QATAR UNIVERSITY

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NOVEL ADSORBENTS FOR THE REMOVAL OF OIL FROM PRODUCED WATER

BY

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ABSTRACT

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Produced water is water that is brought up to the surface of the well during oil and gas operations. Almost all oil and gas wells generate huge amounts of produced water as part of the production process. These large volumes of water are estimated to be over 437 million barrels per day. This number most likely will continue to rise due to the increase in energy demand. For the sustainable development of oil and gas fields, managing produced water in an effective manner is a key issue. There are several methods explored for produced water management including recycle, reinjection and disposal back into the environment and all of which require an effective treatment method prior to reuse. Adsorption, a prominent method for water treatment due its high efficiency at low concentrations, is implemented widely for tertiary treatment. Due to its high adsorption capacity, activated carbon has always been the most commonly used adsorbent in the industries worldwide. However, due to its high cost of regeneration, it is becoming a less attractive option. Recently, synthetic resins are showing potential as an alternative to activated carbon adsorbents. In this study, the application of four commercial synthetic resins for the removal of emulsified oil from produced water was investigated.

Key experimental parameters such as adsorbent dosage, contact time, initial oil concentration and pH were evaluated for Optipore L493, Amberlite IRA 958, Amberlite XAD 7 and Lewatit AF 5. Oil removal rates upwards of 98% were achieved using AF 5, XAD 7 and L493. IRA 958 recorded very modest removal rates of less than 25%. Isotherm data werefurther investigated and fitted using Langmuir, Freundlich, Toth, Flory Huggins and Dubinin-Radushkevich models. The Freundlich model showed the best representation of the adsorption process onto XAD 7. The Toth model presented the best illustration of the adsorption process onto L 493 while Dubinin-Radushkevich best described the removal using AF 5 resin. Kinetic studies assessing the rate of removal for each resin were conducted and results fitted using pseudo-first and second order equations in addition to intraparticle diffusion models. Experimental results were best fitted using pseudo second order kinetics. The study confirmed the applicability of the resins for the removal of oil from produced water.

Chemical regeneration is conducted to study the synthetic resin’s ability for regeneration and reuse. Solvents used for this part of the study include two organic solvents (methanol and ethanol), 1 M NaOH and D.I. water heated to 65 °C. Experimental results indicate that XAD 7 was completely regenerated using both organic solvents. AF 5 was also completely regenerated using methanol and D.I. water, while NaOH completely regenerated L493. To further support this data, resins were further analyzed at a clean state and after regeneration using an organic elemental analyzer.

DEDICATION

To my father and mother who taught me the value of education and to my friends at Qatar university who made this ride an enjoyable one

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

AC	Activated carbon
ACT	Automated chemostat treatment
API	American petroleum institute
BET	Brunauer-Emmett-Teller
BOD	Biological oxygen demand
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
COD	Chemical oxygen demand
D.I. water	Deionized water
DOC	Dissolved organic compounds
DR model	Dubinin-Radushkevich model
DVB	Divinylbenzene
EDX	Energy dispersive X-ray spectroscopy
EPA	Environmental protection agency
FTIR	Fourier transform infrared
MF	Microfiltration

NF	Nanofiltration
NORM	Naturally occurring radioactive materials
PAH	Polyaromatic hydrocarbons
ppm	Part per million
RO	Reverse osmosis
RPM	Rotations per minute
SEM	Scanning electron microscopy
TC	Total carbon
TDS	Total dissolved solids
THM	Trihalomethanes
IC	Total inorganic carbon
TOC	Total organic carbon
TORR	Total oil remediation and recovery
UF	Ultrafiltration
UV light	Ultra-violet light
VOC	Volatile organic compounds

CHAPTER 1: INTRODUCTION

Produced water is generally defined as waste byproduct generated in the exploration and production of oil and gas from offshore and onshore wells [1]. It can also be defined as the water extracted from underground formations and brought up to the surface along with the oil and gas. Due to its high-volume generation, produced water may cause impelling environmental challenges and therefore, it is considered a key factor in the economic exploitation of gas- and oilfields. The presence of this water is mainly due to seawater or freshwater that is trapped along with oil and gas between layers of impermeable rocks in naturally occurring underground hydrocarbon formations [2]. Moreover, it is additional water that is injected into reservoirs to maintain well hydraulic pressure as a technique to enhance oil recovery.

The constituents of produced water depend on natural geological formation and the type of hydrocarbons being produced [3]. Figure 1 gives a brief description of the contaminants that normally exist in produced water [4].

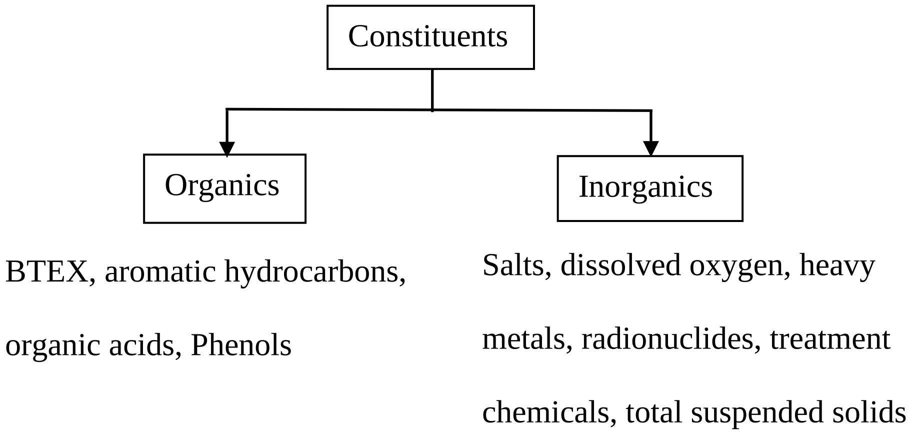

Figure 1. General constituents of produced water

This effluent contains a complex mixture of various pollutants; nonetheless, it can be broadly classified into organics and inorganics.

Oil production normally generates substantial amounts of wastewater during the production phase and the volume typically increases along with the life of the well [5]. Each year 21 billion barrels of produced water are generated from around million wells in the United States alone and more than 50 billion barrels are produced worldwide [6]. It has been reported that for every one barrel of oil there exists 3 to 5 barrels of water on average [3]. As can be seen from Figure 2, in regions where wells are at a higher maturity level, the water to oil ratio increases and in some cases the ratio goes up to 14 as is the case in Canada [7]. Thus, it can be said that the petroleum industry is producing water more than any other fluid.

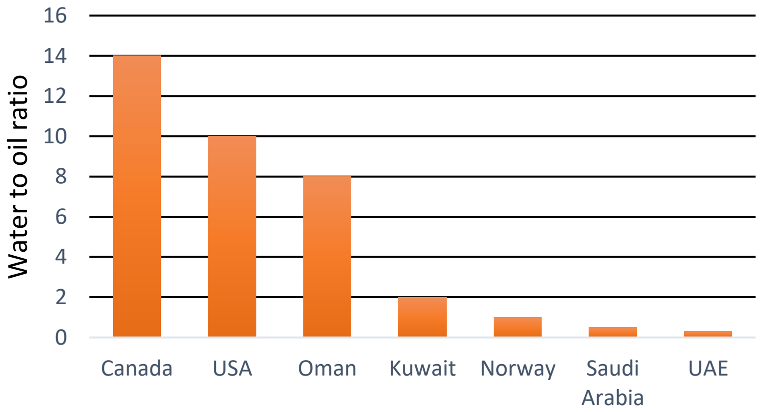

Figure 2. Water to oil ratio by region [7].

There are several methods to manage produced water and among those techniques is discharge back into the environment [2]. Due to the heterogeneity of contaminants present in produced water, strict laws are placed by governmental legislation for discharge limits. The allowable amount of oil and grease in discharge effluents varies from one country to another. The regulatory limit of oil concentration in produced water set by The Department of Energy and Climate Change in the UK is 30 mg/L [8]. US regulations limit produced water discharge to a monthly average of 29 mg/L and a daily maximum of 42 mg/L [9]. Australian EPA permits a maximum allowable petroleum hydrocarbons of 30 mg/L [10]. In south America, the discharge regulations are more stringent. In Ecuador and Colombia, the discharge limit of oil and grease is 15 mg/L. In Argentina, the discharge limit is reduced even further to 5 mg/L [10]. Strict legislation are also applied in the Middle East where the discharge limit for oil and grease is less than 10 mg/L [11].

Due to strict environmental regulations, the cost of treating produced water to the permitted discharge limit is becoming increasingly expensive. Technologies available to treat produced water can be generally classified into two categories: conventional and advanced treatment technologies [12]. Conventional techniques such as hydrocyclones and skimmers are usually employed for the removal of non-dissolved constituents as a primary separation solution where the quality of the exit effluent normally ranges from 150 – 50 mg/L oil in water concentration [13]. As the size of organic compounds decreases, the more difficult it becomes to remove these compounds using conventional oil/water separators. Advanced and more sophisticated technologies are required at this stage of treatment. Among these technologies are membrane [14]–[18] adsorption technologies. Adsorption is a premier and established method for further purifying water as a polishing step. Due to its simplicity, ease of operation, relatively less generation of sludge, and its adequate regeneration capacity, adsorption is increasingly receiving attention in the water treatment industry [19]. Adsorption is currently employed in companies worldwide such as Siemens as a polishing step for produced water treatment prior to discharge utilizing walnut shells as adsorbents [20].

