$

where q_e is the amount of adsorbed oil per unit mass of adsorbent (mg/L), C_e is the concentration of adsorbate in solution at equilibrium (mg/L), q_m is the maximum amount of oil per unit mass of adsorbent (mg/g) and b is the affinity constant to binding sites (L/mg). A plot between the specific adsorption (C_e/q_e) versus the equilibrium concentration C_e will show if the experimental data obeys this model or not [42]. R_L is a unitless separation factor used to describe whether the adsorption process is favourable or not. Table 5 illustrates the essential characteristics of the Langmuir isotherm [43]. The equation below represents this factor:

$$R_L = \frac{1}{1 + bC_i} \tag{8}$$

where C_i is the initial concentration of adsorbate $(mg/L)$and b is the affinity constant to binding sites (L/mg) [42].

Table 5: Essential characteristics of langmuir isotherm [42]

Value of R_L	**Type of isotherm**
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L < 1$	Irreversible

1.2.10.2.2 Freundlich isotherm. The Freundlich isotherm is considered to be an empirical equation that is used to explain a heterogeneous system. The equation is as follows:

$$q_e = k_f C_e^{\frac{1}{n}} \tag{9}$$

A linearized form of equation 9 is:

$$\ln q_e = ln\, k_f + \frac{1}{n} ln C_e \tag{10}$$

where $\boldsymbol{q_e}$is the amount of adsorbed oil per unit mass of adsorbent (mg/g), C_e is the concentration of adsorbate in solution at equilibrium (mg/L), k_f is a Freundlich

constant related to the multilayer adsorption capacity $\left(mg^{(1-\frac{1}{n})}L^{(\frac{1}{n})}/g\right)$ and n is a Freundlich constant related to the intensity of adsorption [43,45,46].

A Plot lnq_e versus lnC_e will give a linear line if the data obeys this model [42].

1.2.10.2.3 Temkin isotherm. Temkin and Pyzhev suggested that some indirect interaction from the adsorbate on the adsorption isotherm may have an impact, which may be the reason why the heat of adsorption decreases linearly with the coverage of adsorbent, and thus they included it in an adsorption model:

$$q_e = \frac{RT}{b}\ln(AC_e) \tag{11}$$

And in the linear form:

$$q_e = BlnA + BlnC_e \tag{12}$$

where, q_e is the amount of adsorbed oil per unit mass of adsorbent (mg/g), C_e is the concentration of adsorbate in solution at equilibrium $(mg/L), B$: RT/b, where b is the Temkin constant related to heat of adsorption $(J/mole)$, A is a Temkin constant (L/mg), R is ideal gas constant $(J/mole.K)$ and T is the absolute temperature (K). A plot of q_e versus lnC_e will yield a straight line where A and B can be obtained from slope and intercept respectively [42].

1.2.10.2.4 Dubinin- Radushkevich (D-R) isotherm. This isotherm model is employed in order to organize the procedure and the energy of adsorption. It also differentiates between the physisorption and chemisorption. The D-R model is given by:

$$lnq_e = lnq_m - B_D\varepsilon^2 \tag{13}$$

where, q_e is the amount of oil adsorbed per unit mass of adsorbent (mol/g), $q_m$is the maximum capacity of adsorption, ε is the Polanyi potential (J/mol), and $B_D$is the D-R constant (mol^2/kJ^2).

Moreover, the relation between C_e and ε is given in equation 14:

$$\varepsilon = RTln[1 + \left(\frac{1}{C_e}\right)] \tag{14}$$

where, T is the absolute temperature, R is a universal gas constant $(J/mol.K)$ and C_e is the equilibrium concentration. If lnq_e versus ε^2 is plotted, a linear relation results with the -B_D and lnq_m as the slope and intercept respectively [45]. E which

is the mean free energy is calculated per molecule of adsorbate [42] as given in equation 15:

$$E = \frac{1}{\sqrt{2B_D}} \tag{15}$$

This E value will present data about the mechanism of the adsorption process. If its value is in the range of 8-16 (KJ/mol), then it is a chemisorption process; otherwise it is a physisorption process as it usually lies below 8 (KJ/mol)) [47].

1.2.10.3 Kinetics of adsorption. Understanding the kinetics of adsorption is very crucial in order to understand to what extent the adsorbent can uptake the adsorbate. In addition, it provides an overview of the time and reaction path to approach equilibrium through the process. This is a function of the properties of the adsorbent as well as the operating parameters of the process [47,48]. This study conducted to treat produced water using graphene, the system is heterogeneous due to presence of two separable phases namely the adsorbent and the adsorbate. Two kinetic models that describe this heterogeneity are presented below:

1.2.10.3.1 Pseudo-first-order model. The pseudo-first-order model (Lagergren Model) is given by this equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{16}$$

which after being linearized becomes:

$$\ln(q_e - q_t) = lnq_e - k_1 t \tag{17}$$

where q_t is the amount of emulsified oil removed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant ($1/min$) and t is the contact time (min).

To determine the rate constant, $\ln(q_e - q_t)$ versus t is plotted [47-49].

1.2.10.3.2 Pseudo-second-order model. The equation describing this model is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{18}$$

Rearranging equation 18 will give the following:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (19)$$

where, q_t is the amount of emulsified oil removed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_2 is the pseudo-second-order rate constant $(g/mg.min)$ and t is the contact time (min). A plot of t/q_t versus t will read $1/q_e$ as the slope and $1/k_2 q_e^2$ as the intercept [50].

Several methods for measuring the concentration of oil in produced water where introduced in the literature with specific limitations for each. In this work, the quantification of oil in produced water is the crucial part for this study. Detailed literature review of these methods is necessary in order to validate a method that is suitable for measuring emulsified oil in produced water. Below is a description of this literature survey.

1.2.11 Quantification of oil in produced water. For measurement of oil in produced water, different instrumental methods are usually used. These methods are based either on physical separation or extraction followed by physiochemical measurements which include the following [8]:

1. UV-Visible spectroscopy.
2. Infrared spectroscopy.
3. Fluorescence spectroscopy.
4. Total Organic Carbon (TOC).
5. Chemical Oxygen Demand (COD).
6. Gravimetric.
7. Gas Chromatography-Flame Ionisation Detection (GC-FID).
8. Gas Chromatography-Mass Spectroscopy (GCMS).

1.2.11.1 UV-Visible spectroscopy. Atoms and molecules are present in certain defined energy levels, and the change of this level will require absorption or emission of energy known as quantum. Samples will absorb energy (photons) and get promoted to a higher energy orbital of energy at a range of wavelength, then this is recorded as absorption spectrum [51]. Regularly, an extracted sample of oil is placed in this instrument where the absorbance is measured. Based on a calibration curve prepared from known concentrations, the amount of oil present in the

extracted sample can be known. The measurements in this instrument are based on the Beer-Lambert Law:

$$A = log\frac{I_o}{I} = ELc \tag{20}$$

where, A is the absorbance, I_o is the incident light intensity, I is the transmitted light intensity, E is a constant, L is the path length and c is the hydrocarbon concentration in the extracted sample. There are two kinds of this instrumental measurement, either by single wavelength, or three wavelengths. These depend on which stretch vibration frequency is required, and as a result, different wavelengths may read the contribution of different compounds [8]. Advantages of this instrument are that the similar cell can be used for all determinations and that the baseline technique can eradicate many likely errors. Disadvantages include the unfeasibility of the instrument to read the molecular weight. Also, the measurements of absorbance are limited by the influence of stray radiation as well as the narrowness of spectra [52]. The UV range of wavelengths are lower than the visible light (400 nm – 10 nm).Typically, UV-Visible spectrophotometer is used to monitor the effluent of the waste stream from industries, specifically to check that organic compounds are less than their threshold. The common management followed is to categorize the organic compounds into three groups: Group A which contains low molecular compounds, organic solvents, proteins, aromatics, and short-chain aliphatics and are detected in UV-Visible spectrophotometer at a range of 250-290 nm, Group B which are humic acids and products of biological removal and are detected in UV-Visible spectrophotometer at a range of 290-350 nm, and lastly, Group C with no divisions to date [53].

1.2.11.2 ***Infrared spectroscopy (IR).*** Infrared absorption is very similar to UV-Visible spectroscopy except that the former is limited to compounds that have small energy variances in the rotational states [54]. It is also based on Beer's law. It deals with the infrared region of the electromagnetic spectrum, which means light with a lower frequency and longer wavelength than the visible light. The wavelengths presenting the infrared absorption where organic compounds absorb are in the range of 2500 to 16000 nm. Molecules experience different vibrational motions which are specific to each component. Based on these motions, organic molecules absorb infrared that corresponds to the energy of these vibrations. This

technique allows obtaining absorption spectra that reflects their molecular construction [55]. Advantages of this method include that IR can almost read any sample in various states like liquids, powder and fibers. The cell used in this technique can be employed for all measurements. However, it is not possible to know the molecular weight of the substance measured [52].

1.2.11.3 Fluorescence spectroscopy. Most molecules have the lowest vibration level of the ground electronic state, at the room temperature. However, when they absorb light, they are excited to new states, to produce either S2 or S2. An important term to understand in this measurement is the quenching which indicates an interaction of the excited state of the fluorophore with its surrounding, leading to a decrease in the intensity [56]. This method is extensively used in measuring the fluorescence of crude oil components in produced water after being extracted. The history of this method in characterizing crude oil goes back to the 1970's. Certain studies were done to diverse oil types using this method [57]. Baszanowska et al. [58] performed a study to identify oil emulsions in water using fluorescence spectroscopy. They prepared synthetic oil-in-water emulsions and then detected different types of oils with different concentrations. They concluded that this method is efficient and easy to use, especially for in-situ measurements [58]. Advantages include flexibility and ease of application [56].

1.2.11.4 Total organic carbon (TOC). Total Organic Carbon (TOC) is a measurement of the total organic compounds present in a sample. . A reaction is required in which these compounds react with oxygen under high temperature, in which carbon dioxide is emitted as a product. Based on carbon dioxide peaks, the TOC can be read for each sample. In addition, a calibration curve of the mean area versus TOC should be prepared for known samples. Usually, high temperatures are required to ensure complete oxidation of the organic compounds. It is necessary to remove the inorganic matter in the sample to avoid any interference, and this is done by acidification and stripping using a carrier gas [59]. This tool is used to identify petroleum contamination in required streams. TOC has a great oxidation potential compared to COD, which can represent more accurately the content or organic matter in a sample. However, TOC are usually related to COD and BOD values, and this requires the knowledge of their values [60].

1.2.11.5 Chemical oxygen demand (COD). The Chemical Oxygen Demand (COD) is a measurement of the organic compounds in a specific sample. The organic compounds are allowed to react with oxygen, which indicates how much oxygen is needed for these compounds, and hence, with more oxygen demand, more organic compounds are there. An advantage of this method includes that it does not require much time to get results; however, the use of toxic chemicals is a concern related to disposal [60].

1.2.11.6 Gravimetric. This method requires that the extracted sample will be put in a flask with a known weight, after which the temperature is controlled in a water bath, and the solvent is evaporated, condensed, and then recovered. Next, the oil left in the flask is dried and weighed, from which the weight of the flask is subtracted. Thus, the amount of the left over (residual) oil is calculated [8]. Advantages include ease of determinations since gravimetric does not require any calibration curve. Also, it normally does not provide instrumental errors, and it can read the atomic mass of any element up to six significant figures. However, it is time consuming and it can only read one element or a limited number of elements at the same time [61]. This tool has been used to identify crude oil presence in samples, but mostly to study the bacterial degradation of crude oil/organic matter [62].

1.2.11.7 GC-FID. This method describes the hydrocarbons present in the sample, unlike the infrared absorption and gravimetric. It consists of the following:

a. Carrier gas supplier
b. Injector
c. Chromatographic column
d. Detector
e. Data handling system.

The extracted sample is dried. Then placed in this instrument, where various hydrocarbons will be detected based on their difference in adsorption. These compounds are moved to the detector by the aid of the carrier gas. After being detected, the compounds are burnt and detected by a Flame Ionization Detector (FIM) [8].

1.2.11.8 GCMS. This device consists of two parts; the first is Gas Chromatography (GC), and the second is Mass Spectrometry (MS). The first part reads all the organic components that are present in the sample of oil. It produces different spectral peaks depending on the existing components in the oil, where the retention time can be used to differentiate between the compounds. The retention time is the time which has elapsed between the injection time and the elution time. In addition, the peaks produced from the GC are directly proportional to the amount of substances in the sample studied. A carrier gas, which is usually an inert gas, is responsible for carrying the sample which is separated and transferred to the MS. For the MS to work, the sample must be in a gaseous phase, after which it gets ionized to different fragments in a mass spectrum, which are matched with the existing library to identify the compound of a specific peak [63]. GCMS is widely used to identify the different organic compounds existing in the sample qualitatively and quantitatively.

1.3 Thesis organization

Chapter 1 presented a background on the need to treat produced water, a detailed literature review on produced water and its characteristics, technologies adopted to treat produced water, graphene synthesis and applications, literature survey of produced water treatment by adsorption, adsorption isotherms and kinetic models and quantification methods of oil in produced water. Chapter 2 describes the experimental work conducted in this research to find the optimum tool for oil quantification as well as to treat produced water by adsorption. Chapter 3 demonstrates the results and discussion of methods examined to quantify oil. Chapter 4 examines the adsorption experimental results of treatment of produced water by graphene to find optimum conditions. It also presents the studied adsorption isotherms, adsorption kinetic models and thermodynamic study. Moreover, Chapter four illustrates graphene regeneration using n-hexane solvent along with the results obtained over two adsorption-regeneration cycles. Chapter 5 concludes the thesis with the main results and findings and presents recommendations for future examinations.

Chapter 2: Experimental

2.1 Materials

All chemicals used in this work were of analytical grade. Heavy crude oil (with API less than 22.3°) was obtained from the Abu Dhabi National Oil Company (ADNOC), UAE. The surfactant was obtained from General Electric (GE), UAE, ENDCOR OCC9783. n-hexane used was obtained from J.T. Baker (Netherelands) with purity > 95 % . Graphene was bought from Grafen Chemical Industries (Grafen Co., Turkey). 1.0 M Sodium hydroxide and 1.0 M hydrochloric acid were used for the pH tunings. 1.0 M NaCl was used for salinity adjustment.

2.2 Instrumentation

UV-Visible measurements were performed on CARY 50 Conc (Varian, Australia). Fluorescence measurements were performed on CARY Eclipse (Varian, Australia). TOC readings were obtained using TOC-V_{CPN} (SHIMADZU, Japan). A stuart vortex mixer was used at 2000 rpm for mixing extracted samples. Samples were centrifuged using Centrifuge (HERMLE Labortechnik GmbH, Germany) at 4000 rpm. Orion 210 A+ basic pH meter and Orion 115A+ basic cond/TDS/salinity meter were used (Thermo Electron Corporation, USA). A temperature controlled flask shaker was used at 150 rpm (Edmund Buhler, Germany). Syringe filters of 0.45 μm were used (PTFE Membrane, Chrom Tech, Germany). Graphene was characterized using SEM (TESCAN VEGA.3-LMU, USA).

2.3 Methods

2.3.1 Preparation and stability of emulsion. In order to mimic natural produced water, stable emulsified oil should be prepared. In this work, the stability of oil emulsion was tested using different percentages of deionized water in water surfactant mixture as follows: 50%, 60%, 80%, and 100% deionized water. For 50.0 mL of each solution, 12.500 mg of oil was added. The stability of the resulted mixture was tested visually and using light scattering technique. The most stable emulsion with minimum light scattering was obtained for 60 % water in water surfactant mixture. This composition was adopted in all follow up measurements for quantification of the efficiency of adsorption by graphene.