The criteria for the selection of novel adsorbents for removal of oils from water is based on several factors that include sorption capacity, sorption rate, recyclability, high porosity, adsorbent cost and surface hydrophobicity [21]. Considerable removal of oil from water is typically associated with the presence of high carbon and oxygen content [21]. Activated carbon, known for its good adsorption capacity, has always been associated with the adsorption process. However, due to its high cost of production and regeneration, researchers are resorting to other alternatives [19]. Low cost adsorbents such as zeolites [22], [23], clay [24], [25], bagasse [26], agricultural waste [27]–[30] or waste products from industrial operations including coal and fly ash have been explored for the removal of dissolved organic compounds from contaminated waters. However, a major disadvantage associated with these adsorbents is availability and regeneration making them impractical for industrial use. Synthetic resins are now viewed as a practical alternative to activated carbon for the removal of oils from wastewater. The key advantage of the adsorption process on synthetic resins is that the binding forces encountered are relatively weak in comparison to the binding forces due to adsorption on activated carbon [31], [32]. Thus, allowing solute recovery through simple means of regeneration such as solvent extraction or steam stripping. Also, due to the controlled process of manufacturing resins, they can be designed with specific functional groups and pore sizes enhancing their performance for specific applications. They are employed in industrial applications such as purifications processes in the food and drug industries, odor control and in wastewater facilities. Moreover, they have been successfully exploited for the removal of individual dissolved organic compounds such as phenols, BTEX and other aromatic compounds [33]–[40]. However, no research has been reported on the removal of oil, a mixture of petroleum hydrocarbons normally extracted from oil or gas wells, from contaminated water using synthetic resins.

The objective of this research work is to evaluate the use of synthetic resins for the removal of oil from water where batch equilibrium studies have been carried out for the adsorption of oil on commercial synthetic resins. The focus of analysis will be on adsorption isotherms of oil on four types of synthetic resins: Optipore L493, Lewatit AF 5, XAD7 and IRA 958 at different contact time, resin dosage, initial oil concentration and pH using empirical equations that describe their adsorption behavior. The objectives of this thesis work are as follows:

- Investigate the potential of synthetic resins to remove oil from produced water that is prepared in the lab
- Predict batch kinetics and adsorption isotherms to evaluate adsorption capacity of the synthetic resins
- Evaluate the ability of synthetic resins to be regenerated through chemical regeneration using two organic solvents methanol, ethanol, 1M sodium hydroxide and D.I. water heated to 65 °C.

In the subsequent chapters, background information regarding produced water and its characteristics and management is provided in the literature review chapter along with a review of current technologies for produced water treatment. The method applied to carry out this research work is developed in chapter 3. The results and discussion of experimental work is provided in chapter 4. The last chapter, chapter 5, encompasses conclusions and future work pertaining to this study.

CHAPTER 2: LITERATURE REVIEW

1.1 Produced water

1.1.1 Definition

Produced water is generally defined as waste byproduct generated in the exploration and production of oil and gas from offshore and onshore wells. Multiple reasons contribute to the presence of produced water, which include seawater or freshwater that is trapped along with oil and gas between layers of impermeable rocks. in naturally occurring underground hydrocarbon formations - this water is normally known as formation water. In addition, as a technique to enhance oil recovery, additional water is injected into reservoirs to maintain well hydraulic pressure due to the extraction of oil and gas. Thus, produced water is the combination of formation water and injected water that are brought up to the surface along with oil and gas products.

1.1.2 Characteristics of produced water

The constituents of produced water could broadly be divided into organic and inorganic compounds. The physical and chemical properties of produced water depends greatly on geological formation and location, lifetime of the well, the nature of the chemical additives added in order to enhance oil recovery and the type of hydrocarbons that are produced [41]. The major component of produced water is the salt content which is expressed in terms of conductivity, total dissolved solids (TDS) or salinity. Other constituents that are also present which include oil and grease normally expressed as hydrocarbons or organic compounds. In addition to metals, radioisotopes and a wide variety of chemical additives all of which will be explained below. Comprehending the constituents of a produced water sample is vital towards selecting the appropriate water treatment technology and abiding by regulatory compliance.

1.1.2.1 Dissolved and dispersed oils

Dissolved and dispersed oils or total organic compounds (TOC) encompass a wide variety of different families of organic compounds. These compounds typically consist of petroleum hydrocarbons which could also be further classified into saturated hydrocarbons and aromatic hydrocarbons [42]. The one-ring aromatic hydrocarbons that usually include benzene, toluene, ethylbenzene, and xylene (BTEX) and low molecular weight saturated hydrocarbons are the most abundant organic compounds in produced water [42]. Other compounds also include polyaromatic hydrocarbons (PAH) and phenols. It was shown that there is a strong correlation between the concentrations of dispersed oil in produced water and the concentration of aromatics and phenols[43]. The connection found was that the distribution of oil in the water phase varies differently with different organic compounds. The concentration of PAH and alkylated phenols ($C_6 – C_9$) are strongly correlated to the content of dispersed oil while alkylated phenols ($C_0 – C_3$) and BTEX are not associated with the concentration of dispersed oil. Which follows that as the molecular weight of hydrocarbons increase, their solubility in water decreases. Dissolved and dispersed oils will have a detrimental effect on the environment if not managed according to regulations.

1.1.2.2 Dissolved solids

Dissolved minerals or inorganic compounds are divided into the following categories: cations and anions, heavy metals and naturally occurring radioactive constituents [1]. Samples of produced water typically comprise of high levels of dissolved salts with salinity values that range from 100 to 300, 000 mg/L as total dissolved solids (TDS) [4]. Cations usually include but are not limited to: sodium, calcium, magnesium, and potassium ions where sodium and chloride ions are the major contributors to the water salinity [4]. Anions normally include chloride, sulfate, carbonate and bicarbonate ions.

Metals that are of higher toxicity to the environment also exist in produced waters which are cadmium, cobalt, copper, lead, mercury, and nickel however, they normally occur at lower concentrations [2].

Naturally occurring radioactive materials (NORM) are also commonly found in produced water samples. Radium-226 and radium-228 are the most abundant radionuclides and are derived from the radioactive decay of uranium-238 and thorium-232 that are accompanied by specific types of rocks and clays that are normally present in the hydrocarbon wells [44]. Uranium and thorium are part of the core of the rock matrix, thus, they are insoluble in reservoir fluids. Radium is somewhat soluble in water and because it has similar chemical properties as barium and strontium, it has the ability to co-precipitate in the extraction process as sulfates [44]. Solid precipitates either deposit through scale formation or discharged into the environment.

1.1.3 Produced water management

Produced water is normally managed through a three-tiered pollution prevention hierarchy [2]:

1. Minimizing the production of produced water
2. Recycling and reuse
3. Disposal as a final option if above tiers not practical

Arthur et al. [45] proposed some options to oil and gas operators on produced water management and are as follows:

- Injection: produced water can be reinjected back into the formation from which is oil produced or in other formations

- Reuse in oil/gas operations: produced water can be reinjected back into the well to maintain well pressure
- Beneficial reuse: produced water can be consumed in beneficial uses such as irrigation, cattle and animal consumption and drinking water
- Disposal: produced water can be discharged back into the environment

Prior to managing produced water through any of the above-mentioned methods, produced water should be treated to meet the required quality specifications for further reuse or the environmental legislations for discharge. The subsection below details current technologies on the treatment of produced water.

1.1.4 Produced water polishing treatment technologies

Produced water contains contaminants of different nature and that will require the application of a chain of different water treatment units. A single process is not sufficient to remove all types of contaminants present in produced water. It is crucial to identify the constituents of produced water prior to treatment in order to determine the required technologies needed to design the water treatment process. Generally, the treatment of produced water consists of three stages: pre-treatment, primary and secondary treatment and the final polishing step. The pre-treatment step involves the removal of large oil droplets and coarse particles. The primary stage is designed to remove smaller oil droplets and it usually consists of API separators skim tanks and plate pack interceptors. The secondary treatment step of the treatment removes even smaller oil droplets and particles by employing gas flotations, hydro-cyclones and centrifuges. The last stage is the polishing step which is employed for the removal of ultra-small oil droplets and dispersed hydrocarbons using membranes or adsorption columns. Other technologies used in the polishing step recommended by American Petroleum Institute (API) include also air stripping, ultra-violet light, chemical oxidation and biological treatment [46]. A detailed discussion on each technology is given in the following subsections.

1.1.4.1 Membrane technologies

Membrane technologies have been employed for the treatment of produced water. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are all pressure driven processes that can be applied for oil field and refined produced water treatment [47]. There are several advantages to using this technology which include small footprint, ease of operation, high quality permeate, removal of low molecular weight organics and dissolved contaminants [1]. Nonetheless, the disadvantages this technology also entails are the following: membrane fouling that leads to lower productivity, high energy cost, membranes require periodic chemical cleaning, waste generated due to the cleaning process and backwash require further treatment or disposal [1], [48].

Different kinds of membranes have been explored for the treatment of produced water. Membranes from polymeric materials and inorganic ones have been reported in the literature. Kose et al. [49] explored ceramic and polyacrylonitrile for oil in water separation using synthetic produced water. A percentage removal of hydrocarbons achieved was 99%; however, the drawbacks faced were membrane fouling and chemical treatment was required for the cleaning process. Abadi et al. [50] tested a MF system with a tubular ceramic membrane (α-AL_2O_3) for the treatment of oily wastewater. The technology exhibited a TOC removal of 95 %; nonetheless, organic fouling caused the flux to decrease to 50 % of its original value. Zsirai et al. [18] conducted a pilot-scale study of real produced water obtained from oil platforms operating on the Arabian Gulf to assess the optimum membrane characteristics to meet the required water quality specifications. It was reported that in order to produce the desired water quality an effective method of chemical cleaning should be applied; thus, the study indicates that fouling is a persisting problem with membrane technologies. Overall, fouling is an issue that is common among all membrane processes

Limited data is published on large scale membrane processes for the treatment of produced water. However, there are three large-scale up and running treatment plants that employ RO as a polishing treatment in Chennai Petroleum company limited with a flow of 430,000 L/h, San Ardo water reclamation project in California with a flow of 331,223 L/h and oilfield in Wellington, Colorado with a flow of 14,763 L/h [47]. Figure 3 is an example of a produced water treatment plant where each membrane unit is utilized depending on the quality specifications and target destination of treated water. For instance, UF is used in case the treated water is to be disposed back into the environment. NF is used when the treated water is to be reinjected back for reuse in oil and gas operations.

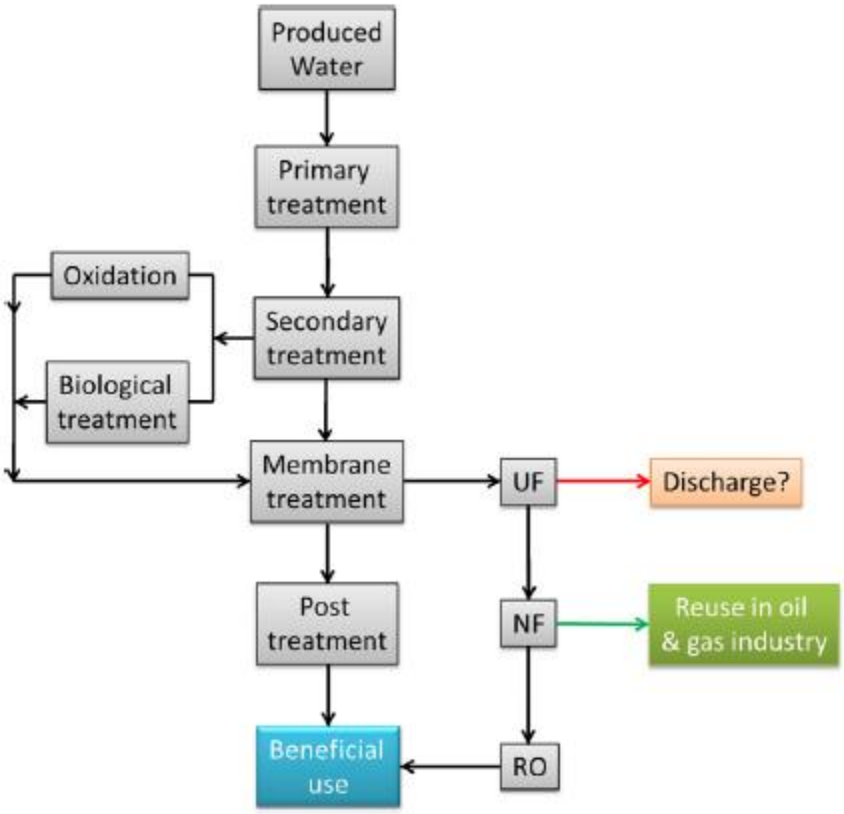

Figure 3. A schematic diagram of a produced water treatment plant with a membrane unit as a polishing step [43].

1.1.4.2 Chemical oxidation

Chemical oxidation is an effective and reliable technique for the removal of organic and inorganic compounds from produced water. This technique uses strong oxidants such as ozone and hydrogen peroxide, irradiation and catalysts such as photocatalysts to oxidize organic compounds to their highest stable oxidation state to reach complete mineralization, the oxidation state being carbon dioxide and water [51]. Advantages to using this technology is the ease of operation, it can treat a wide range of contaminants including hydrocarbons, acid, base and neutral organics, volatile and non-volatile, and low energy requirements are needed. Drawbacks to using this technology include catalyst fouling due to the presence of oil, high energy requirement if ozone used as oxidant and sludge and toxic residues may form [46].

1.1.4.3 Biological treatment

Biological treatment has been employed for the removal of organic compounds from produced water. Different processes such as biological aerated filters, activated sludge and batch reactors have been used for produced water treatment. The main method of treatment is through microorganisms that disintegrate organic compounds. This technique is effective when the feed has a COD of < 400 mg/l and BOD of < 50 mg/L [52]. It has been reported that with Bacillus sp bacteria, the COD removal efficiency went up to 90% while treating produced water [53]. Tellez et al. [54] reported that the percentage removal of total petroleum hydrocarbons (TPH) reached 99 % via an activated sludge system with a retention time of 20 days.

Although biological treatment is an effective treatment for removal of biodegradable hydrocarbons, there are disadvantages of using this technique. These disadvantages include build-up of oil that may hinder biological activity, long residence time may be required to reach the desired quality, aeration causes calcium scale to form and accumulation of sludge that will need further treatment [46].

1.1.4.4 Air stripping

Air stripping has shown to be a promising potential for the treatment of produced water to meet regulations on TOC. Hydrocarbons dissolved in water are removed through interphase mass transfer [55]. This technique can be accomplished using three technologies that include: a tank with spargers that provide air bubbles in produced water, the second technology consists of a packed column that facilitates contact between air and produced water in a countercurrent flow, lastly, the third technology encompasses a tray column where air bubbles rise through flowing produced water [55]. All three technologies are also commonly used in petroleum refining and gas-processing industries. The advantages of using this technique include the complete removal of volatile organic compounds including benzene, toluene, naphthalene and phenols. Also, the technology works on low energy requirements, low weight and small footprint. However, the risk of fouling may occur by oil, risk of calcium scaling and a gaseous waste stream may rise that will need further treatment [46].

1.1.4.5 Ultra-violet light

UV treatment is now a popular choice for disinfection in produced water treatment. Stepnowski et al. [56] studied the process of oil degradation using hydrogen peroxide from wastewater obtained from a refinery plant. It was shown that the addition of UV light accelerated the degradation process due to the formation of hydroxyl radicals where complete removal was achieved after 24 hours of treatment. Philippopoulos et al. [57] assessed the process of ultraviolet irradiation and hydrogen peroxide as a polishing treatment for oily wastewaters. It was reported that almost all present organic compounds were decomposed to organic acids. As a result, the COD efficiency reached only 45 % removal due to the formation of organic acids. This technique has the ability to remove both volatile and non-volatile organic compounds, no waste generation, can handle waste with high concentrations. Nevertheless, it does not treat dispersed oils, formation of toxic residues if peroxide is used, UV lamps may need high energy requirements and may also undergo fouling [46].

1.1.5 Commercial technologies for removal of oils from produced water

1.1.5.1 TORR^{TM}

The total oil remediation and recovery (TORR) technology manufactured and developed by a Canadian company, Earth Canada corporation, for the removal and recovery of oil from produced water. This technology encompasses a multi-stage adsorption processes followed by a separation one. Adsorbents used for the adsorption process are a polyurethane – based material referred to as the reusable petroleum adsorbent (RPA) that facilitates the removal of both large and small oil droplets by adsorbing oil emulsions, followed by agglomeration of oil droplets and then desorbing them as large oil droplets. During the separation process, oil and water are then gravitationally separated in the separation chamber [58].

1.1.5.2 BioPetroClean: ACT^{TM}

Automated chemostat treatment (ACT) technology is a biological wastewater treatment solution that is based on sustaining a group of microorganisms for the degradation of organic compounds in a chemostat system. This technology consists of a continuous flow reactor where low concentrations of bacteria is used to avoid the formation of sludge. The advantage of using this technology is that it can be used on-site decreasing operational and maintenance cost [59]

1.1.5.3 Prosep inc: C-TOUR™

This technology is used for the removal of dispersed oil and water soluble organic using the method of solvent extraction through condensate injection into produced water streams. The technology operates by injecting condensate into produced water streams extracting available pollutants. Both the condensate and pollutants agglomerate to form bigger oil droplets that are later separated mechanically or hydraulically from the produced water streams. According to performed operation using this technology, removal efficiency of dispersed oil is around 70 % whereas phenol removal was around 60 % [60].