2.3.2 Quantification of emulsified oil. Several methods were described in the literature to quantify oil in produced water such as Fluorescence spectroscopy, gravimetric and others which were discussed in section 2.7. In this study, three methods were examined as analytical tools to quantify emulsified oil in produced water. These instruments are Fluorescence spectroscopy, UV-Visible spectroscopy and Total Organic Carbon (TOC).

2.3.2.1 Calibration curve of oil in n-hexane. A stock solution of 1200 ppm was prepared by introducing 30.0 mg of oil into 25.0 mL n-hexane. Standard solutions of different concentrations were prepared by dilution ranging from 10.0 ppm to 60.0 ppm. A fluorescence spectroscopy was used to read these standard samples at an excitation of 260 nm. The intensities were used to prepare a calibration curve at two wavelengths 330 nm and 372 nm. Another stock solution was prepared by introducing 25.0 mg of oil in 50.0 mL n-hexane. This produced a stock solution of 500 ppm, after which different concentrations were prepared by dilution ranging from 50.0 ppm to 450 ppm. These standard solutions were diluted ten times in n-hexane, and then read spectrophotometrically by measuring the absorbance of each solution at 275 nm using the UV-Visible spectroscopy.

2.3.2.2 Calibration curve of surfactant in n-hexane. A 50.0 ppm standard solution of surfactant in n-hexane was prepared out of which concentrations in range of 5.00 ppm – 20.0 ppm were prepared. The solutions were mixed on the vortex for 5 minutes then read using the fluorescence spectroscopy at an excitation of 260 nm. A calibration curve was performed using the data from the spectroscopy.

2.3.2.3 Extraction of oil from emulsified produced water by n-hexane. A known concentration of oil in the range 10.0 – 60.0 ppm was prepared in a 60%:40% deionized and surfactant respectively. 5.0 mL was taken each solution and extracted using 5.0 mL n-hexane. Two replicates of the stock solution with concentration of oil 1200 ppm were similarly extracted with 5.0 mL n-hexane. The samples were shaken for 5 minutes using the vortex, and centrifuged for 6 minutes, and the oil in the n-hexane layer was determined using a Fluorescence spectroscopy. The hexane layers of samples after extraction were combined, which accounted for 30.0 mL, 5.0mL each, and read on the Fluorescence spectroscopy. Samples read on fluorescence spectroscopy at excitation 260 nm. The extraction procedure was repeated three times for statistical analysis. A similar extraction procedure was done

on prepared oil concentration in range of 50.0 – 450 ppm, but instead extracted with 9.0 mL of n-hexane. The concentration of oil extracted in n-hexane layer for each sample was determined using UV-Visible spectroscopy at wavelength of 275 nm. Also, the extraction procedure was repeated three times.

On the other hand, a 200.0 mL of deionized water and surfactant solution with the ratio 60%:40% respectively was prepared to serve as a correction for the extracted emulsified oil in n-hexane. It was extracted three times and diluted ten times in n-hexane for the first extraction, two times for the second, and not diluted for the third. The concentration of surfactant extracted in n-hexane from the sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm using UV-Visible spectroscopy.

2.3.2.4 Total organic carbon. Standard solutions were prepared with the use of KHP (potassium hydrogen phthalate). Standards of emulsified oil in deionized water and surfactant with the ratio 60%:40% respectively were diluted 100 times with deionized water and prepared in vials for the TOC test. Three replicates of surfactant with deionized water solution (No oil) was diluted 100 times and also read in the TOC for the sake of comparison, as blanks. Samples were then tested in the TOC machine at a temperature of 720 ℃.

2.3.3 Adsorption study. All experiments were done in a batch adsorption mode. A known concentration of emulsified oil solution was prepared using the above water surfactant ratio (60%). The pH and salinity of this solution was adjusted to the required values by addition of either 1.0 M HCl, 1.0 NaOH and 1.0 M NaCl solution. 50.0 mL of this solution was transferred to erlenmeyer flask. A known mass of graphene was added to produce the required adsorbent dosage. The flasks and its contents were incubated at the required temperature and shaken for a specific time interval. At specific predetermined times, 5.0 mL of this solution was drawn and filtered using 0.45 μm syringe filters. The oil in this sample was extracted using 9.0 mL of n-hexane for three times. The oil content was quantified using UV-Visible spectroscopy. The effect of adsorbent dosage, contact time, pH, salinity, temperature and initial concentration of emulsified oil were optimized for the removal of oil by graphene. Below is the description of procedure for each studied parameter.

2.3.3.1 Effect of adsorbent dosage. Produced water was prepared in the laboratory using a 600.0 mL solution of water and surfactant (60%:40%)

respectively with an initial concentration of crude oil of 250 ppm. 50.0 mL of this solution was introduced into 100.0 mL conical flasks. To determine the effect of adsorbent dosage, different masses of graphene in the range of 0.0500-0.3500 g were introduced into each flask under identical conditions. The initial pH was 7.98±0.05, contact time was 120 minutes, and temperature was 25.0 ℃. Each flask was then shaken in a thermostated shaker at 150 rpm. For each dosage, two runs and a control were prepared. Samples were filtered, and then 5.000 mL of each filtrate was extracted three times using 9.0 mL n-hexane. Samples were mixed on the vortex for 5 minutes and then centrifuged for 6 minutes. The concentration of oil extracted in n-hexane for each sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm. The corresponding concentration was evaluated from the calibration curve. The percent removal of oil by graphene was then calculated. A detailed sample calculation is described in Appendix A.1 for the removal efficiency of emulsified oil by the optimum graphene dosage of 3.00 (g/L) .

2.3.3.2 Effect of contact time. 50.0 mL of the prepared produced water was introduced in a 100.0 mL erlenmeyer flask. The optimum adsorbent dosage of graphene 3.00 (g/L) was then introduced into the flask. The pH was 7.98±0.05 and the temperature was kept constant at 25.0 ℃. The contact time was varied between 5-120 minutes. Each flask was then shaken in a thermostated shaker at 150 rpm. For each time, two runs and a control were prepared. Samples were filtered, and then 5.0 mL of each sample was extracted three times using 9.0 mL n-hexane. Samples were mixed on the vortex for 5 minutes and then centrifuged for 6minutes. The concentration of oil extracted in n-hexane for each sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm. The removal efficiency of emulsified oil at each time was calculated similarly as described in Appendix A.1.

2.3.3.3 Effect of initial pH. To assess the effect of initial pH, 50.0 mL of the prepared produced water was introduced in different 100.0 mL conical flasks. The pH was adjusted to the desired value ranging from 4.00-12.00 using either 1.0 M HCl or 1.0 M NaOH solutions. The optimum graphene dosage of 3.00 (g/L) was then introduced into each flask and kept in contact at the optimum contact time of 60 minutes at the constant temperature of 25.0 ℃. Each flask was then shaken in a

thermostated shaker at 150 rpm. For each sample, two runs and a control were prepared. Samples were filtered and then 5.0 ml of each sample was extracted three times using 9.0 mL n-hexane. Samples were mixed on the vortex for 5 minutes and then centrifuged for 6minutes. The concentration of oil extracted in n-hexane for each sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm. The removal efficiency of emulsified oil was calculated similarly as described in Appendix A.1.

2.3.3.4 Effect of salinity. To consider the effect of salinity on the percent removal of oil by graphene, 25.0 mL of the prepared produced water was introduced into different 50.0 mL volumetric flasks. For each flask, the pH was adjusted to the optimum value of 10.00 ± 0.05 using 1.0 M NaOH solution; the salinity was adjusted to the desired values in the range of 500-2000 ppm using 5000 ppm stock solution of NaCl. The volume was then completed to the mark with prepared deionized water and surfactant solution of ratio 60%:40% and transferred to a 100.0 mL conical flask. The optimum dosage of graphene 3.00 (g/L) was then added and left in contact at the optimum contact time of 60 minutes at 25.0 ℃ in a thermostated shaker at 150 rpm. For each sample, two runs and a control were prepared. Samples were filtered, and then 5.0 mL of each filtrate was extracted three times using 9.0 mL n-hexane. Samples were mixed on the vortex for 5 minutes and then centrifuged for 6minutes. The concentration of oil extracted in n-hexane for each sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm. The removal efficiency of emulsified oil was calculated similarly as described in Appendix A.1.

2.3.3.5 Effect of temperature. To assess the effect of temperature on the percent removal of oil from produced water, the same procedure as described in section 2.3.4.4 was followed. The pH was adjusted to 10.00 ± 0.05; the salinity was adjusted to the optimum value of 1500 ppm using the same stock solution of NaCl. The volume was then increased to the mark with prepared deionized water and a surfactant solution of ratio 60%:40% and transferred to a 100.0 mL conical flask. The content of each volumetric flask was then transferred to a 100.0 mL conical flask to which was added the optimum dosage of graphene of 3.00 (g/L). The solution was kept in contact for 60 minutes and the temperature was varied between 25.0 ℃- 40.0 ℃. Each flask was then shaken in a thermostated shaker at 150 rpm.

For each sample, two runs and a control were prepared. Samples were filtered and then 5.0 mL of each filtrate was extracted three times using 9.0 mL n-hexane. Samples were mixed on the vortex for 5 minutes, and then centrifuged for 6 minutes. The concentration of oil extracted in n-hexane for each sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm. The removal efficiency of emulsified oil was calculated similarly as described in Appendix A.1.

2.3.3.6 Effect of initial concentration of oil. To obtain the adsorption isotherms, four different concentrations of oil in produced water were prepared in the range of 100-1000 ppm. 25.0 mL of each solution was introduced into 50.0 mL volumetric flasks, and the optimum salinity and pH were adjusted using 5000 ppm NaCl and 1.0 M NaOH solutions, respectively. The volume was then adjusted to the mark with prepared deionized water and surfactant solution of ratio 60%:40%. The solutions were then transferred to 100.0 mL conical flasks to which was added the optimum dosage of graphene of 3.00 (g/L). Each solution was shaken at the contact time of 60 minutes at a constant temperature of 25.0℃ in a thermostated shaker at 150 rpm. For each concentration, two runs and a control were prepared. Samples were filtered, and then 5.0 mL of each filtrate was extracted three times using 9.0 mL n-hexane. Samples were mixed on the vortex for 5 minutes and then centrifuged for 6 minutes. The concentration of oil extracted in n-hexane for each sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm. The removal efficiency of emulsified oil was calculated similarly as described in Appendix A.1.

Chapter 3: Results and Discussion - Method of Quantification of Oil in Produced Water

The presence of surfactant in produced water revealed the Fluorescence and TOC methods to be not suitable for quantification of oil in the produced water. The UV-Visible spectroscopy with wavelength selectively locked mode at 275 nm was used for oil measurements. Using this selected wavelength rendered the UV-Visible spectroscopy technique as the optimum analytical tool for quantifying the oil in produced water. Detailed results and discussion of each of the Fluorescence, UV-Visible and TOC are described below.

3.1 Fluorescence Spectroscopy

The Fluorescence spectra for oil in n-hexane at different concentrations is shown in Figure 6. Inspection of this figure reveals that two optimum analytical wavelengths can be selected for quantifying oil in n-hexane. These wavelengths are 330 nm and 372 nm.

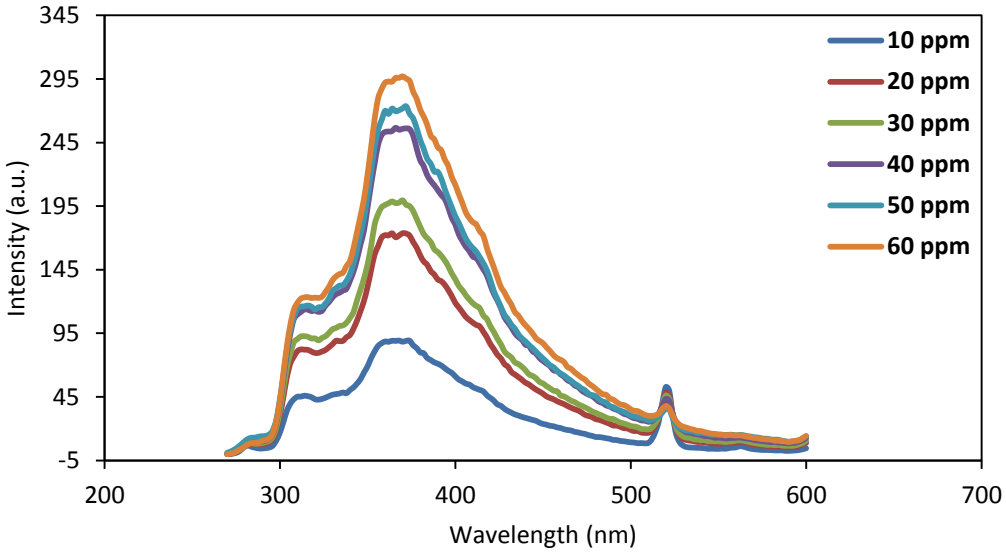

Figure 6: Fluorescence spectra of oil in n-hexane, excitation 260 nm

Standard solutions of oil in n-hexane were prepared and the fluorescence was measured at these wavelengths. A calibration curve was obtained at each wavelength and is shown in Figure 7.

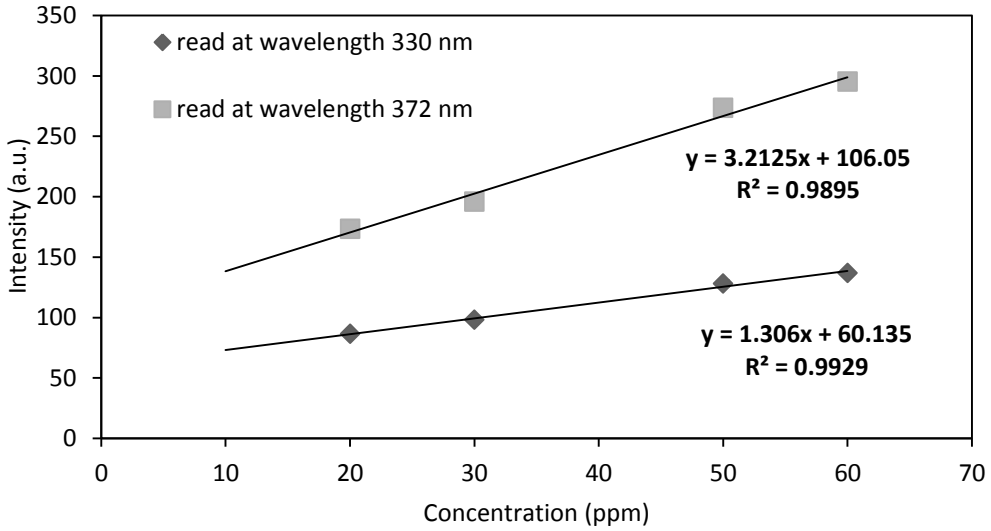

Figure 7: Calibration curve of oil in n-hexane, fluorescence spectroscopy at excitation 260 nm, λ = 330 nm and 372 nm

Same procedure was used to obtain the calibration curve for surfactant in n-hexane (Figures 8,9). Inspection of Figure 8 reveals that the fluorescence intensity of surfactant in n-hexane decreases with increasing concentration. This inverse proportionality between intensity and concentration can be explained by the presence of other components within the surfactant solution, where their fluorescence intensity is concentration dependent. Hence, it was impossible to use the fluorescence technique to quantify the extracted oil from produced water, since the surfactants are interfering negatively with the concentration of oil at the selected wavelengths and the obtained results have serious deviation from the true value.