1.2 Adsorption technology

The principle of adsorption - in specific the concept that some solid materials have the ability to remove dissolved compounds has been around for a very long time. As such, process or produced waters containing dissolved organic compounds can be purified by the passage of this contaminated water through a column containing these solid materials normally known as adsorbents. The adsorption technology never lost its credibility in its utilization in the water treatment industry. To a broader extent, it has also been recently employed in new field applications such as groundwater remediations and enhanced wastewater treatment where it competes with well-established process technologies such as distillation and absorption [61].

1.2.1 **Adsorbents**

In order to achieve an effective separation process, whether a bulk separation or a polishing step, several factors should be considered that pertain to choosing the ideal adsorbent for the separation system. These factors include high internal volume which allows an easy access of components to be removed [62]. Also, Considering that adsorption is a surface phenomenon, the surface area of the adsorbent is a key quality parameter in the selection process [61]. High surface area generates the high capacity required for a separation or purification process to be successful. Adsorbents can be created with internal surface areas which can range from 100 m^2/g to about 300 – 1200 m^2/g [62]. Adsorption kinetics are crucial to the system for adsorbents must be capable in transferring molecules to the active sites in a rapid manner. Also, in most applications it is desirable to achieve an effective regeneration of the system without damaging the mechanical and adsorptive properties of the adsorbents [62].

1.2.1.1 Activated carbons

Activated carbons (AC) are known to exhibit outstanding adsorptive properties. Its application dates centuries back starting with the discovery that charred materials have the ability to remove tastes, odor and color from water. activated carbon is now widely employed in industrial applications including water treatment, hydrogen purification, volatile organic control and decoloring sugar solutions. AC are generally synthesized from a wide range of carbonaceous materials through a thermal decomposition process followed by an activation process. Raw materials include coal, coke, wood, coconut shell. The manufacturing process can be divided into two methods, gas activation and chemical activation [62]. Gas activation basically involves two steps. First, pores are formed by heating in the absence of air to a temperature between 400 – 500 °C to drive off volatile compounds. Second, the activation step is then carried out using steam (other gases can also be used such as CO_2) at a temperature between 800 and 1000 °C. The chemical activation method involves the use of chemicals zinc chloride or phosphoric acid to produce AC directly from the raw material. AC exists in two forms, granular AC and powdered AC. Pore size diameter ranges from less than 2 nm to greater than 50 nm and pore volumes are normally of the order of 0.3 cm^3/g [63].

ACs have been employed for the removal of organic compounds such as phenols, aromatic and other organic compounds. There has been a flow of applications designed to remove organic compounds from water. In general, activated carbon yields a higher adsorption intensity than typical resins [33]. However, the main advantage that synthetic resins have over other adsorbents is the ease of regeneration. Also, resins can be tailored for other specific applications including pharmaceutical and semiconductor industries [63].

Other adsorbents have also reported for the removal of organic compounds, such as molecular sieves, silica gel, clay materials and zeolites [62].

1.2.1.2 Synthetic resins

Synthetic resins (focus of this work) are primarily employed in aqueous applications for the efficient and selective removal of organic compounds. They normally come in bead form with a defined pore structure and high surface area. Polymeric resins are synthesized based on styrene crosslinked by divinylbenzene (DVB) or co-polymers of acrylic acid esters/divinyl benzene (see Figure 4) [62]. The type of interaction that occurs between the adsorbent and the molecules to be removed depends on the nature of the surrounding conditions such as pH, heat and competing molecules among other conditions. The key initiation that influences the adsorption of molecules onto a resin matrix is the driving force between molecules and these forces include: Van der Waals, hydrogen bonds, ionic, and hydrophobic interactions [64]. These forces are induced depending on the type of polymers used for the synthesis process. For example, if primary amine groups were to be used for the polymeric synthesis; henceforth; the major forces responsible for adsorption are hydrogen bonds interactions. Thus, if the resin is a non-functional resin, which means its hydrophobic (example XAD 4, L 493 and AF 5), Van der Waals interactions will take place.

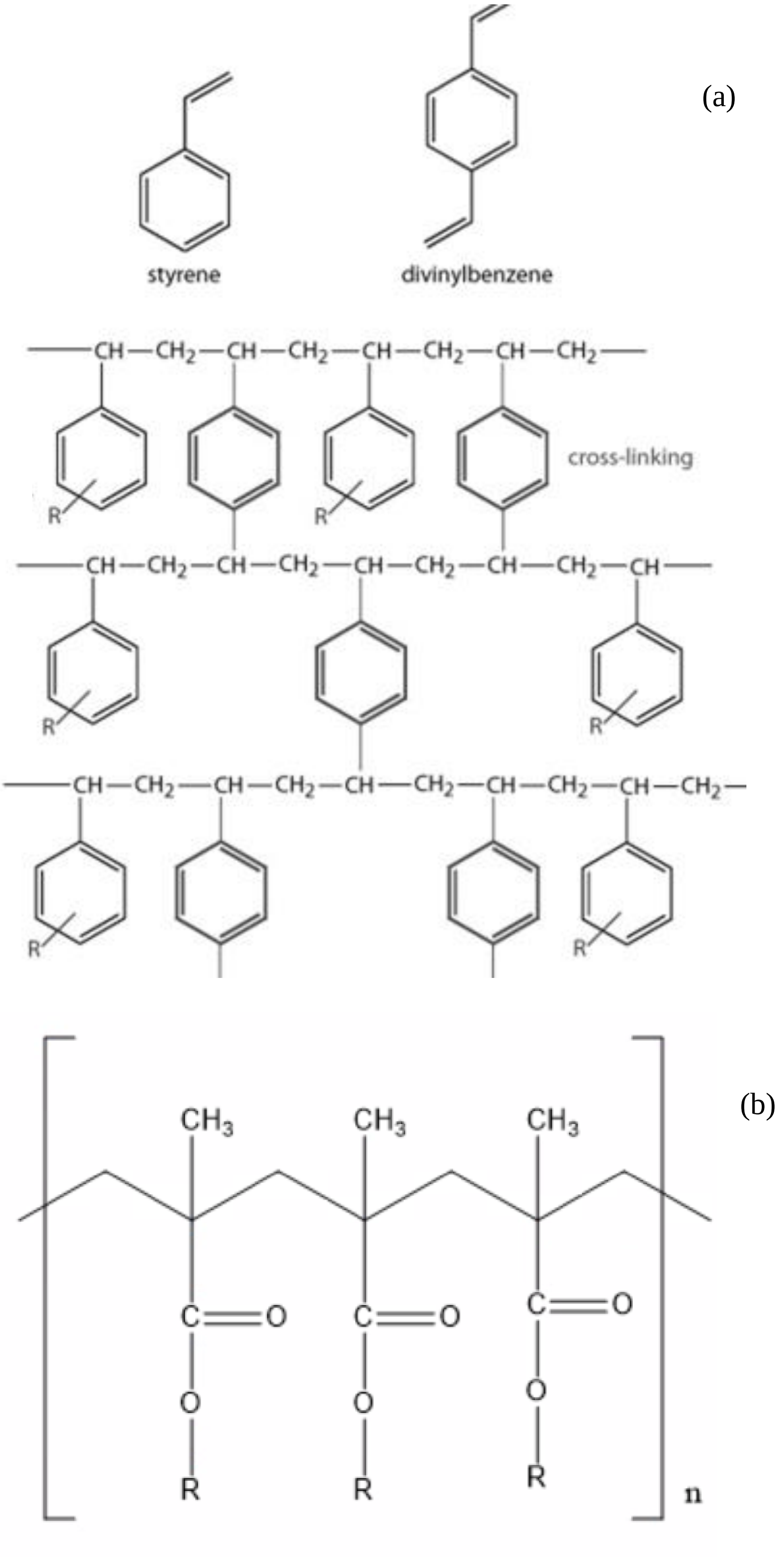

Figure 4. Examples of basic matrices of polymeric resins (a) polystyrene – DVB (b) polymethacrylate

A wide selection of resins possess ion exchange properties which aid in applications such as wastewater treatment. Synthetic resins are classified into the following categories: strong base anion, weak base anion, strong acid cation and weak acid cation and nonionic. The nonionic group of resins are nonfunctionalized which means no functional group has been added to the structure as opposed to strong base anion and strong acid cation where the chemical matrices of both resins are functionalized with three methyl groups (or one ethanol group replaces one of the methyl groups) and a sulfonic acid functional group respectively [65]. The weak acid cation resin contains carboxylic acid as the functional group and weak base anionic resin has a functional group of secondary or tertiary amines [65]. Table 1 summarizes the resins than have been experimented in the literature on a lab scale. As can be seen, both resins Optipore L493 and XAD 4 exhibit a neutral ionic form because no functional groups have been added into their matrices.

The difference between resins synthesized based on strong acids/bases or weak acids/bases is that resins based on strong acids/bases tend to exhibit lower ion exchange capacities than those based on weak acids/bases. Also, regeneration is performed differently for both. Strong acids/bases tend to be more convenient and require only a one step regeneration method. However, weak acid/base resins require a two-step regeneration method where the first step resins must be soaked with a strong mineral acid such HCl for H^+ to be exchanged followed by a neutralization step by NaOH to switch H^+ with Na^+ [63].

Table 1. Summary of Resins Studied in The Literature

Resin name	Hydrophobicity	Resin matrix	Functional group	Ionic form
Optipore L493	Non-ionic	Styrene-DVB	None	Neutral
A500P	Strong base anion	Styrene-DVB	Quaternary amine	Chloride
A860	Strong base anion	Crosslinked acrylic	Quaternary ammonium	Chloride
MN 200	Non-ionic	Styrene-DVB	None	Neutral
Amberlite XAD4	Non-ionic	Styrene-DVB	None	Neutral
Amberlite IRA 958	Strong base anion	Crosslinked acrylic	Quaternary ammonium	Chloride
Amberlite XAD 7	Weakly polar	Acrylic Ester	None	None

1.2.2 Synthetic resins for removal of organic compounds

Synthetic resins have exhibited 5 to 10 times the capacity of granular activated carbon in water purification especially for the removal of volatile organic compounds with low concentrations. [63]. There is very limited research on the removal of oil from water through the use of commercial synthetic resins, however they have been successfully utilized for the removal of natural organic matter (NOM), total organic compounds (TOC) and dissolved organic compounds (DOC). A summary of applications of synthetic resins for the removal of specific organic compounds such as phenolic compounds or BTEX compounds which are normally found in oils or in produced and process waters is given below.

One of the most commonly explored commercial resins for the removal of organic compounds in the literature is the Amberlite XAD 4 polymeric adsorbent. It is chemically synthesized by the copolymerization of styrene and divinylbenzene. XAD 4 resin is hydrophobic and has a nonpolar network, therefore, the main driving force for molecules from the bulk solution into the adsorbent phase are Van der Waals interactions [66]. This resin exhibited substantial potential for their ability to effectively remove organic compounds from water, [32], [40], [67]

The adsorption of phenolic compounds from an aqueous solution onto XAD 4 resin has been investigated [37]. The experiments were carried out under different operating conditions including pH variations. Their observations indicated that the adsorption behavior of phenols by XAD 4 could be described by both Langmuir and Freundlich models. The removal of phenols was highly pH dependent due to species distribution of phenols in solution. Phenols were effectively removed under acidic conditions where molecular phenol species are dominant as opposed to the alkaline medium where the removal efficiency decreased due to the dominating presence of the negatively charged phenols.

The combined mechanisms of adsorption and ion exchange has been explored [36]. The removal of phenols has been tested with a nonfunctionalized hyper-cross-linked polymer Macronet MN200 and two ion exchange resins Dowex xz, a strong anion exchange resin, and AuRIX 100, a weak anion exchange resin. The equilibrium experimental data were effectively fitted to the Langmuir and Freundlich isotherms at different pH values for phenol adsorption was affected. The nonfunctionalized resin exhibited maximum loading adsorption under acidic conditions where the molecular phenol form is the dominant species. This supports the fact that the nonfunctionalized resin has high affinity towards hydrophobic compounds. In contrast, the ionic exchange resins conveyed maximum loading under alkaline conditions where the phenolate is the dominant species. Also, it was reported that the pH effect establishes a combined effect of both adsorption and ion exchange mechanisms under alkaline condition.

The adsorption of phenol was experimented with different polymeric adsorbents that included XAD 4, NDA 103 and Amberlite IRA96C [40]. The aminated adsorbent NDA 103 yielded the highest adsorption capacity due to the combined effect of hydrogen bonding (due to tertiary groups that provide proton acceptors) and Van der Waals interactions (due to the resin's hydrophobic surface). Owing to XAD 4's non-polarity, the only driving force is Van der Waals interaction while IRA96C, a weak base adsorbent, the adsorption process is mainly driven by hydrogen bonding. The adsorption isotherms were adequately fitted by Langmuir and Freundlich equations.

Methyl tert-butyl (MTBE) is commonly used as gasoline oxygenate and its major degradation product tert-butyl alcohol (TBA) have been investigated for their sorption affinity towards synthetic resins [39]. Kinetic and equilibrium adsorption experiments were conducted on four synthetic resins. Single and binary systems were explored. For single solute experiments, the investigated adsorbents showed higher recovery for MTBE in the following order: Ambersorb 563, Optipore L493, Amberlite XAD 4, and Amberlite XAD 7. In the binary mixture where o-xylene was introduced into the system, adsorption competition among particles occurred towards available sites. This competition primary depends on the nature of the resin employed. Optipore L493 has favorable adsorption towards moderately polar compounds while Ambersorb 563 favors highly polar compounds. It has been noted that pretreatment of synthetic resins with alcohol may reduce the adsorption capacity.

XAD 4 was also experimented by along with four other resins in order to explore their adsorption and desorption features towards an aqueous solution of ten phenolic compounds[67]. Desorbing agents tested include water, methanol and ethanol under basic and acidified conditions. Adsorption isotherms were determined, and the data fitted satisfactorily with the Langmuir isotherm model. The highest adsorption percentages were obtained by the polar resins however, higher desorption ratios occurred with nonpolar resins. The study confirmed that the polarity of compounds to be adsorbed plays a major role in system recovery. The adsorption capacity of a nonpolar resin increases with decreasing compounds polarity and vice versa.

The performance of Purolite A500P was evaluated through the removal of effluent organic matter [68]. This Purolite resin is macroporous strong anion exchange resin and was assessed through adsorption equilibrium, kinetics and fluidized bed experiments. The results showed that A500P had higher affinity towards hydrophilic compounds with percentage removal of 73.1 % and 55% removal for hydrophobic compounds. Prior to performing the experiments, A500P was crushed into four different sizes 150 µm, 150 – 300 µm, 300 – 420 µm and 420 – 600 µm in order to study the effect of particle size on the adsorption process. It was found that particle sizes with 150 – 300 µm exhibited the highest DOC removal.

In a research work performed by Víctor-Ortega et al., the recovery of phenols from an aqueous solution was evaluated using two synthetic resins, Amberlyst A26, a strong base anion resin and Amberlite IRA67 a weak base anion resin[35]. It was revealed that the equilibrium data fitted adequately with the Langmuir isotherm as it provided the best correlation for both resins. As for the kinetic studies, they have been analyzed using particle diffusion model which proved satisfactorily. It was concluded that the strong base anion demonstrated higher removal capabilities in comparison to the weak base anion resin.

Adsorption isotherms of phenol and 4-chlorophenol on their removal from water have been studied by Juang et al. on both Amberlite XAD 4 and XAD 7 with a temperature range of 288 – 318 K [69]. The experimental results failed to fit with conventional parameter equations due to the sharp rise of concentration of phenol adsorbed at equilibrium which is a result of multilayer adsorption. Therefore, the Brunauer-Emmett-Teller (BET) equation was employed as it adequately describes this adsorption mechanism. This type of adsorption phenomenon is not common among research practitioners given XAD 4 is commonly tested. Adsorption decreases gradually towards equilibrium due to the occupation of available sites by adsorbates allowing no room for further adsorption to occur. Researchers who performed this work explained that the reason behind these unusual results is due to the pore-blockage mechanism which mainly states that at low concentrations of phenols, the solutes adsorb on sites nearest to the surface of the resin. While at high phenol concentration, the initial flux is high which allows for the solute to shoot deep into the resin matrix. They have also reported that the adsorption capacity per unit area of XAD 7 is relatively higher due to the fact that the specific area of XAD 7 (450 m^2/g) is much smaller than XAD 4 (725 m2/g) which agrees with works reported earlier.

Just recently, synthetic resins have also been tested for the removal of benzene, toluene, ethylbenzene and isomers of xylene (BTEX) compounds by Makhathini et al. [34]. The resin explored in this research experiment has not been studied before PAD 910 polystyrenic resin. Batch studies were performed to evaluate the effects of the following experimental parameters: mixing strength, contact time, internal diffusion, adsorbates and initial concentration on the removal of BTEX compounds. The equilibrium data fitted well with the linearized Dubinin-Radushkevich and the Langmuir model at pH 5.86. However, it has been reported that the latter is the most practical model in representing the adsorption of aromatic compounds. the pseudo-second order rate model fitted well to the adsorption kinetics.

Only two research groups have investigated pH as an important criterion for the recovery of organic compounds from water using synthetic resins. According to Caetano et al. and Ku et al., who both reported similar results, that nonfunctionalized resins tend to be more effective under acidic conditions where the molecular form is the dominant species and functionalized ones tend to exhibit maximum loading under alkaline conditions where ionic form is the most dominant species [36], [37]. These findings prove that pH plays a crucial role in the adsorption process. Therefore, pH needs to be considered as a judging parameter to be able to effectively evaluate resins for the system employed. However, this is not the case as most of the research projects tend to ignore pH as a method of assessment.

Table 2. Summary of Experiments Performed on Commercial Synthetic Resins for The Removal of Organic Compounds.