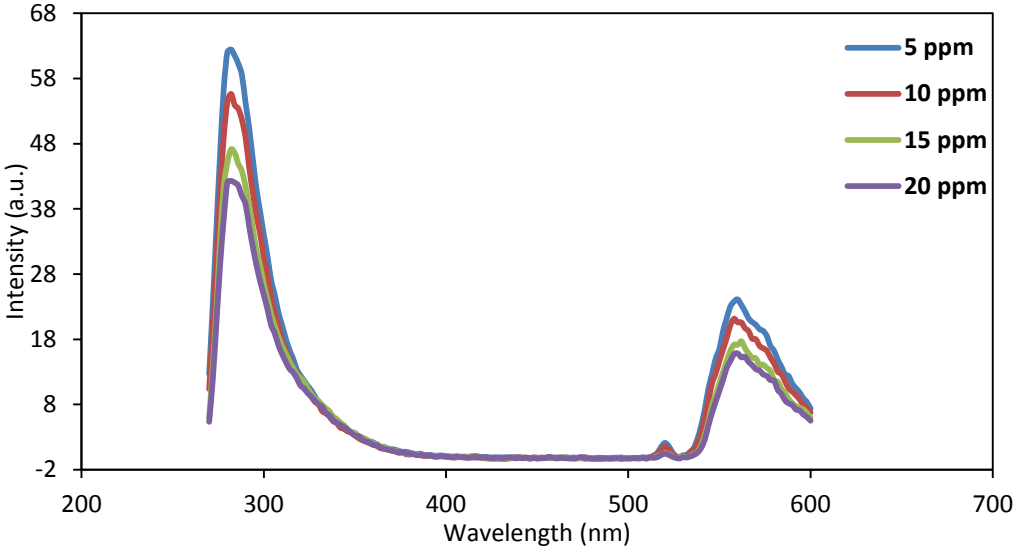

Figure 8: Fluorescence spectra of surfactant in n-hexane, excitation 260 nm

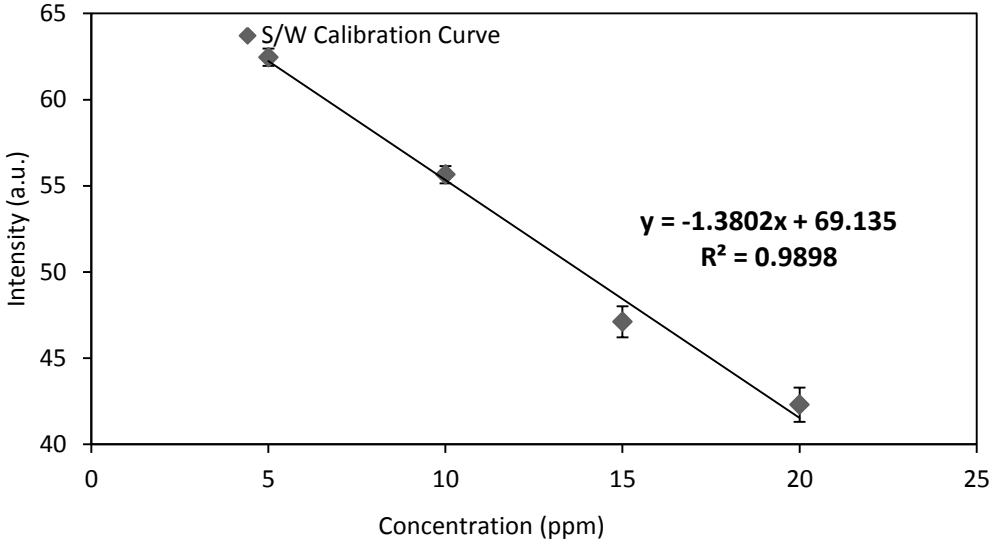

Figure 9: Calibration curve of surfactant in n-hexane, fluorescence spectroscopy at excitation 260 nm, λ = 330 nm

This conclusion was reached based on the results of extraction of emulsified oil by n-hexane. Figures 10-12 represent the Fluorescence spectra of oil extracted by n-hexane layers from emulsified water, which show that this multiple extraction is not consistent with the normal behaviour of the immiscible liquid. This could be explained by either n-hexane might be dissolving partially in the emulsion of the surfactant/deionized water, leading to the observed serious discrepancy between the measured value and the standard value. On the other hand, it could be also explained by the presence of other components in surfactant solution that might be extracted by n-hexane which may also lead to the same observation. Consequently, the Fluorescence spectroscopy technique used to analyze the surfactant/water system was not producing the expected logical results, but rather conveying that the system is behaving differently from expectation.

To sum up, evaluating the quantity of oil in real produced water that contains surfactants using the Fluorescence spectroscopy is inappropriate, and hence other techniques should be used.

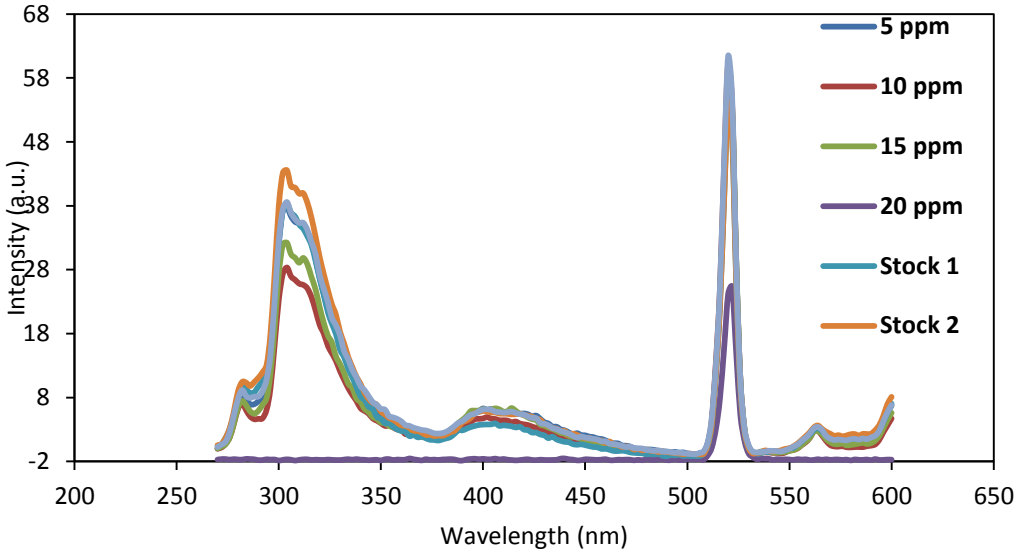

Figure 10: Fluorescence spectra of emulsified oil in n-hexane layer – first extraction, excitation 260 nm

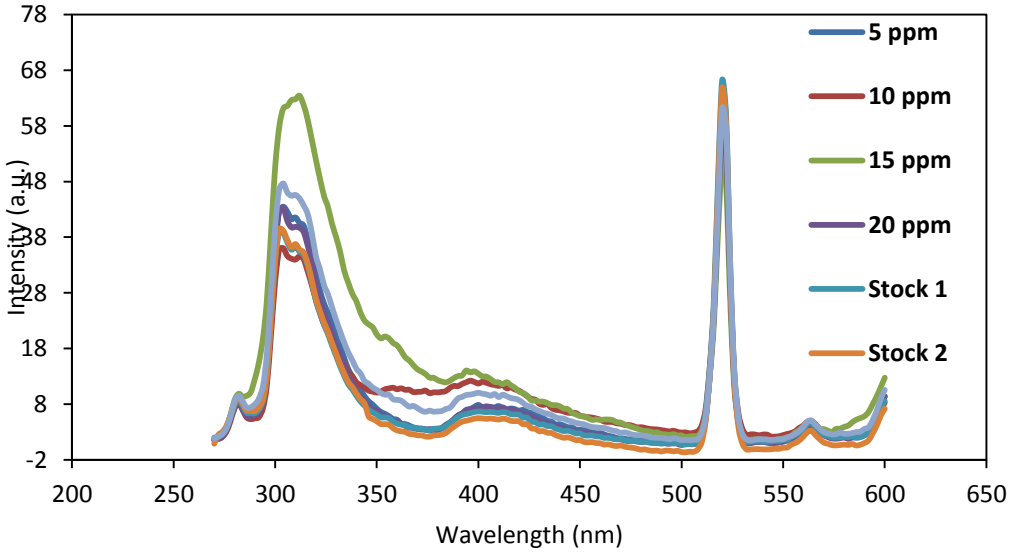

Figure 11: Fluorescence spectra of emulsified oil in hexane layer – second extraction, excitation 260 nm

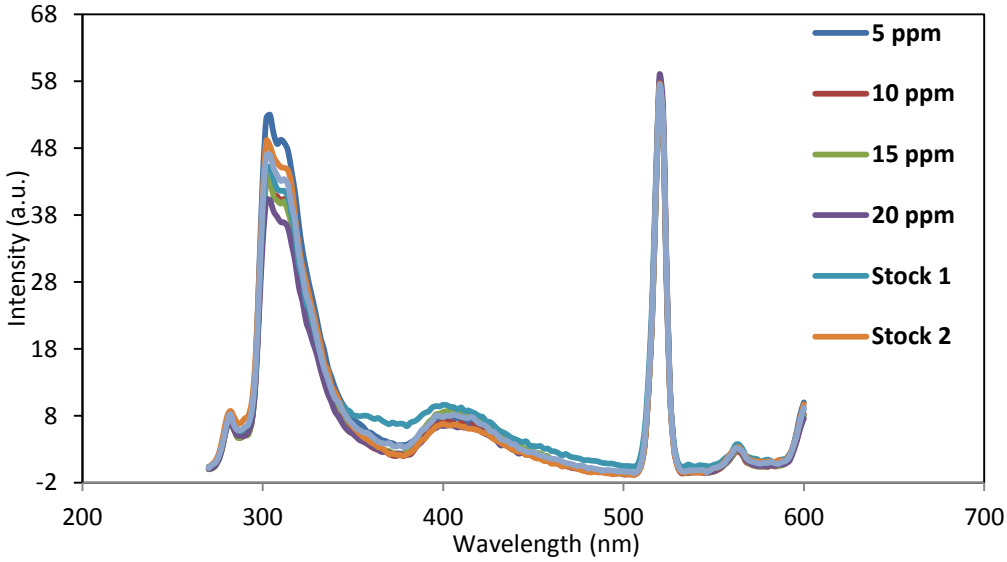

Figure 12: Fluorescence spectra of emulsified oil in n-hexane layer – third extraction, excitation 260 nm

3.2 TOC

The calibration curve presented in Figure 13 shows a linear trend of emulsified oil concentration with the mean area. In Table 6, the TOC of the samples prepared increased with the increase of emulsified oil, and even demonstrated an almost linear relationship as shown in Figure 14. Nonetheless, the TOC of the surfactant and water alone (SW) have a high value and even higher than the samples which have emulsified oil in them. This suggests that the hydrocarbons existing in the sample of emulsified oil were not completely digested, as they need higher temperature for a complete digestion of the emulsified oil samples. The TOC machine available in the laboratory can only operate at two temperatures; 680℃ and 720℃. Higher temperatures are not possible and this is a reason this technique could not be applied to this research work. Therefore, this method is not suitable for usage in this research using the existing instrument in the lab. Hence, it is recommended to conduct similar study on TOC instrument that can reach 1200℃.

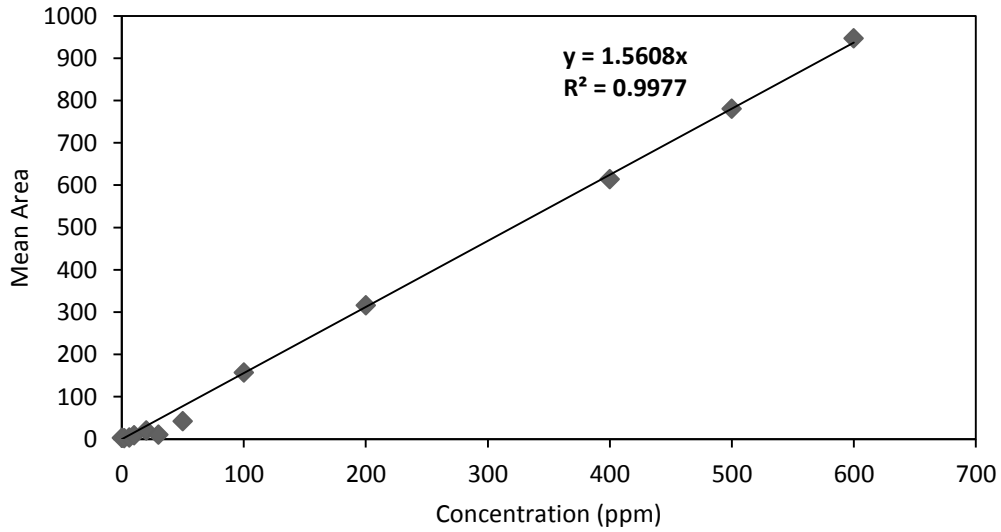

Figure 13: Calibration curve of the KPH standards, TOC at 720 ℃

Table 6: TOC for diluted concentrations of oil in surfactant/water solution, along with TOC of a no oil

Concentration (ppm), (diluted 100 times)	**TOC ($\frac{mg}{L}$)**
50	72.2
150	233
250	321
350	506
450	536
SW 1	400
SW 2	620
SW 3	670

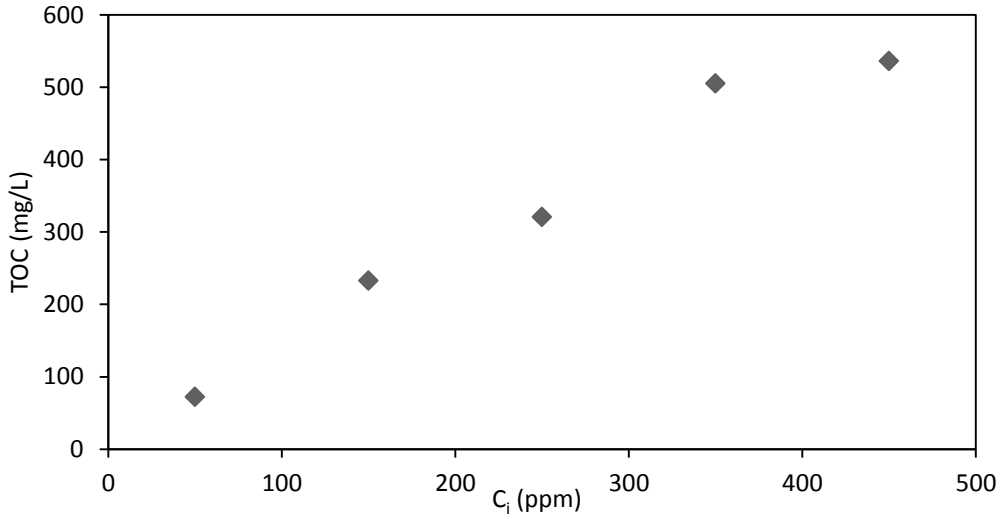

Figure 14: TOC versus concentration of oil in deionized water/ surfactant, TOC at 720 ℃

3.3 UV-Visible Spectroscopy

The UV-Visible spectra for oil in n-hexane at different concentrations are shown in Figure 15. Furthermore, the UV-Visible spectra for extracted surfactant in n-hexane are also displayed in Figure 16. Inspection of these figures reveals that at wavelength 275 nm, the absorbance is primarily due to the n-hexane extracted fraction of oil. Hence, this wavelength was used to lock the absorbance of oil in oil extracted samples. Figure 17 displays the calibration curve of oil in n-hexane at this wavelength. The limit of detection (LOD) of the calibration curve was calculated using equation 21 and was found to be 0.262 ppm [64].