Synthetic resin used	Quality of water	Experimental conditions and % removal
XAD 4 [37]	Nine phenolic compounds were used: phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 2-methylphenol, 2,4-dimethyl phenol	Experiment were conducted under room temperature in a shaker water bath.
XAD 4, NDA 103 and IRA 96C [40]	Phenol was purchased from Shanghai Chemical station. It was then dissolved in deionized water in the batch adsorption runs without pH adjustment. Surface area 0.305 nm^2/molecule, Cross-sectional distance = 0.43 nm and conc. 925 mol/m^3. pKa: 9.89	Batch experiments performed at different temperatures: 293, 303 and 313 K., 0.05 g were added to a 100 ml flask with 50 ml of aqueous solution phenol with conc. ranging from 0.15 to 2 mmol/L and shaken under 150 rpm for 24 hr

Synthetic resin used	Quality of water	Experimental conditions and % removal
Ambersorb 563, Optipore L493, XAD 4 and XAD 7 [39]	Millipore water was used Chemicals used: MTBE, TBA, o-xylene and perdeuterated tert-butyl alcohol	Experiment was carried out at 20 °C. For MTBE: mass of Ambersorb 563 was added to vials with 0.01 g and mass of other resins was 0.06 g. Conc. Of MTBE was 11.5 mg/l. For TBE: mass of all adorbents is 0.06 g with initial conc. of TBA is 7.71 mg/l. The rest approached equilibrium after 24 hr. TBA sorption to Ambersob 563 reached in 48 hr. L493, XAD7 and XAD4 reached in 24hr. Ambersorb 563 had the highest sorption potential and XAD7 had the lowest

Synthetic resin used	Quality of water	Experimental conditions and % removal
XAD 4, XAD 7, XAD 16, IRA96 and Isolute ENV+ [67]	Ten phenolic acids were experimented gallic acid, 4-hyroxybenzoic acid, 4-hydroxyphenilacetic acid, vanillic acid, syringic acid, p-coumaric acid, ferulic acid, 3,4-dimethyloxybenzoic acid, 3,4,5-trimethoxybenzoic acid and cinnamic acid.	Batch experiments conducted at pH of 4.5 solutions placed in a rotary shaker operating at 180 rpm at 25 °C for 1 hr. IRA89: 89% and XAD resins: 45.4 - 49.8%
Amberlyst A26 and IRA67 [35]	The aqueous solution was synthesized with analytical grade reagents. Phenol was dissolved in double distilled water	The effect of the initial concentration of phenols was examined in the range 1 – 200 mg/L until equilibrium was achieved at constant resin dosage 7 g/L.
XAD 4 and XAD 7 [69]	The synthesized solution was prepared by dissolving analytical grade phenol in deionized water without pH adjustment	A fixed amount of resin 0.1 g was placed in a fixed amount of volume of solution 0.1 dm^3 in glass stoppered flask and shaken at 130 rpm for 5 days

Synthetic resin used	Quality of water	Experimental conditions and % removal
Purolite A500P [68]	Synthetic water was used and it had the following characteristics: DOC: 10 mg/L and pH 7.3, Humic acid: 4.2 mg/L, Tannic acid: 4.2 mg/l, Arabic acid (polysaccharide): 5.0 mg/L	Different doses of purolite was added in 200 ml synthetic wastewater and were mixed at 110 rpm for 72 hr continuously. For the fluidized bed contractor, four different particle sizes were used to pack the bed column. The wastewater was pumped at fluidization rates of 2, 6 and 10 m/hr. A500P removed 76.4 of hydrophilic compounds, humic substances 86.5%, and low molecular weight of neutrals 83.3% and 55% hydrophobic
PAD 910 [34]	The aqueous solution was synthetically prepared where a stock solution of diluted concentrations of BTEX compounds were within the range of 0.35 – 14.47 ppm.	Batch experiments were conducted at room temperature (25 ◦C) it was determined that the resin adsorbed 98% of benzene, 59% ethylbenzene, 84% of p-xylene and 90% o-xylene at an initial concentration of 14.47 mg/L.

Synthetic resin used	Quality of water	Experimental conditions and % removal
MN200, Dowex XZ and AuRIX 100 [36]	The aqueous solution was synthetically prepared in the lab with different concentrations of phenols ranging from 5 to 2000 mg/dm^3	Batch experiments were performed at room temperature. Samples of 0.2 – 0.3 g were mechanically mixed in an aqueous solution of 20 cm^3 at different phenol concentrations. Regeneration was achieved with 90% resin recovery using a solution of methanol and water

1.3 Adsorption equilibrium isotherms

In the process of exploring novel adsorbents in achieving an ideal adsorption system, it is important to establish the most ideal equilibrium correlation. This correlation aids in interpreting adsorption parameters and quantitative comparison of adsorbent behavior for different adsorption systems at varied experimental conditions [70], [26]. Equilibrium relationships, generally known as adsorption isotherms, can be defined as the ratio between the amount adsorbed onto the adsorbent to the amount remaining in the solution when an adsorbate in the solution phase has been in contact with the adsorbent for a sufficient amount of time [71]. The adsorption isotherms are determined by several mathematical formations that are typically based on experimental fittings while generating data that pertains to the physical properties and the type of process involved in the system. Below are the major equilibrium adsorption isotherm models that have been employed for the removal of hydrocarbons in the literature.

1.3.1 Langmuir isotherm model

The Langmuir isotherm model was initially employed in describing the gas-solid phase adsorption of activated carbon. However, it was then extended to mathematically describe equilibrium relationships between a bulk liquid phase and a solid phase [72]. This model predicts a monolayer adsorption process where one active site can only be occupied by one adsorbate molecule (no further adsorption takes place) with no interaction or steric hindrance from adjacent occupied sites [72]. It is a homogeneous adsorption mechanism where all sites have equal affinity towards adsorbate molecules, thus, all adsorbed molecules have equal enthalpies and activation energy [73]. This model is normally expressed as equation 1 where q_m is the maximum adsorption capacity and b represents energy for the adsorption process.

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

1.3.2 Freundlich isotherm model

In contrast to the Langmuir isotherm model, this empirical formula predicts a multilayer adsorption with non-uniform affinities over the heterogeneous surface [71]. In the early stages of development, it has been used for the adsorption of animal charcoal to validate that the ratio of the adsorbate onto a given mass of adsorbent to the solute at different solution concentrations was not constant [74]. However, it is now extensively utilized in heterogeneous systems in particular for organic compounds or highly interactive species on activated carbon and molecular sieves [75]. Nonetheless, this model lacks a fundamental thermodynamic basis as it does not reduce to Henry's law at low concentrations [76]. The model is denoted as equation 2 where K_f and n are the Freundlich constants that represent adsorption capacity and favorability of the adsorption process respectively.

$$q_e = K_f C_e^{1/n} \tag{2}$$

Other isotherms used in this study include Toth, Dubinin-Radushkevich (DR) and Flory-Huggins. The Toth model is normally applied to predict heterogeneous processes with multi-layer adsorption that is useful in satisfying both low- and high-end boundary of adsorbate concentrations [72]. The Toth isotherm model can be expressed using equation 3. The constant, t, provides an indication of the level of heterogeneity of the system The system is said to be heterogeneous if the value of t deviated away from 1 [77].

$$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}} \tag{3}$$

The Flory-Huggins model addresses the characteristics of the degree of surface coverage of the contaminant on the surface of the adsorbent [72]. Equation4 expresses the empirical form of the isotherm model. θ expresses the degree of surface coverage and K_{FH} is used to determine the Gibbs free energy, which is expressed as equation 5. This model is also useful in governing the feasibility and spontaneity nature of the process [78].

$$\frac{\theta}{C_e} = K_{FH}(1-\theta)^{n_{FH}} \tag{4}$$

$$\Delta G^\circ = -RTln(K_{FH}) \tag{5}$$

DR model is a three-parameter model that is based on the assumption that adsorption mechanism occurs on a heterogeneous surface with a Gaussian energy distribution [79]. The isotherm is denoted as equation 8 where k_{ad} is the activity coefficient related to the sorption mean free energy, E (kJ/mol). E is related the mean free energy of adsorption per molecule of adsorbate that is transferred from infinity in the solution to the solid phase.

$$q_e = q_s \exp\left(-k_{ad}\varepsilon^2\right) \tag{6}$$

1.4 Regeneration methods

Most studies found in the literature focus on adsorption and very minimum is said on regeneration studies. Regeneration is a must in order to have a successful commercialization of adsorbent materials. Also, a successful regeneration run does not only recover target contaminants, it should recover the adsorbent’s original capacity without altering the porous structure of the adsorbent and no substantial amount of mass should be lost [80]. During the adsorption process, a fraction of the removed contaminants may become irreversibly adsorbed preventing the adsorbent from its potential reuse. Henceforth, it is vital to perform regeneration and assess whether the adsorbents can be reused for the maximum number of cycles. Regeneration can be accomplished via the following methods all of which will be explained in the following subsections:

- Chemical regeneration
- Thermal regeneration
- Biological regeneration

1.4.1 Chemical regeneration

Chemical regeneration is one of the important regeneration methods. This method encompasses an extensive variety of reagents to remove contaminants. Regeneration can be performed using water, organic solvents and supercritical regeneration are all under the umbrella of extraction mechanism as seen in Figure 5. Also, electrochemical and NaOH regeneration are governed by changes in pH or degradation of adsorbed contaminants [81]. Moreover, oxidative regeneration involves the degradation of contaminants through an oxidation reaction. Regeneration of synthetic resins are commonly performed through solvent extraction which will be the focus of the following discussion.