$$LOD = 3.3 * \frac{standard\ deviation\ of\ blank}{slope\ of\ calibration\ curve} \tag{21}$$

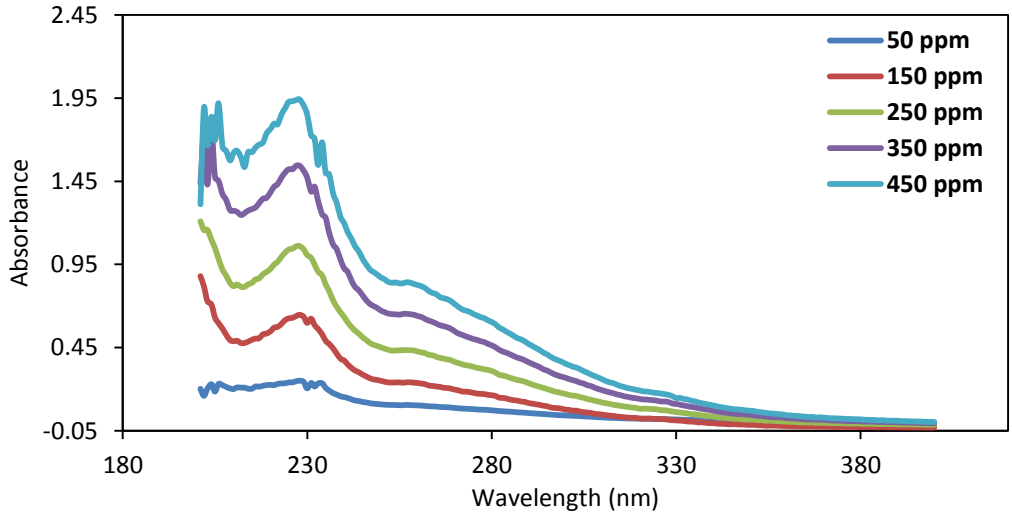

Figure 15: UV-Visible spectra of oil in n-hexane

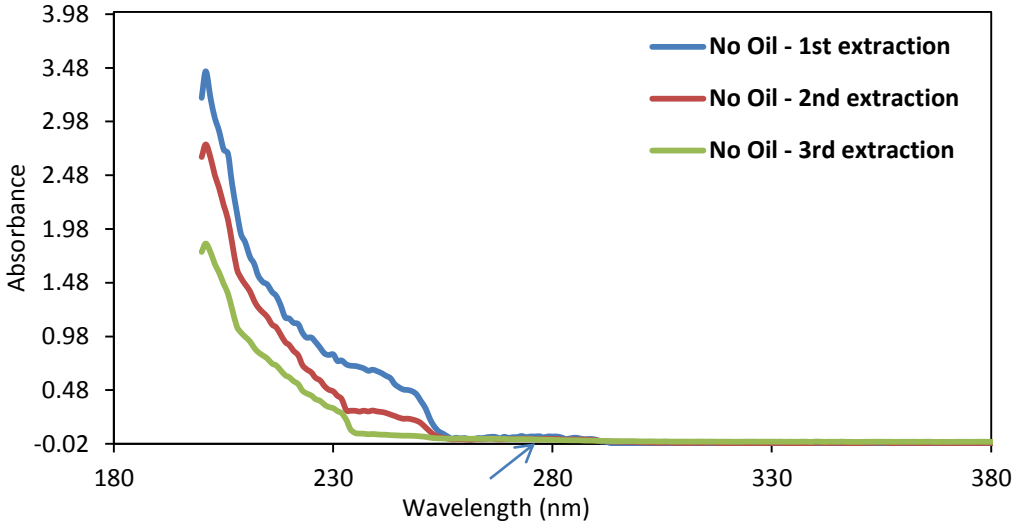

Figure 16: UV-Visible spectra of surfactant extracted in n-hexane

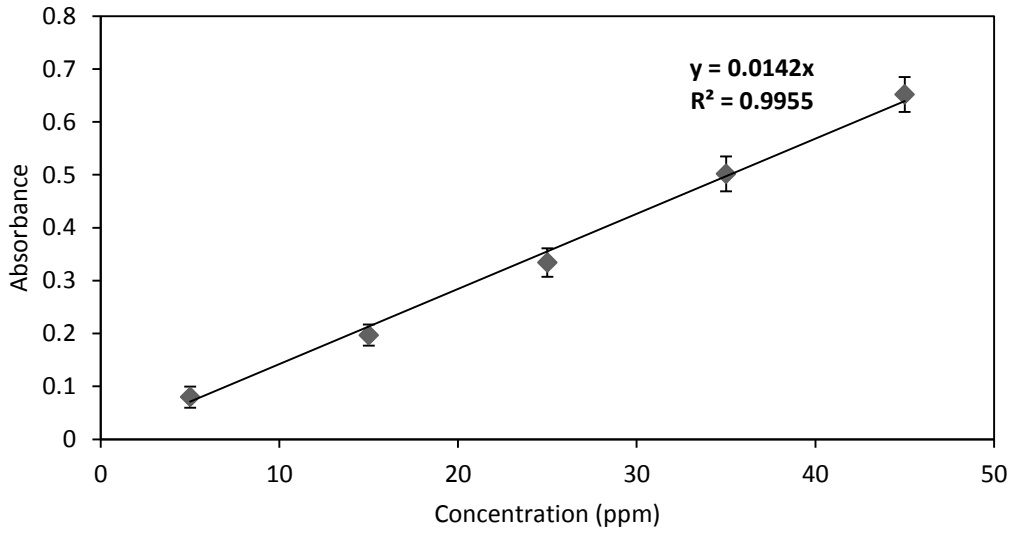

Figure 17: Calibration curve of oil in n-hexane, λ= 275 nm. The LOD: 0.262 ppm

Figures 18-20 illustrate the spectra of emulsified oil in n-hexane at different concentrations for the first extraction, second extraction, and the third. It is clear that as the third extraction was approached, the concentration of emulsified oil in the n-hexane layer was lower than the second extraction, and the latter was lower than the first extraction, and these results are consistent.

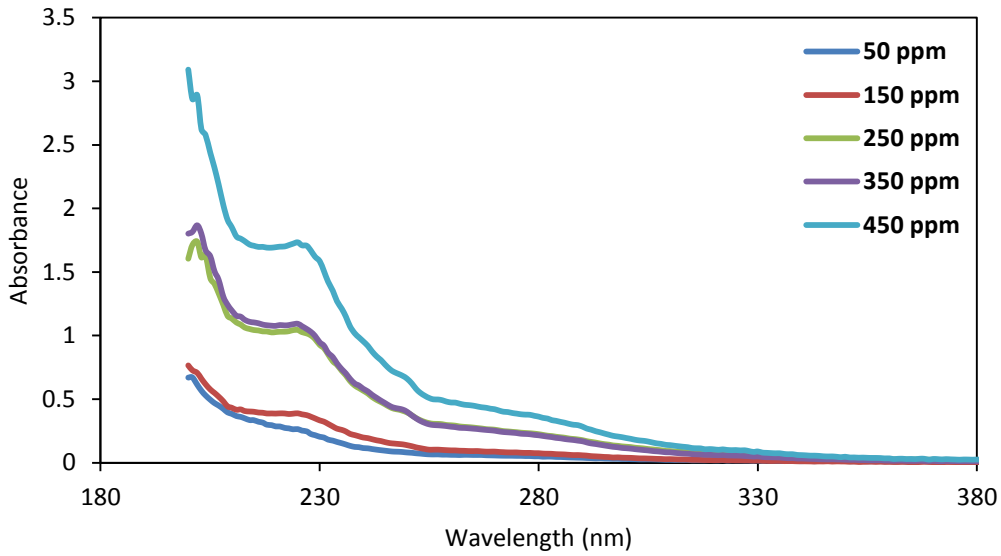

Figure 18: UV-Visible spectra of oil in n-hexane – first extraction, diluted 5 times

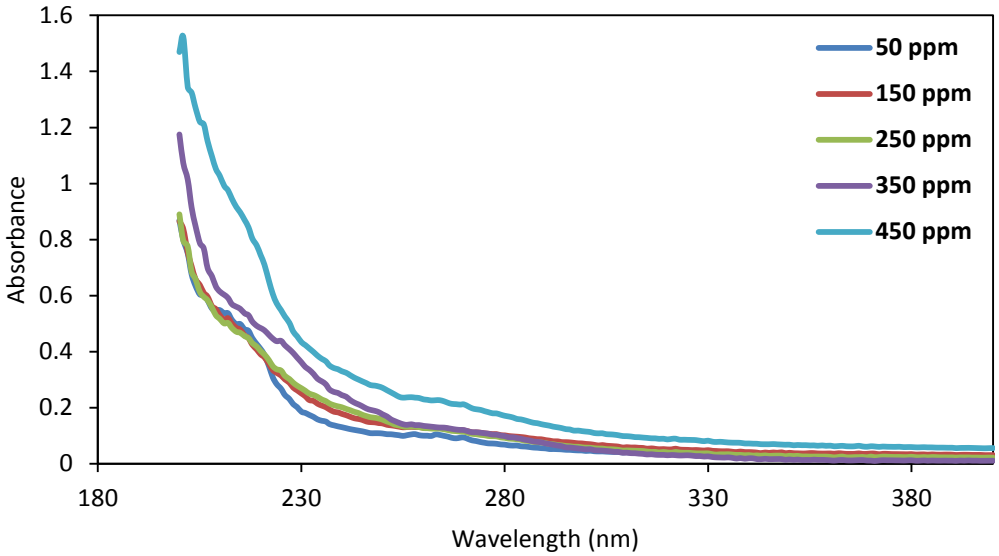

Figure 19: UV-Visible spectra of emulsified oil in n-hexane – second extraction

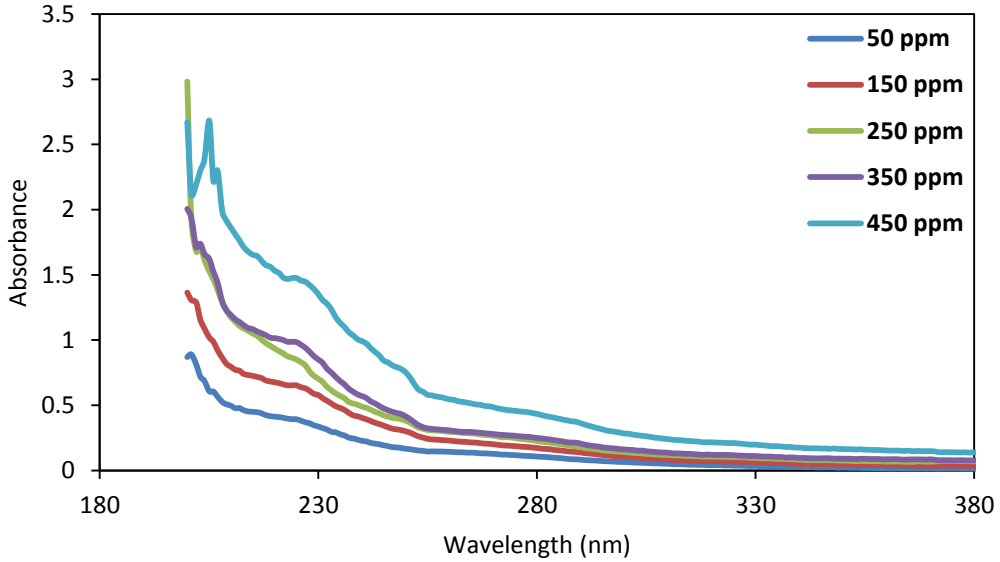

Figure 20: UV-Visible spectra of oil in n-hexane – third extraction

To validate the UV-Visible method, known concentrations of oil in emulsified water were prepared and the percent recovery by n-hexane extraction; followed by quantification using the above calibration curve (Figure 17) were determined. Tables 7-8 summarize the results as function of different extraction cycles. The results point out that the total percent recovery reaches almost 100 % for 50 ppm, and lowest at 150 ppm (50%). This renders this method as a powerful method to quantify oil in produced water. The percent oil recovery of n-hexane was calculated based on masses and not concentrations. So the final concentration for each sample was changed to mass by the multiplication of concentration into volume used. The trend shown in Figure 21 is not linear, but can underline the influence of emulsified oil concentration to its recovery. Higher concentrations may mean lower recoveries; however, a clear conclusion is made after studying the adsorption capacity of graphene that is able to treat emulsified oil in produced water, and, hence, the real recovery will be conveyed by how much an adsorbent can uptake.

Table 7: Concentrations of oil before and after n-hexane extraction, UV-Visible spectroscopy, λ= 275 nm

	Sample Concentration (ppm)	Final Concentration without correction (ppm)	Final Concentration (ppm)
	No oil	3.42	0.00
First Extraction	50	19.0	15.6
	150	28.6	25.2
	250	84.6	81.2
	350	96.3	92.9
	450	136	133
	No oil	1.90	0.00
Second Extraction	50	10.4	8.52
	150	13.2	11.3
	250	17.5	15.6
	350	18.8	16.9
	450	32.2	30.3
	No oil	0.80	0.00
Third Extraction	50	4.27	4.47
	150	6.22	5.42
	250	7.16	6.36
	350	7.67	6.87
	450	13.2	12.4

Table 8: Oil recovery by n-hexane, UV-Visible spectroscopy, λ= 275 nm

Sample Concentration (ppm)	Initial mass of oil (g)	Final mass of oil (g)	% Oil Recovery
50	2.48	2.50	99.2
150	3.77	7.50	50.2
250	9.29	12.5	74.3
350	10.5	17.5	60.0
450	15.8	22.5	70.1

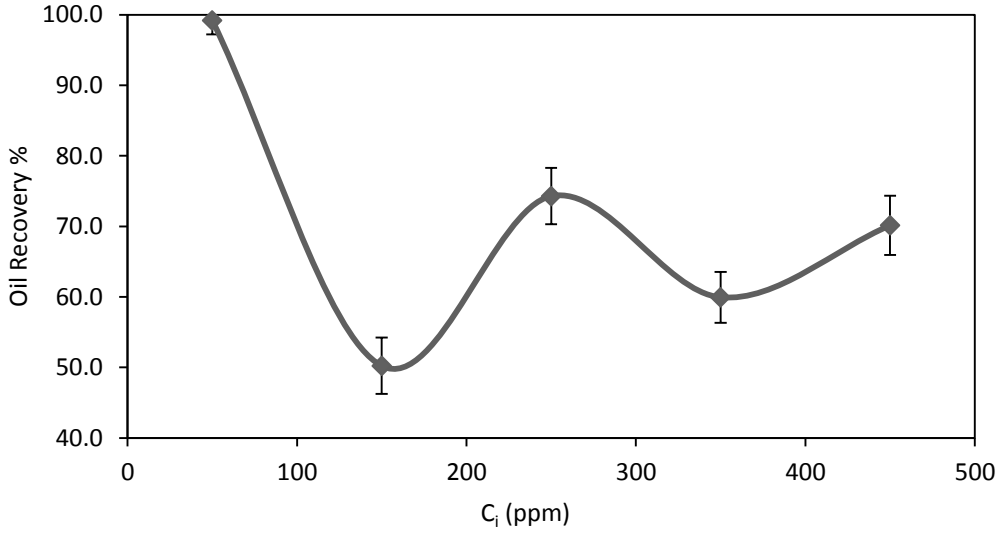

Figure 21: Oil recovery by n-hexane at different initial oil concentrations. Oil concentration measured by UV-Visible spectroscopy at λ= 275 nm

In conclusion, the UV-Visible spectroscopy in wavelength locked mode proved to eliminate the complexity of the sample read, and produce logical data compared to results obtained from the Fluorescence spectroscopy. On the other hand, the use of the Fluorescence spectroscopy to quantify emulsified oil has limitations due to the presence of surfactant, and as a result it is not an appropriate tool to quantify the emulsified oil in produced water. It should be pointed out that the Fluorescence technique is widely used to monitor oil in produced water [65]. Our finding points out that one should be careful in applying this technique due to the possibility of contaminants that might interfere with the Fluorescence of oil which will lead to serious deviation in the measured quantities.