Regeneration of synthetic resins is commonly performed via solvent extraction where target contaminants are desorbed back into the solvent through the same method adsorption occurs. One of the key advantages synthetic resins have over other adsorbents is their ability to be recycled and reused. Several solvents have been reported in the literature that have successfully regenerated different kinds of adsorbents including synthetic resins.

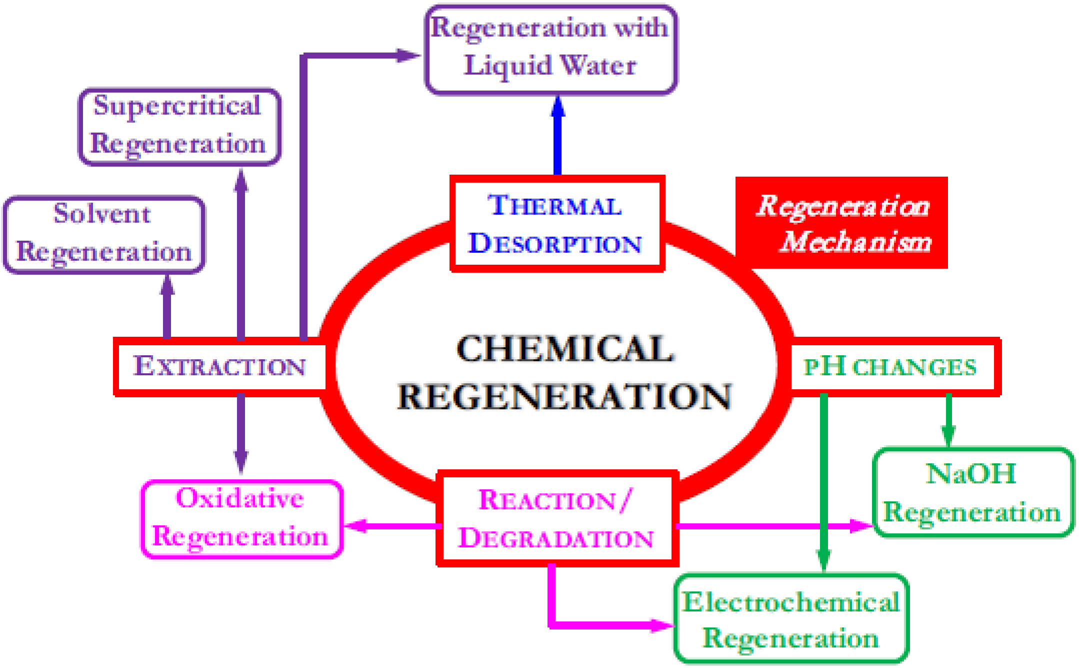

Figure 5. Summary of the chemical method for regeneration [72].

Caetano et al. [36] was able to recover 90% of adsorbed phenols onto a polymeric resin with 50% methanol in water solution after 1 hour. However, very poor recovery was observed when using NaOH. Another desorption study encompassed testing a group of synthetic resins (XAD 4, XAD 7, XAD 16, IRA 96 and Isolute ENV+) by

Ferri et al. [67]. Desorbing agents used in the study include water, ethanol, methanol acidified ethanol and basified ethanol. The results showed that after a few successive desorption cycles, nonpolar (XAD 16 and ENV+) and weakly polar (XAD 7) were best desorbed using ethanol and the polar resin IRA 96 was best desorbed using acidified ethanol.

Desorption characteristics of Optipore L493 was investigated by Erping et al. [39] using water as the regenerant. Their data indicated that it took ten days to reach equilibrium. Greluk et al. [82] assessed the desorption of dye adsorbed on the anion exchange resin IRA 958 using different solutions including aqueous and aqueous methanol solutions of HCl, NaOH and NaCl. The results indicated that only 44% and best desorption was obtained with 1M HCl in 50% methanol solution. It is worth mentioning that the low desorption value was due to the strong electrostatic attractions between the trimethyloammonium groups of the synthetic resin and the sulphonic groups of the dye. Due to these strong attractions, poor results were reported on the desorption experiment. This shows that desorption depends on whether the adsorption mechanism is a strong binding force such as ionic interactions or a weak binding force such as van der Waals interactions. Crook et al. [83] tested both acetone and methanol for the regeneration of XAD 4 and XAD 7 loaded with phenols. It was reported that both solvents are efficient where the regeneration efficiency determined was between 95 – 100 %. Liu et al. [84] observed a desorption efficiency of 98 % with 6 hours of treatment with 0.1 M NaOH on Optipore L 493 loaded with trihalomethanes (THM). Five cycles were carried out with a minimum loss in the resin’s capacity indicating L 493’s good capacity for regeneration and reusability.

1.4.2 Thermal regeneration

Another regeneration method is thermal regeneration. This regeneration method can be performed via traditional ways using inert gases and steam or non-traditional ways using a microwave, UV radiation or electric currents [85]. Although this technique is economically favorable and most commonly used in industries, thermal regeneration does not effectively regenerate, and it has the tendency to damage the structure of adsorbents losing mass in the process [80]. Generally, this method provides heat to remove target pollutants that are adsorbed onto the surface of the adsorbent material. There are three regeneration mechanisms that fall within thermal regeneration:

- Thermal desorption techniques
- Desorption and decomposition technique
- Gasification technique

The thermal desorption technique operates by providing heat to break the link between the adsorbent and adsorbate across all adsorption sites without altering the chemical structure of target contaminants. This technique is widely used for the regeneration process to recover VOC’s [86]. There are three common ways to provide heat, such as through an inert gas, steam and electrical current [80]. The desorption and decomposition method operates by applying hot inert gas such as N_2, He or Ar where regeneration occurs through heating these hot gaseous streams gradually until high temperature are reached, normally around 700 – 900 °C s [80]. This method is commonly applied in the industry due to design simplicity; nonetheless, there are crucial drawbacks to this technology. Pollutants decompose during the regeneration process due to the application of high temperatures [87]. Mass losses from 2.5 % to 5.9% have also been reported in addition to decrease in specific area and micropore volume up to 10 % [87]. The last method is the gasification method. This technique is applied after the desorption and decomposition method because of the fact that heating at high temperatures regularly will likely leave behind carbonaceous residue on the surface of the adsorbent (this mostly happens with AC adsorbents) thereby, decreasing the adsorption capacity through continues destruction and blockage of the porosity of adsorbents. Consequently, the gasification method's main target is to remove these residues to fully recover the adsorbent's capacity prior to the adsorption process. This method usually employs CO_2 and steam at temperatures around 800 °C or higher. Due to the application of these high temperatures, it is important to monitor the extent of the gasification process to avoid major mass losses of adsorbents.

Table 3. List of Studies for The Desorption of Organic Compounds from Using Thermal Regeneration

Type of adsorbent	Eluent	Regeneration method	Adsorption cycles	Reference
AC fiber cloth	Styrene + BTEX	Electrothermal thermal	-	[88]
AC filter	Mixture of VOC's	Electrothermal heating	5	[89]
BAC	Alkanes	Thermal heating	-	[90]
ACFC	Mixture of organic compounds	Electrothermal heating	5	[91]
AC	Toluene	Thermal heating	-	[92]
Hydrochar AC	Thiophene	Thermal + chemical	3	[93]

The above described thermal regeneration methods are among the traditional methods in the field of regeneration and are commonly used in the industry, specifically heating with inert gases and the steam gasification process. Despite the disadvantages pertaining to these technologies, they are still favored for industrial purposes on the basis that they are clean and highly efficient.

1.4.3 Biological regeneration

Biological regeneration involves two methods of regeneration. In the first method, adsorbents are inoculated with microorganisms prior to the adsorptions step. The adsorbents are first put in contact with a microorganism culture that grows developing a biofilm that envelops the outer surface of the solid adsorbent [94]. Adsorption and regeneration are employed simultaneously, when contaminants are in direct contact with the adsorbents through the adsorption process, they are directly consumed by microorganisms that are attached to the surface of the solid. This method may promote regeneration; however, because the microbial growth happens before the adsorption process, it hinders the adsorption activity due to the blockage of the adsorbents' pores.