UV-Visible spectroscopy is the optimum analytical tool for quantifying emulsified oil in produced water and will be used to quantify emulsified oil concentrations through the treatment of produced water in this research.

Chapter 4: Results and Discussion - Treatment of Emulsified Produced Water by Graphene

Several adsorbents were used to treat produced water (see section 1.2.10) as mentioned in the literature survey. Adsorption was found to be a powerful method for such purpose. In this work, the nanomaterial graphene was tested for its efficiency for removal of oil from emulsified produced water samples. The scanning electron microscope (SEM) presented a clear difference of the graphene surface before and after adsorption of emulsified oil. In addition, the effect of adsorbent dosage, contact time, initial pH, salinity, temperature and initial concentration of emulsified oil were investigated. Moreover, the adsorption isotherms and adsorption kinetics were also studied. The results are discussed below.

4.1 Characterization of Graphene

Characterization of graphene by SEM before and after adsorption illustrates the presence of oil onto the surface of graphene, which indicates the occurrence of adsorption. In Figure 22 (a) the voids and cavities of graphene are clear, where as in Figure 22 (b), the surface of graphene depicts that oil has occupied these voids. This is better visualized by the arrows in Figure 22 (a)-(b). Table 9 shows the main properties of graphene used in this study.

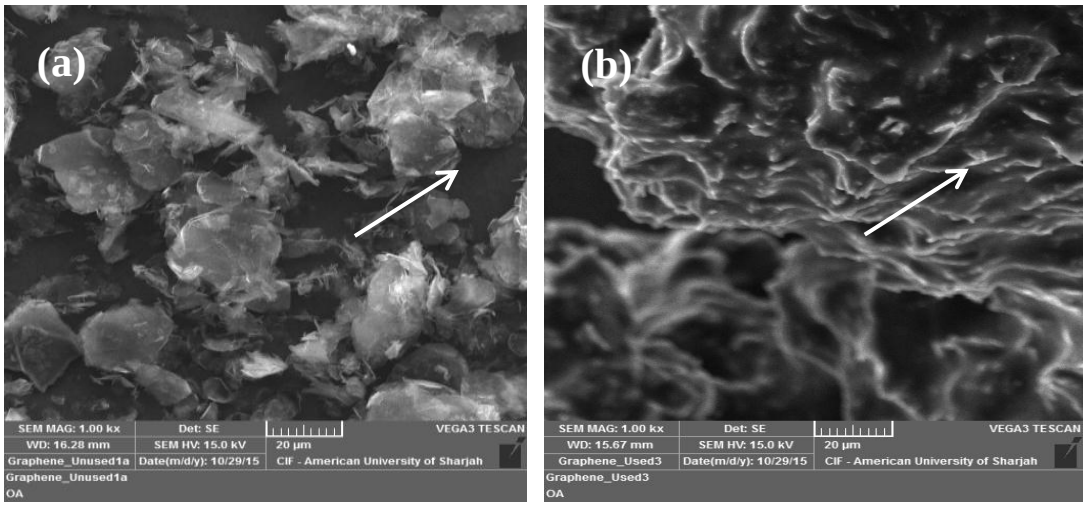

Figure 22: SEM of graphene (a) before and (b) after adsorption

Table 9: Properties of graphene used in this study [35]

Thickness	5 - 10 nm
Diameter	5 - 10 μm
Purity	< 99%
Density (Powderous)	~ 0.05 g/cm^3
Raman Spectra ID/IG Ratio	0.08
XRD 2-theta 26° peak	Negligible

4.2 Effect of Adsorbent Dosage

Figure 23 shows the removal efficiency of emulsified oil as a function of graphene dosage. Initially, removal efficiency increased with increasing in the graphene dosage. The removal efficiency remained constant for a dosage of graphene ≥ 3.00 (g/L) with a maximum efficiency of 70.0%. This could be due to the saturation of graphene, where all sites had adsorbed the maximum mass of oil. Therefore, 3.00 (g/L) of graphene was chosen as the optimum adsorbent dosage for this study.

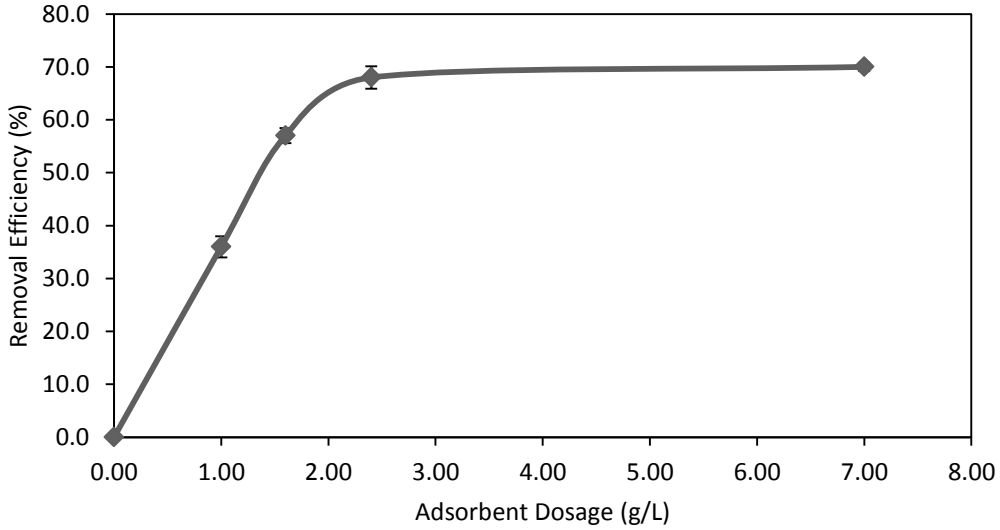

Figure 23: Effect of adsorbent dosage on the removal efficiency of emulsified oil by graphene. Initial oil concentration = 200 ppm, initial pH = 7.98±0.05, temperature = 25.0 ℃, contact time = 120 minutes, and shaking rate = 150 rpm

4.3 Effect of Contact Time

Figure 24 shows the removal efficiency of emulsified oil as a function of contact time while fixing the other parameters including the initial concentration of emulsified oil, adsorbent dosage, pH, and temperature. The removal efficiency of emulsified oil on graphene attained equilibrium in the first period of the process after 40 minutes. So at the beginning, increasing the contact time increased the removal efficiency of emulsified oil rapidly, after which any increase in contact time had no improvement in the removal. This is because adsorption was fast initially as the surface sites on graphene were empty, but after some time, graphene became saturated with emulsified oil. Also, it could be that repulsion between the graphene and emulsified oil molecules has occurred, causing no more adsorption to occur [66]. In this study one hour was chosen as the optimum time contact.

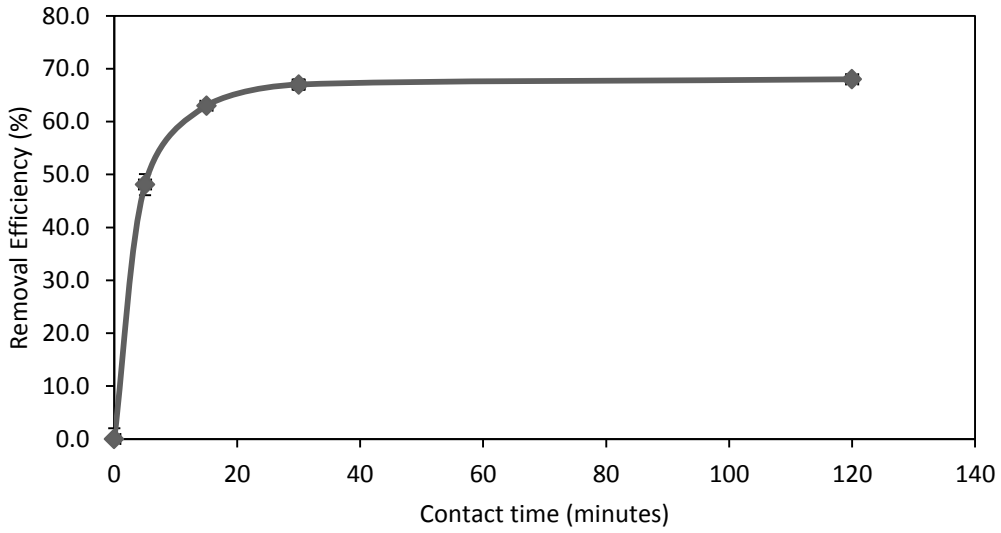

Figure 24: Effect of contact time on the removal efficiency of emulsified oil by graphene. Initial oil concentration = 200 ppm, initial pH = 7.98±0.05, temperature = 25.0 ℃, adsorbent dosage = 3.00 g/L and shaking rate = 150 rpm

4.4 Effect of Initial pH

Figure 25 shows the removal efficiency of emulsified oil as a function of initial pH. Other parameters including adsorbent dosage, contact time, and temperature were fixed. Lower pH decreases the removal efficiency while increasing the pH from 7.98 to 10.00 increases the removal efficiency from 70.0 % to 75.0 %.

This indicates that the removal efficiency of emulsified oil from the produced water is influenced by the pH, and this could be attributed to two reasons, the first is the presence of organic acids in ionic form at basic conditions, and the second is the possible influence of basic medium on the surface chemistry of graphene. Ions will tend to be unstable within the aqueous solution and thus binding on graphene's surface will provide the emulsified oil a better stable position [67]. pH higher than 10.00 had negligible effect on the removal efficiency. Hence, pH 10.00 was chosen to be the optimum initial pH for this study.

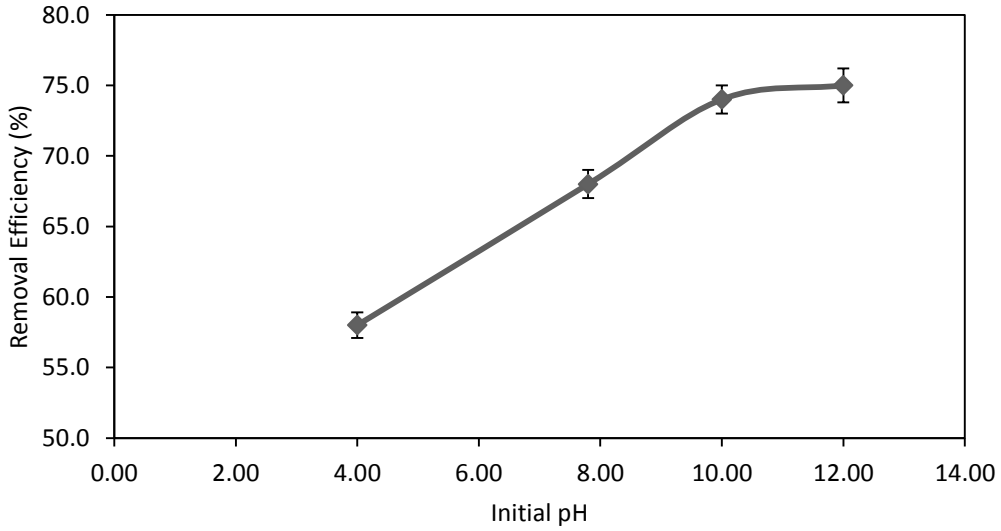

Figure 25: Effect of initial pH on the removal efficiency of emulsified oil by graphene. Temperature = 25.0 ℃, contact time = 60 minutes, adsorbent dosage = 3.00 g/L and shaking rate = 150 rpm

4.5 Effect of Salinity

Figure 26 presents the removal efficiency of emulsified oil as a function of salinity of the emulsion water. Other parameters including adsorbent dosage, contact time, initial pH, and temperature were fixed at optimum values. When the concentration of NaCl increased, the removal efficiency of emulsified oil was higher until 1500 (mg/L) where no relevant change in the removal efficiency was noticed. When the concentration of NaCl increases in the synthetic produced water, oil will become less stable within the aqueous phase and gets adhered on the surface of graphene easier. Water molecules will dissolve the NaCl with a higher affinity than it will dissolve the oil, and this might affect the stability of the emulsion, whence

increasing the chance of adsorption of oil onto the surface of graphene [47]. In this study, 1500 (mg/L) was chosen as the optimum NaCl concentration added.

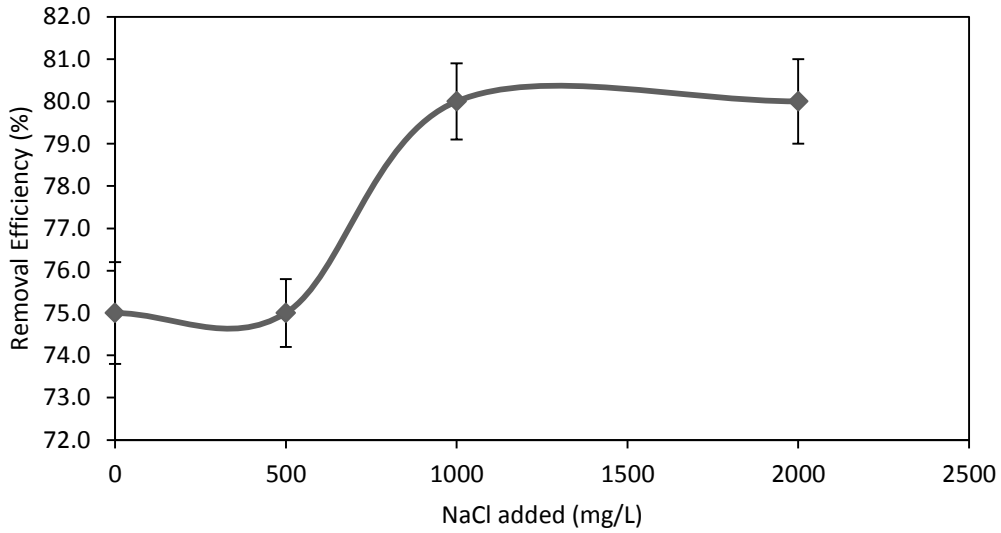

Figure 26: Effect of NaCl added on the removal efficiency of emulsified oil by graphene. Initial pH = 10.00±0.05, temperature = 25.0 ℃, contact time =60 minutes adsorbent dosage = 3.00 g/L, and shaking rate = 150 rpm

4.6 Effect of Temperature

Figure 27 presents the removal efficiency of emulsified oil as a function of temperature. Other parameters including adsorbent dosage, contact time, initial pH and NaCl added were fixed. When the temperature is increased from 25.0 ℃ to 40.0 ℃, the removal efficiency of emulsified oil decreases from 80.0 % to 60.0 %. This suggest that the physisorption process is exothermic, which means lower temperatures favor the adsorption of oil on graphene. In the next chapter, a thermodynamic study was conducted to better analyze the behavior of the adsorption process at these different temperatures.

4.7 Effect of Initial Concentration of Oil

Figure 28 demonstrates the decline in removal efficiency of emulsified oil when the initial concentration of this oil was increased. High removal efficiency of emulsified oil was shown at lower initial concentrations of oil, for instance, at 50.0 ppm; around 90.0 % of oil was removed, whereas around 70.0 % was removed at higher initial concentrations of oil in the range of 400-410 ppm. This may be due to the fact that the adsorbent activity sites were saturated with oil, thus reducing the chance of

oil to get adsorbed from the solution onto the graphene surface when the initial concentration of emulsified oil was increased.

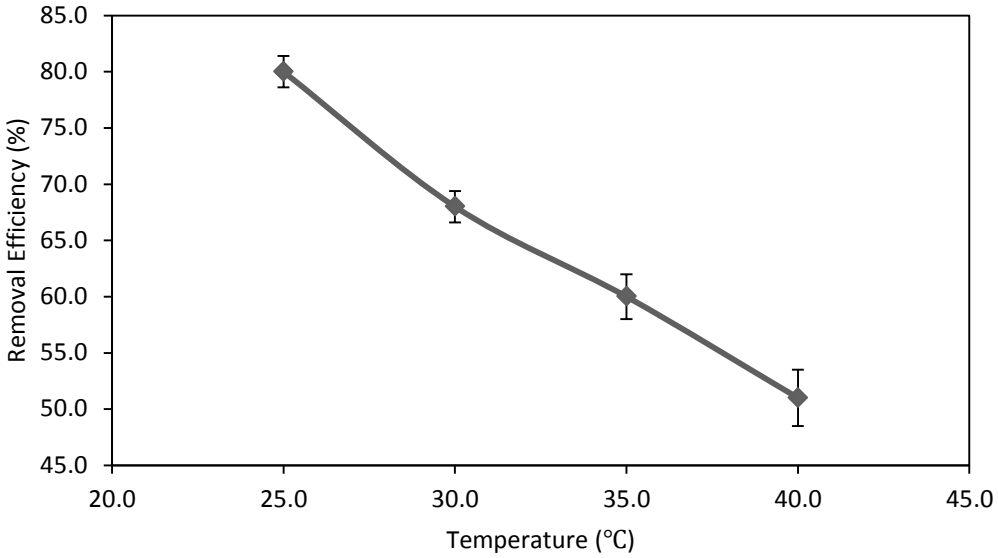

Figure 27: Effect of temperature on the removal efficiency of emulsified oil by graphene. Initial pH = 10.00±0.05, contact time = 60 minutes, NaCl added = 1500 mg/L, adsorbent dosage = 3.00 g/L, and shaking rate = 150 rpm

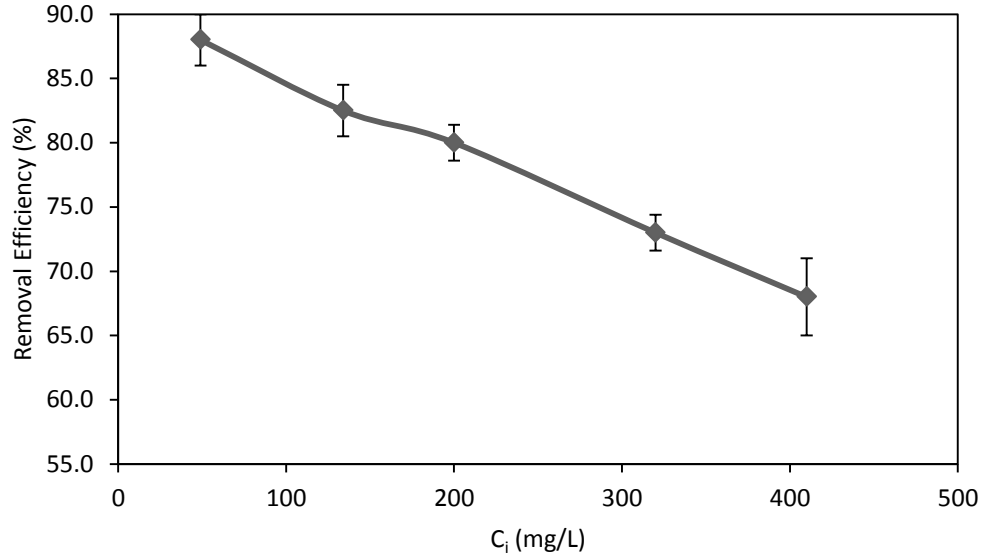

Figure 28: Effect of initial concentration of emulsified oil on the removal efficiency of emulsified oil by graphene. Initial pH = 10.00±0.05, temperature = 25.0 ℃, contact time =60 minutes, NaCl added = 1500 mg/L, adsorbent dosage = 3.00 g/L, and shaking rate = 150 rpm

4.8 Adsorption Isotherms Models

Adsorption isotherms are used to correlate the mass of adsorbed material per unit mass of the adsorbent at uniform surrounding conditions. To model the adsorption isotherms, the initial concentration of the emulsified oil were varied where other parameters were kept fixed including contact time, temperature, graphene dosage, initial pH and NaCl added. The equilibrium data were fitted using four different isotherms (see section 1.2.10.2):

Langmuir isotherm (Equation 7).

Freundlich isotherm (Equation 10).

Temkin isotherm (Equation 12).

Dubinin- Radushkevich (D-R) isotherm (Equation 13).

4.8.1 Langmuir isotherm. Figure 29 presents the Langmuir adsorption isotherm of the emulsified oil by graphene. As shown in table 10, the maximum adsorption capacity was obtained as 130 (mg/g). The R^2 value (0.988) of the Langmuir model may suggest that this model applies on the adsorption of emulsified oil onto graphene, however no final conclusion can be made until other isotherm models are examined.

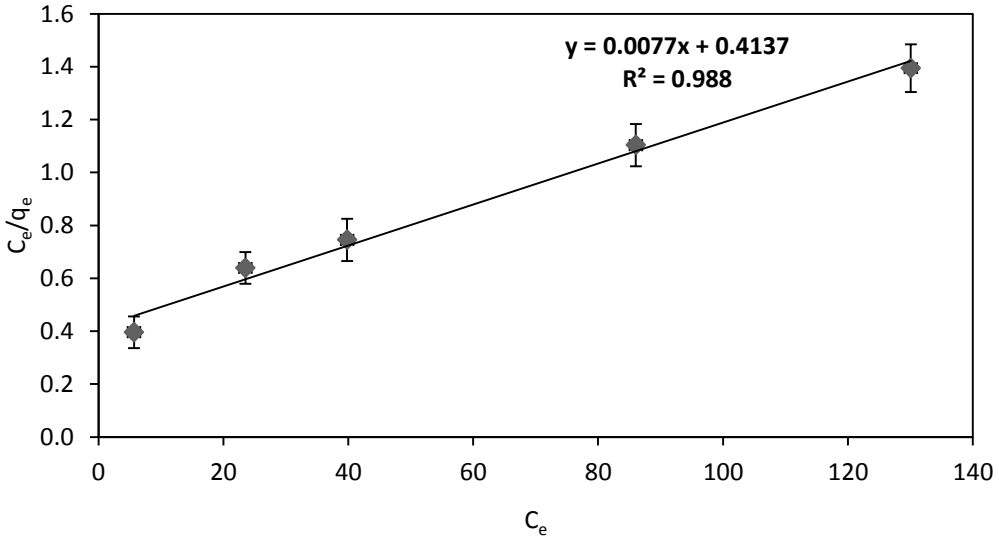

Figure 29: Langmuir adsorption isotherm for adsorption of emulsified oil on graphene. Initial pH= 10.00±0.05, temperature = 25.0 ℃, adsorbent dosage = 3.00 g/L, contact time = 60 minutes, NaCl added = 1500 mg/L and shaking rate = 150 rpm

4.8.2 Freundlich isotherm. In Figure 30, the value of k_f and n are found from the intercept and the slope respectively. k_f is an indication for the adsorption capacity of the adsorbent and usually used to compare the adsorption capacities of different adsorbents in a certain study, whereas $(1/n)$ indicates the influence of concentration on the adsorption capacity as well as the adsorption intensity [68]. If n = 1, the adsorption is linear and the adsorption energy is similar to all sites [69]. If the value of $(1/n)$ is less than one, it means favorability of adsorption [45], and that as the adsorption density increases, the attraction of adsorbate to the adsorbent rises. If the value of $(1/n)$ is greater than one, it indicates that the average binding strength will decrease if the surface coverage increases [70]. Generally, the value of n between 1-10 means good adsorption [71]. It should be pointed out that this isotherm shows a very good fit into linear form, with a high R^2 (0.9926).

4.8.3 Temkin isotherm. Figure 31 below presents the Temkin isotherm from which the slope reads the constant B, and from the intercept the constant A is calculated. The R^2 value is 0.962 which is lower than the value of R^2 obtained from Langmuir and Freundlich isotherms. This indicates that the equilibrium data of the adsorption of oil onto graphene is not well described by the Temkin isotherm. This is further proved by the non-linearity found in fitting this data (Figure 31). On the other hand, the Temkin isotherm is known to inappropriately present the data of liquid phase adsorption,which leads to the conclusion that the liquid phase adsorption is more complex than the gas phase adsorption [43].

4.8.4 Dubinin-Radushkevich (D-R) isotherm. Figure 32 illustrates a low value for R^2 (0.915), which is the lowest among the other isotherms namely Langmuir, Freundlich and Temkin isotherms. . This suggests that the equilibrium data of adsorption of oil onto graphene does not fit D-R isotherm. Also, the fitting of experimental data in this model presents a high deviation from linearity and this further shows that this isotherm cannot describe the removal of emulsified oil by graphene from produced water.

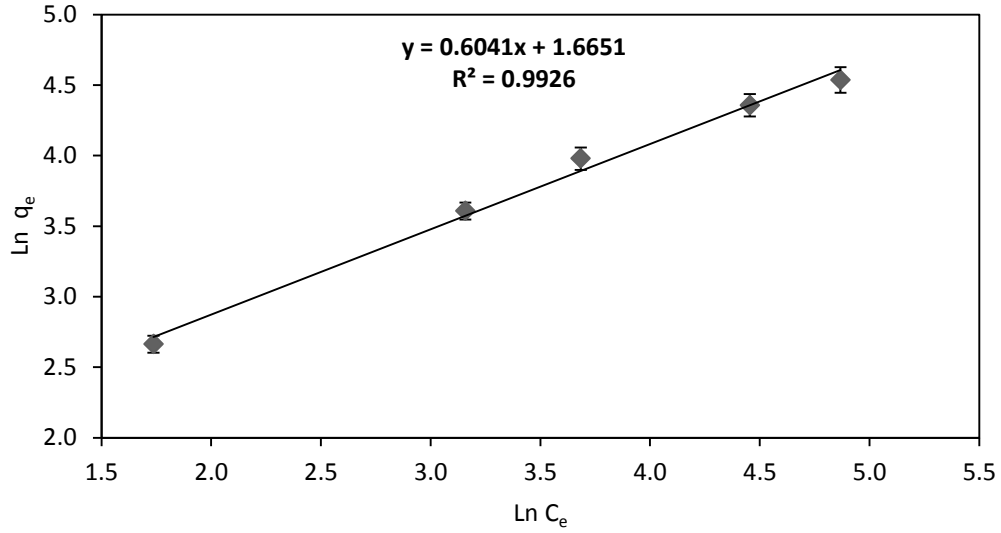

Figure 30: Freundlich adsorption isotherm for adsorption of emulsified oil on graphene. Initial pH= 10.00±0.05, temperature = 25.0 ℃, adsorbent dosage = 3.00 g/L, contact time = 60 minutes, NaCl added = 1500 mg/L and shaking rate = 150 rpm

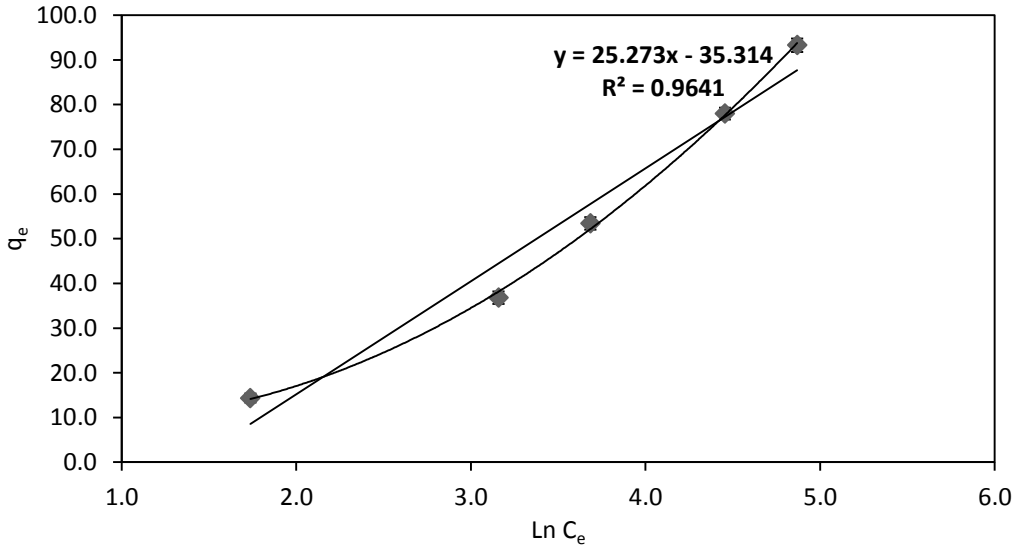

Figure 31: Temkin adsorption isotherm for adsorption of emulsified oil on graphene. Initial pH= 10.00±0.05, temperature = 25.0 ℃, adsorbent dosage = 3.00 g/L, contact time = 60 minutes and shaking rate = 150 rpm

Table 10 shows that the Freundlich isotherm model best fits the data obtained experimentally with the highest R^2 (0.993). This indicates that the adsorption of emulsified oil on graphene follows the heterogeneity of adsorption sites [43]. The produced water being a combination of versatile oil mixtures and organic compounds, their adsorption onto graphene will be different, and this is presented by Freundlich isotherm data, which describes well mixed wastes [72].

Table 10 presents the constants of the Freundlich isotherm; the value of n being more than 1 (1.66) suggests the favorability of adsorption of emulsified oil onto graphene.

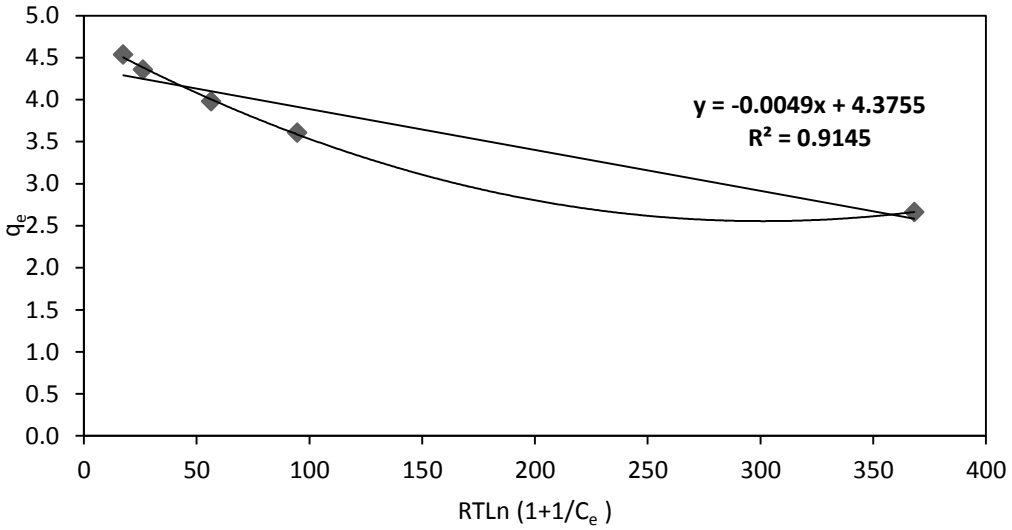

Figure 32: D-R adsorption isotherm for adsorption of emulsified oil on graphene. Initial pH= 10.00±0.05, temperature = 25.0 ℃, adsorbent dosage = 3.00 g/L, contact time = 60 minutes, NaCl added = 1500 mg/L and shaking rate = 150 rpm

Throughout this study, the adsorption capacity was calculated using Equation 22:

$$q_e = \frac{m_i - m_f}{m_g} \tag{22}$$

However, the maximum adsorption capacity of graphene following the Freundlich isotherm is calculated from the model using equation 23:

$$q_e = k_f C_e^{\frac{1}{n}} \tag{23}$$

where $k_f = 5.29$ and $n = 1.66$, the calculated maximum adsorption capacity q_m achieved at initial concentration of emulsified oil = 410 ppm equals 100 (mg/g). Appendix A.2 shows the data used for plotting the above isotherms.

Table 11 presents oil sorption capacities of different adsorbents in g oil / g adsorbent. Carbon nanotubes sponges and graphite showed high sorption capacities for treating oil. Adsorbents used to treat emulsified oil (oil with surfactants) had relatively lower sorption capacities, yet graphene used in this study had a higher sorption capacity compared to organo-clay and modified bentonite. It should be

noted that graphene used in this study is of industrial grade and its surface area is lower (~150 m^2/g) than graphene's theoretical surface area (2630 m^2/g).

Table 10: Equilibrium adsorption parameters of four different isotherm models for the removal of oil from synthetic produced water using graphene

Adsorption Isotherm Model	**Parameters**		**R^2**
Langmuir Isotherm	**b** $(\frac{\mathbf{L}}{\mathbf{mg}})$	0.019	0.988
	$\mathbf{q_m}$ $(\frac{\mathbf{mg}}{\mathbf{g}})$	130	
Freundlich Isotherm	$k_f\left(\frac{\mathbf{mg}^{(1-\frac{1}{n})}\mathbf{L}^{(\frac{1}{n})}}{\mathbf{g}}\right)$	5.29	0.993
	n	1.66	
Temkin Isotherm	$\boldsymbol{B}$ $(\frac{J}{mole})$	23.0	0.962
	A $(\frac{L}{mg})$	0.280	
D-R isotherm	$\boldsymbol{B_D}$	0.005	0.915
	$\boldsymbol{q_m}$ $(\frac{mg}{g})$	79.5	

Table 11: Oil sorption capacities of different adsorbents

Adsorbent	**Type of oil removed**	**Sorption capacity** $(\frac{g}{g})$	**Reference**
Carbon nanotube sponges	Oil spills	92.300	[73]
Magnetic expanded graphite	Crude oil	35.720	[74]
Acetylated rice straw	Machine oil	24.000	[75]
Hydrophobic silica aerogels	Liquid oil	15.100	[46]
Modified oil palm leaves	Crude oil	1.200	[76]
Barley straw	Standard mineral oil	0.583	[77]
	Canola oil	0.613	
Egg Shells	Crude oil	0.109	[37]
Organo-clay	Emulsified oil	0.067	[78]
Modified bentonite	Emulsified oil	0.049	[44]
This study -graphene	Emulsified oil	0.100	

4.9 Kinetic studies for the adsorption process

It is important to understand the kinetics of the adsorption process as this will assist in scaling up this system. Different predictive models are available in literature to exhibit the performance of the adsorption process when the contact time is varied between the adsorbent and the adsorbate. In this study, pseudo-first-order (Lagergen model) and pseudo-second-order kinetics were employed using data obtained from the experimental results (see Section 1.2.10.3).

4.9.1 Pseudo-first-order kinetics model (Lagergren model). Figure 33 below illustrates the experimental data fitted into Lagergren Model, and it is clear from the value of R^2 (0.891) that this model has a low response variable variation and hence, it cannot be used to predict kinetic data [79]. Furthermore, it shows non-linearity behavior and this verify the scattering of data out of the linear range.

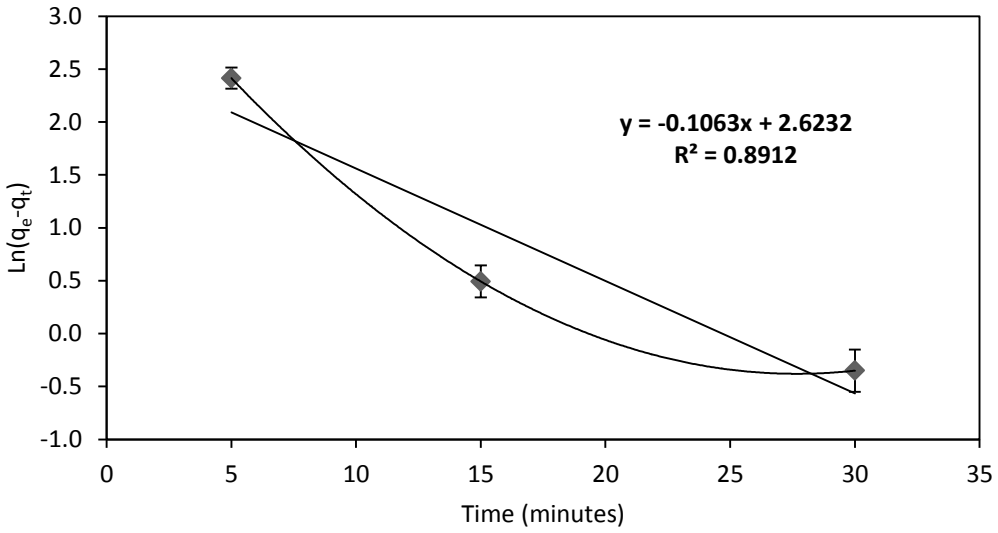

Figure 33: Pseudo-first-order kinetic model for adsorption of emulsified oil on graphene. Initial pH= 10.00±0.05, temperature = 25.0 ℃, adsorbent dosage = 3.00 g/L, contact time = 60 minutes, NaCl added = 1500 mg/L and shaking rate = 150 rpm

4.9.2 Pseudo-second-order kinetics model. In Figure 34, the R^2 (0.999) is high, and it means that 99.9 % of the variation in the response variable can be described in this model [79]. Also, the model showed a linear trend with an excellent fitting of data. This enforces that the experimental data fits the pseudo-second-order kinetic model.

Table 12 illustrates the parameters calculated using the kinetic models. The q_e value calculated by the pseudo-second-order model is closer to the experimental value of q_e (45.4 (mg/g)) by percentage difference 1.00% compared to the pseudo-first-order model with a very high percentage difference 106 %. Also, the R^2 (0.999) for the pseudo-second-order model is higher than that obtained from the Pseudo-first-order model (0.891). Hence, the adsorption process of emulsified oil on graphene follows the pseudo-second-order kinetic model. Appendix A.2 shows the data used for plotting the above kinetic models.

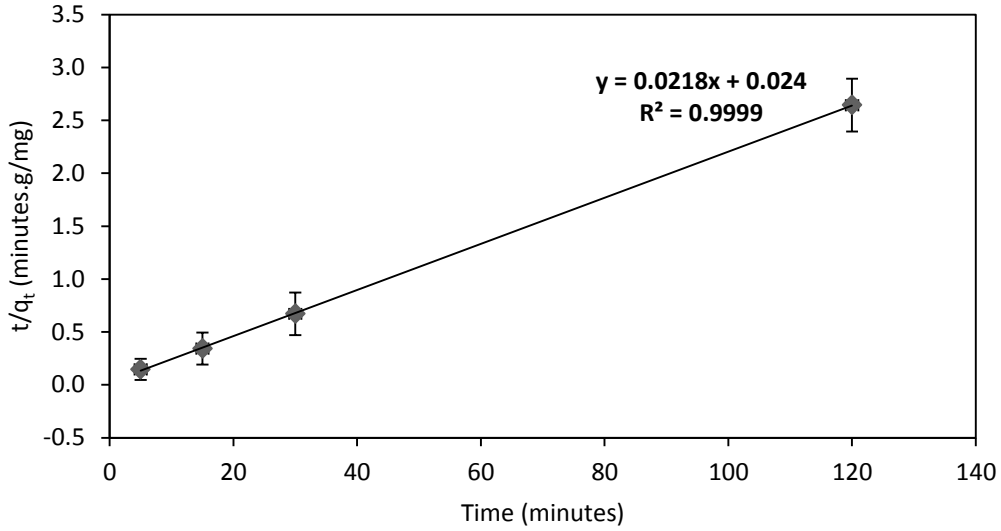

Figure 34: Pseudo-second-order kinetic model for adsorption of emulsified oil on graphene. Initial pH= 10.00±0.05, temperature = 25.0 ℃, adsorbent dosage = 3.00 g/L, contact time = 60 minutes, NaCl added = 1500 mg/L and shaking rate = 150 rpm

Table 12: Kinetic parameters of oil adsorption on graphene by pseudo-first-order and pseudo-second-order models

Adsorption kinetic Model	$\mathbf{C_{i(}}(\frac{mg}{L})$	200	$\mathbf{R^2}$
	$\mathbf{q_{exp}}(\frac{mg}{g})$	45.4	
	Parameters		
Pseudo-first-order kinetic model	k_1 $(\frac{1}{min})$	0.106	0.891
	$q_{e,calc}$ $(\frac{mg}{g})$	13.8	
Pseudo-second-order kinetic model	k_2 $(\frac{g}{mg\ min})$	0.020	0.999
	$q_{e,calc}$ $(\frac{mg}{g})$	45.9	

4.10 Thermodynamic Study

It is significant to understand the thermodynamic behavior of the adsorption process, and this can be done by calculating certain thermodynamic parameters including Gibbs free energy $\Delta G'$, enthalpy $\Delta H'$ and entropy $\Delta S'$. The equations below describe the mentioned parameters:

$$\Delta G' = -RTlnK' \tag{24}$$

$$K' = \frac{C_a}{C_e} \tag{25}$$

where, $\Delta G'$ is the apparent change in Gibbs free energy (J/mol), R is an ideal gas constant (used as 8.314 $(J/mol.K)$), T is the temperature in Kelvins (K), K' is the apparent equilibrium constant found using equation 25, C_a is the concentration of adsorbate on graphene at equilibrium (mg/L) and C_e is the concentration of adsorbate in solution at equilibrium (mg/L) [80].

$$lnK' = -\frac{\Delta H'}{RT} + \frac{\Delta S'}{R} \tag{26}$$

where, $\Delta G'$ is the apparent change in Gibbs free energy (J/mol), $\Delta S'$ is the apparent change in entropy $(J/mol.K)$, $\Delta H'$ is the apparent change in enthalpy (J/mol).

Plotting lnK' versus $(1/T)$ will yield $-\Delta H'/R$ as the slope and $\Delta S'/R$ as the intercept, from which the change in enthalpy and change in entropy can be read as shown in Figure 35. Equation 27 describes the adsorption/desorption process of emulsified oil on graphene, where [A] is the concentration of adsorbate (emulsified oil) and [S] is the concentration of graphene added. The compound [AS] is the adsorbed emulsified oil on graphene.

$$[A] + [S] \Leftrightarrow [AS] \tag{27}$$

There are two types of equilibrium constants; the first is the thermodynamic equilibrium constant which is equal to the multiplication of activity of products over the multiplication of activity of reactants. The second equilibrium constant is the apparent equilibrium constant which uses the concentrations rather than the activities multiplied by an activity coefficient. However, in this study, the equilibrium constant was calculated specifically at a constant equilibrium

concentration of emulsified oil at a constant temperature. Different apparent equilibrium constants were evaluated in order to process with the thermodynamic calculations.

Figure 35 shows a linear relationship of lnK' versus $(1/T)$ with the slope reading the apparent change of enthalpy. Table 13 presents the thermodynamic parameters calculated using equations 24-26. The results match the conclusion that the adsorption process is exothermic in nature because the apparent change in enthalpy is negative. Typically, the physisorption range of free energy values $(\Delta G^{'})$ is between −20.0 and 0 (KJ/mol) whereas the chemisorption range of free energy values is between −80.0 and −400 (KJ/mol) [81]. Because the values of $(\Delta G^{'})$ for this study are between -20 and 0 (KJ/mol); it means the process is physisorption. The apparent change in Gibbs energy $(\Delta G^{'})$ increases as the temperature is increased which means low feasibility of adsorption at higher temperatures. Furthermore, the apparent change in entropy being negative means a decline in the randomness of the solid/solution boundary of the adsorption process [82]. Appendix A.2 shows the data used for plotting the below Figure.

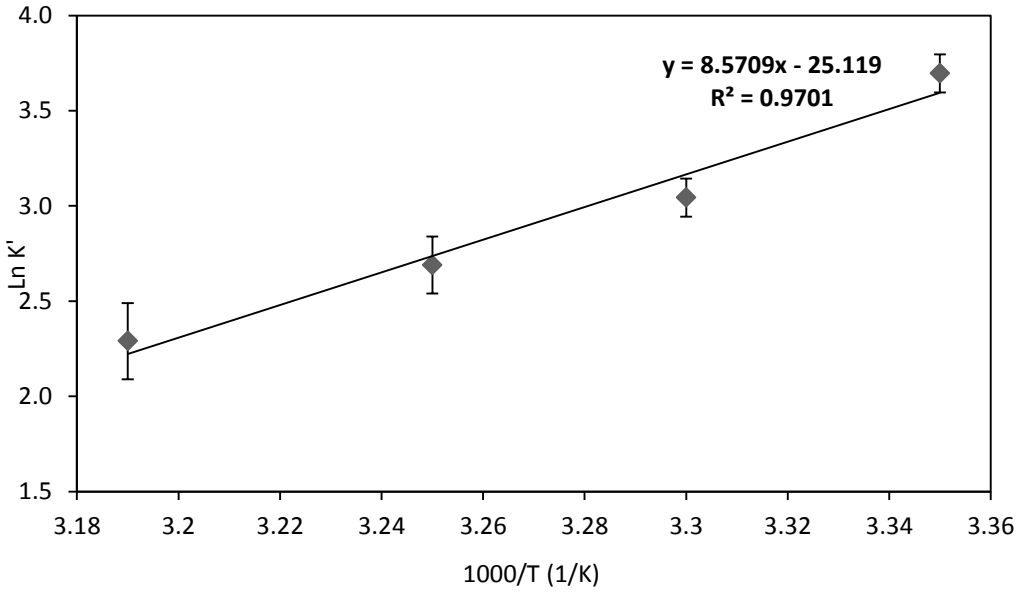

Figure 35: Thermodynamic study for adsorption of emulsified oil on graphene. Initial pH= 10.00, temperature = 25.0 ℃, adsorbent dosage = 3.00 g/L, contact time = 60 minutes, NaCl added = 1500 mg/L and shaking rate = 150 rpm

Table 13: Thermodynamic parameters of emulsified oil adsorption on graphene

$\Delta G'$ $(\frac{kJ}{mol})$					
$\mathbf{298.15\,K}$	$\mathbf{303.15\,K}$	$\mathbf{308.15\,K}$	$\mathbf{313.15\,K}$	$\mathbf{\Delta H'}$ $(\frac{kJ}{mol})$	$\mathbf{\Delta S'}$ $(\frac{kJ}{mol.K})$
-9.16	-7.67	-6.89	-5.96	-71.3	-0.21

4.11 Graphene Regeneration Study

4.11.1 Experimental. Produced water was prepared in the laboratory using a 225.0 mL solution of deionized water and surfactant with ratio of 60%:40% respectively and with an initial concentration of oil 500 ppm. 25.0 mL of each solution was introduced into 50.0 mL volumetric flasks and the optimum salinity and pH were adjusted using 5000 ppm NaCl and 1.0 M NaOH solutions, respectively. The volume was then adjusted to the mark using 60%:40% ratio of deionized water and surfactant. The solutions were then transferred to 100.0 mL conical flasks to which was added the optimum dosage of graphene of 6.00 (g/L) . Each solution was shaken at the contact time of 60 minutes at constant temperature of 25.0℃ in a thermostated shaker at 150 rpm. For each concentration, two runs and a control were prepared. Samples were filtered and then 5.0 mL of each filtrate was extracted three times using 9.0 mL n-hexane. The concentration of oil extracted in n-hexane for each sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm. After that, graphene was filtered and dried from the samples, then washed with n-hexane slowly to recover emulsified oil adsorbed by graphene. This graphene was then re-used similarly on prepared samples of produced water with an initial concentration of emulsified oil 250 ppm. The above procedure was repeated. It was found that n-hexane can recover up to 95.0 % of the adsorbed emulsified oil onto graphene after being used once, and 98.0 % after being used twice. On balance, graphene passed two cycles of adsorption/desorption process through which its percent removal efficiency of emulsified oil was tested.

4.11.2 Results. Figure 36 describes the impact of regeneration on removal efficiency of emulsified oil. The percent removal efficiency of emulsified oil was calculated similarly as described in appendix A.1 and it decreased from 80.0 % to 75.9% and from 75.0 % to 71.5 % over the two adsorption-regeneration cycles respectively. Since n-hexane did not recover 100.0 % emulsified oil from graphene, some voids in graphene were occupied after being used, and hence decreasing the chance for more oil molecules to get adsorbed on regenerated graphene. However, results imply that graphene can be re-used without significant change in its adsorption capacity.

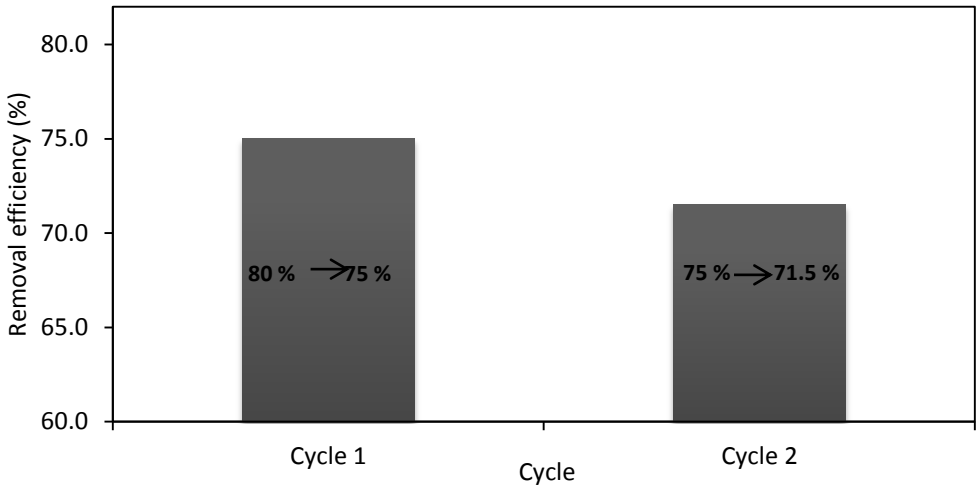

Figure 36: Regeneration study of graphene on removal of emulsified oil. Initial pH= 10.00±0.05, temperature = 25.0℃, adsorbent dosage for cycle 1 = 3.00 g/L, adsorbent dosage for cycle 2 = 1.50 g/L, contact time = 60 minutes and shaking rate = 150 rpm

4.12 Real Produced Water

Real produced water was obtained from Abu Dhabi National Oil Company (ADNOC), UAE. 50.0 mL of this produced water was introduced into three 100.0 mL conical flasks, after which the optimum adsorbent dosage of graphene 3.00 (g/L) was added into two of the samples, and the third served as a control. Samples were shaken in a thermostated shaker at 150 rpm. Then samples were filtered and 5.0 mL of each sample was extracted three times using 9.0 mL of n-hexane. The concentration of oil extracted in n-hexane for each sample was determined spectrophotometrically by measuring the absorbance of each solution at 275 nm. Results revealed that the initial concentration of emulsified oil in the real produced water was 268 (mg/L). The percent removal efficiency of emulsified oil was found to be 90.0 % and it was calculated similarly as described in Appendix A.1.

Chapter 5: Conclusions and Recommendations

In this work, a thorough literature review was completed which highlighted the importance of treating produced water, and some of the common techniques followed in the process of treatment. Below are the important conclusions regarding the treatment of produced water using graphene:

- UV-Visible spectroscopy is the optimum analytical tool to quantify emulsified oil in comparison with fluorescence spectrophotometer and Total Organic Carbon (TOC).
- Batch adsorption experiments for the adsorption of emulsified oil from synthetic produced water were studied by the use of graphene. Results collected present the following: Optimum adsorbent dosage = 3.00 (g/L) , optimum contact time = 60 minutes, optimum initial pH = 10.00, and optimum temperature = 25.0 ℃.
- The removal efficiency of emulsified oil increases with the increase of salinity in the synthetic produced water.
- Increasing the initial concentration of emulsified oil decreases the removal efficiency of emulsified oil.
- The experimental data obtained in this study best fits the Freundlich isotherm model, and follows the Pseudo-second-order kinetic model.
- The thermodynamics study conducted demonstrated that the adsorption process of emulsified oil onto graphene is rather physisorption, and that higher temperatures will decrease the removal efficiency of emulsified oil.
- Regeneration of graphene was done by using n-hexane to remove adsorbed emulsified oil on graphene. Throughout the two cycles of adsorption-desorption, the percent removal efficiencies of emulsified oil were 75.0% and 71.5% respectively.
- Graphene was able to treat a real sample of industrial produced water with an initial concentration of emulsified oil = 268 ppm, and reduce it to 26.8 ppm, which is equivalent to 90.0 % removal efficiency of oil.
- Maximum adsorption capacity of graphene was found to be 100 (mg/g) was evaluated using the Freundlich isotherm model.

- In this study, graphene as an adsorbent is capable of treating produced water efficiently and because it is economical to be employed in large scale applications, it can be an alternative to other adsorbents that treat emulsified oil in produced water. In spite of the relatively low adsorption capacity of graphene in removing emulsified oil, the percent removal efficiency at the concentrations calculated and those usually obtainable in the environment suggest that graphene can be useful for reducing the concentration of emulsified oil in produced water streams.
- It is recommended to use TOC instrument that can reach 1200 ℃ in order to achieve complete digestion of hydrocarbons present in the oil.
- Study using flow method was not achieved in this work due to the graphene structure which is very fine powder with small thickness (5 – 10 nm). Stabilizing the bed was difficult, as neither glass wool nor sand were able to prevent graphene from flowing out with the effluent. As a recommendation, the packed bed column requires granular particles of graphene, unlike the graphene that was used for the batch experiments.

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Appendix

A.1 Sample calculation for optimum adsorbent dosage

For the control:

Table 14: The three hexane layers for the control - optimum adsorbent dosage

First Extraction	Run no.	Absorbance	Final Concentration after dilution 10 times (ppm)	Final Concentration before dilution (ppm)	Mass of oil in hexane layer (mg)		Final Mass in hexane layer(mg)
	Run 1	0.11823	8.326	83.26	0.749	Average	0.784
	Run 2	0.12919	9.098	90.98	0.819		
Second Extraction	Run no.	Absorbance	Final Concentration after dilution 2 times (ppm)	Final Concentration before dilution (ppm)	Mass of oil in hexane layer (mg)		Final Mass in hexane layer(mg)
	Run 1	0.12983	9.143	18.286	0.165	Average	0.155
	Run 2	0.11283	7.946	15.892	0.143		
Third Extraction	Run no.	Absorbance	Final Concentration after dilution (ppm)	Final Concentration before dilution (ppm)	Mass of oil in hexane layer (mg)		Final Mass in hexane layer(mg)
	Run 1	0.10823	7.622	7.622	0.067	Average	0.072
	Run 2	0.11919	8.394	8.394	0.076		

Run 1:

Final concentration with dilution 10 times:

$$\frac{Absorbance}{slope\ of\ calibration\ curve} = \frac{0.11823}{0.0142} = 8.32606\ ppm$$

Final concentration with correction of dilution:

$$= 8.32606 * 10 = 83.2606\ ppm$$

Mass of oil in hexane layer:

$$Final\ concentration\ in\ hexane\ layer * volume\ of\ hexane\ used = 83.2606 * 0.009 = 0.749\ mg$$

Final mass in hexane layer:

$$\frac{mass\ of\ oil\ in\ hexane\ layer\ for\ Run\ 1 + mass\ of\ oil\ in\ hexane\ layer\ for\ Run\ 2}{2} = 0.784\ mg$$

Concentration of oil in the water layer:

$$\frac{Mass\ of\ oil\ in\ hexane\ layer}{Volume\ of\ water\ layer\ extracted} =$$

$$\frac{0.784\ mg + 0.155\ mg + 0.072\ mg}{0.005\ L} = 202\ ppm$$

Final mass of oil:

$$Concentration\ of\ oil\ in\ the\ water\ layer * initial\ volume\ of\ sample\ prepared = 202\ ppm * 0.05\ L = 10.1\ mg\ of\ oil.$$

Initial mass of oil:

$$Initial\ concentration\ of\ oil\ of sample * initial\ olume\ of\ sample\ prepared = 250.0\ ppm * 0.05\ L = 12.5\ mg\ of\ oil.$$

Oil recovery % by hexane:

$$\frac{Final\ mass\ of\ oil}{Initial\ mass\ of\ oil} * 100 = \frac{10.1\ mg}{12.5\ mg} * 100 = 80\ \%$$

So n-hexane can read 80 % of the oil, which is equivalent to 10 g.

For adsorbent dosage 3.00 (g/L):

Table 15: The three hexane layers for graphene dosage 3.00 g/L - optimum adsorbent dosage

First Extraction	Run no.	Absorbance	Final Concentration (ppm)	Mass of oil in hexane layer (mg)		Final Mass in hexane layer(mg)
	Run 1	0.26027	18.326	0.165	Average	0.165
	Run 2	0.26074	18.362	0.165		
Second Extraction	Run no.	Absorbance	Final Concentration (ppm)	Mass of oil in hexane layer (mg)		Final Mass in hexane layer(mg)
	Run 1	0.13687	9.639	0.087	Average	0.088
	Run 2	0.13837	9.747	0.088		
Third Extraction	Run no.	Absorbance	Final Concentration (ppm)	Mass of oil in hexane layer (mg)		Final Mass in hexane layer(mg)
	Run 1	0.10788	7.597	0.068	Average	0.067
	Run 2	0.10234	7.207	0.065		

Run 1:

Final concentration with dilution 10 times:

$$\frac{Absorbance}{slope\ of\ calibration\ curve} = \frac{0.26027}{0.0142} = 18.326\ ppm$$

Mass of oil in hexane layer:

$$Final\ concentration\ in\ hexane\ layer * volume\ of\ hexane\ used = 18.326 * 0.009$$
$$= 0.165\ mg$$

Final mass in hexane layer:

$$\frac{mass\ of\ oil\ in\ hexane\ layer\ for\ Run\ 1 + mass\ of\ oil\ in\ hexane\ layer\ for\ Run\ 2}{2}$$
$$= 0.165\ mg$$

Concentration of oil in the water layer:

$$\frac{Mass\ of\ oil\ in\ hexane\ layer}{Volume\ of\ water\ layer\ extracted} =$$

$$\frac{0.165\ mg + 0.088\ mg + 0.067\ mg}{0.005\ L} = 64.0\ \text{ppm}$$

Final mass of oil:

$$Concentration\ of\ oil\ in\ the\ water\ layer * initial\ volume\ of\ sample\ prepared\ = 64.0\ ppm * 0.05\ L = 3.2\ mg\ of\ oil.$$

Initial mass of oil:

$$Initial\ concentration\ of\ oil\ of sample * initial\ olume\ of\ sample\ prepared = 250.0\ ppm * 0.8 * 0.05\ L = 10.0\ mg\ of\ oil.$$

Removal efficiency % by graphene:

$$= \frac{initial\ mass\ of\ oil - final\ mass\ of\ oil}{Initial\ mass\ of\ oil} * 100 = \frac{10.0 - 3.2}{10.0} * 100 = 68\ \%$$

Table 16: Optimum parameters of removal of emulsified oil using graphene

Parameters studied	Optimum value
Graphene dosage	3.00 g/L
Contact time	60 minutes
Initial pH	10.00
Salinity	1500 mg/L
Temperature	25.0℃

A.2 Tables for isotherms, kinetics and thermodynamics

Table 17: Values used in isotherm models

C_i (ppm)	C_e (ppm)	q_e $(\frac{mg}{g})$	C_e/q_e $(\frac{L}{g})$	R_L
49.00	5.68	14.3	0.396	0.523
134.0	23.5	36.8	0.639	0.286
200.0	39.8	53.4	0.745	0.218
320.0	86.0	78.0	1.10	0.144
410.0	130.1	93.3	1.40	0.116

Table 18: Values used in kinetic models

C_i (ppm)	200					
m_i (mg)	10.0					
Time (minutes)	C_e (ppm)	q_e $(\frac{mg}{g})$	q_t $(\frac{mg}{g})$	$q_e - q_t$ $(\frac{mg}{g})$	$\ln(q_e - q_t)$	t/qt $(\frac{g.mins}{mg})$
5	97.3	45.4	34.2	11.2	2.41	0.146
15	68.7	45.4	43.8	1.64	0.493	0.343
30	65.9	45.4	44.7	0.704	-0.351	0.671
120	63.8	45.4	45.4	0.00		2.64

Table 19: Values used in the thermodynamic study

T (℃)	T (K)	q_e $(\frac{mg}{g})$	Mass of oil adsorbed (mg)	C_a (ppm)	C_e (ppm)	K'	lnK'	1/T
25	298.15	53.4	8.01	160	39.8	40.3	3.70	0.00335
30	303.15	41.4	6.21	124	59.2	21.0	3.04	0.00330
35	308.15	32.4	4.87	97.3	66.1	14.7	2.69	0.00325
40	313.15	22.5	3.46	69.2	68.2	9.12	2.21	0.00319

VITA

Lamis Abou Chacra was born on July 10, 1992 in Dubai, United Arab Emirates. She graduated from high school in 2009 from Al Ma'arifa International School. She studied for her Bachelor's degree in Chemical Engineering at the American University of Sharjah and graduated in fall 2013, with a minor in Enviromental and Water engineering. In Spring 2014, she started her graduate studies at the American University of Sharjah for the Masters in Chemical Engineering, and has been awarded a funded scholarship as well as graduate assistantship. She contributed to two published papers: "Group Contribution Methods for Estimation of Ionic Liquid Heat Capacities: Critical Evaluation and Extension. Chemical Engineering & Technology" and "Adsorption Process of Sulfur Removal from Diesel Oil Using Sorbent Materials." In addition, she successfully completed ISO/TS 29001 Lead Implementer training course in spring 2015.