The second biological regeneration method is commonly referred to bioregeneration. This method is more convenient as microbial inoculation occurs after the adsorption process. Exhausted adsorbents are put in direct contact with a microorganism culture where contaminants are degraded through microbial activity. The advantages pertaining to this method is that it is simple to operate, eco-friendly and cost effective [95]. On the other hand, disadvantages of this method have been reported in the literature. Some contaminants may reach the inner pores of the adsorbent, large microbes may not be able to penetrate into the porous structure; thereby, reducing the effectiveness the desorption process [81]. Also, in order to promote and sustain microbial growth and degradation of contaminants, there are specific conditions to be met. Such as delivering and sustaining the right temperature, pH, and oxygen amounts. Lastly, microbials require 10 – 20 days to reach maximum microbial activity making the regeneration process rather time consuming [96].

CHAPTER 3: MATERIALS AND METHODS

An experimental plan was constructed to meet the objectives of this research. The experimental plan was divided into different subdivisions and are presented as follows:

- Synthesis of produced water with concentration of oil around 30 ppm that is suitable feed for a tertiary system or a polishing step
- Prior to adsorption experiment, some resins required pretreatment for them to perform at their best capacities. Methanol and distilled water were used for the treatment.
- Batch experiments were conducted at laboratory scale to establish the synthetic resin's adsorption capacity for oil and to study the kinetic behavior of the adsorption of oil onto synthetic resins under different operating conditions such as resin dosage, contact time, initial oil concentration and pH
- Regeneration of synthetic resins mainly through chemical regeneration with two organic solvents (methanol and ethanol), 1 M NaOH and D.I. water heated to 65 °C.

1.5 Materials

Table 4 lists all chemicals used along with their specifications throughout this study. All solutions were prepared using D.I. water obtained from Millipore's Milli-Q Integral Water Purification System. Gasoline was obtained from Woqood petrol station grade Octane 95. As for the process of glassware cleansing, a three-step procedure was followed. First, they were washed with laboratory detergent, then they were washed and rinsed thoroughly with distilled water, lastly, they were dried in the oven at 70 °C overnight. Glass bottles used for the adsorption experiment were rinsed with sulfuric acid to avoid adsorption on the walls of the bottles.

Table 4. Chemicals Used and Specifications

Chemical name	Chemical formula	Vendor	Specifications
Ethanol	C_2H_5OH	VWR	99.7 – 100%
Methanol	CH_3OH	VWR	99.8%
Sodium Hydroxide	$NaOH$	Fisher Scientific	≥ 98 %
Sulfuric Acid	H_2SO_4	Fisher Scientific	≥ 98 %
Ethylene tetrakis tetrol	$[-CH_2N[(-CH_2CH_2O-)_x[-CH_2CH(CH_3)O-]_yH]_2]_2$	Sigma Aldrich	2% v/v, density 1.02g/ml, HLB between 1-7 and surface tension of 36 dyn/cm

Adsorbents used in this study are commercial synthetic resins of different hydrophobicity. Optipore L493 and Lewatit AF5 (has not been experimented on before) non-polar resins and Amberlite IRA958 polar resin were obtained from Sigma-Aldrich. Amberlite XAD7 slightly polar resin was acquired from Fisons. The chemical and physical properties of the synthetic resins used in this study are obtained from the material data sheet provided by the manufacturer.

Table 5. Physical Properties of Resins Used in This Study

Physical/chemical properties	XAD 7	L 493	AF 5	IRA 958
Resin type (Hydrophobicity)	Intermediate polarity	Nonpolar and hydrophobic	Nonpolar and hydrophobic	Strong base anion – chloride form
Resin matrix	Acrylic ester (Aliphatic, methyl methacrylate)	Styrene-Divinylbenzene	Styrene-Divinylbenzene	Crosslinked acrylic
Functional group	None	None	None	Quaternary ammonium
BET Surface area (m^2/g)	450	1100	1200	-
Average pore diameter (Å)	90	46	80	64.7

1.6 Experimental methods

1.6.1 Synthesis of produced water

The first step in synthesizing produced water in the lab is the selection of oil to act as the source of hydrocarbons that are normally found in produced waters extracted from oil and gas wells. The basis of selection was on the nature of water to be introduced into the adsorption unit. Since the adsorption unit is to be located in the tertiary treatment sector, the goal is to synthesize an oil in water emulsion that acts as a suitable feed. Water leaving the secondary treatment generally constitutes of oil particles that cannot be removed at early stages of treatment. Normally, huge particles of oil, that contain long chains of hydrocarbons that are the most difficult to dissolve in water, are easily removed at early stages of treatment. The difference between oil particles removed at early and final stages of treatment is the length of carbon chains. The longer the carbon chain, the formation of stable emulsions is less likely to occur. Thus, the separation process is easier and can be accomplished through conventional means. However, smaller carbon chains that tend to form stable emulsions are most difficult to remove using the same conventional treatment.

Choosing the kind of oil to be utilized depends primarily on the target length of carbon chains. Gasoline was chosen to be the source since it contains carbon chains that range from C_5 to C_{11}. Whereas diesel or kerosene contain carbon chains from C_{12} and above. Therefore, the shorter carbon chains are most likely to remain in the water coming from the secondary treatment, and gasoline was found to be the best representative of these organic compounds.

In order to have a stable homogeneous emulsion, the addition of a surfactant was an essential step. The name of the surfactant used in this study is ethylenediamine tetrakis. During early stages of this study, experimental tests were performed to obtain the desired oil in water concentration (30 – 50 ppm). The emulsion was formulated with deionized water. To obtain the desired oil in water concentration, the surfactant, see Figure 6 for chemical structure, acting as another source of organic compounds was also considered. Thus, several trial and error experiments took place in order to obtain the right amounts of surfactant and oil to generate the desired oil in water concentration while having a stable emulsion that lasts for a long period of time. The degree of stability relies on the amount of surfactant used. The higher the amount, the more stable the emulsion will be. A ratio of 1:1 of oil and surfactant was found to be the best ratio. Knowing that the surfactant is soluble in water and not in oil, it was dissolved in distilled water. First, 1 g of surfactant was measured out using an analytical balance supplied by Adam Equipment (model: AE680593, UK) with a maximum capacity of 210 g and a readability of 0.0001 g and mixed with 1 L of water using a Fischer Scientific homogenizer (type: FSH 1000 W/08451671, Switzerland) until a homogeneous mixture was observed. Next, the amount of oil needed, 1 g, was weighed out and added to the surfactant/water mixture in a dropwise manner. Lastly, the oil in water emulsion was mixed continuously for 7 minutes in order to have a stable homogenous emulsion

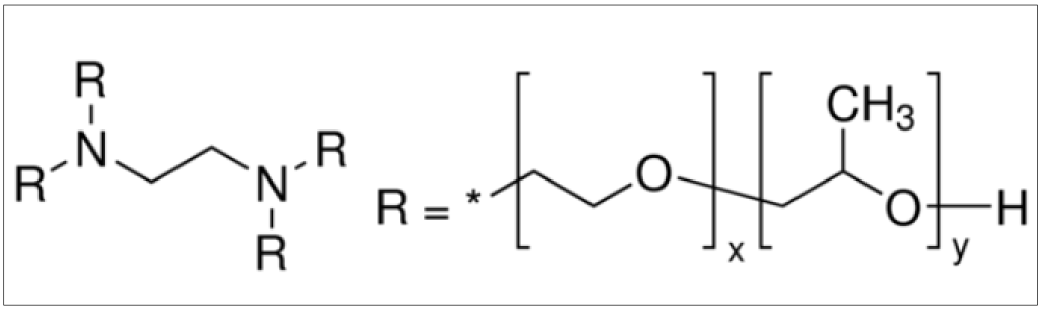

Figure 6. Chemical structure of ethylenediamine tetrakis

1.6.2 Adsorbent pretreatment

Synthetic resins are typically manufactured and stored in plastic containers. In some resins, bacteria tend to grow within. To prevent this from happening, additives are added in order to preserve the resins and keep them from rotting. These additives act as barriers during the adsorption process; henceforth, the resin’s capacity decreases not yielding the expected performance. A pretreatment step is required to remove these unwanted barriers.

A trial experiment was performed to identify the resins that required pretreatment prior to the adsorption experiment. Two trial runs were carried out, one with pretreatment while the other without. The results showed that AF 5 and L 493 did not required any pretreatment – percentage removals for both runs were very close. Contrarily, XAD 7 and IRA 958 needed pretreatment as the results from the trial with pretreatment showed significant improvement relative to the trial where pretreatment was not performed.

The pretreatment method followed was obtained from the literature [69]. First, the resins were washed with methanol and stirred for 15 minutes on the magnetic stirrer. Next, the resins were then washed with distilled water for another 15 minutes and were left to dry in the oven at a temperature of 323 K for 24 hours.

1.6.3 Adsorption experiments

The potential of synthetic resins to remove oil from water was investigated by varying the adsorbent dosage, contact time, initial oil concentration and pH for the four different resins. The experiments were conducted in triplicates at room temperature and pressure and at a fixed volume along with a control sample to see if gasoline can be lost due to handling and shaking. Resins were placed in glass bottles with a volume of 50 ml of synthetic produced water. The bottles were then placed in a KS 501 orbital shaker and agitated for 24 hours at a fixed shaking speed of 180 rpm at pH 6.7. Figure 7 gives a brief illustration of the experimental procedure performed in the lab.

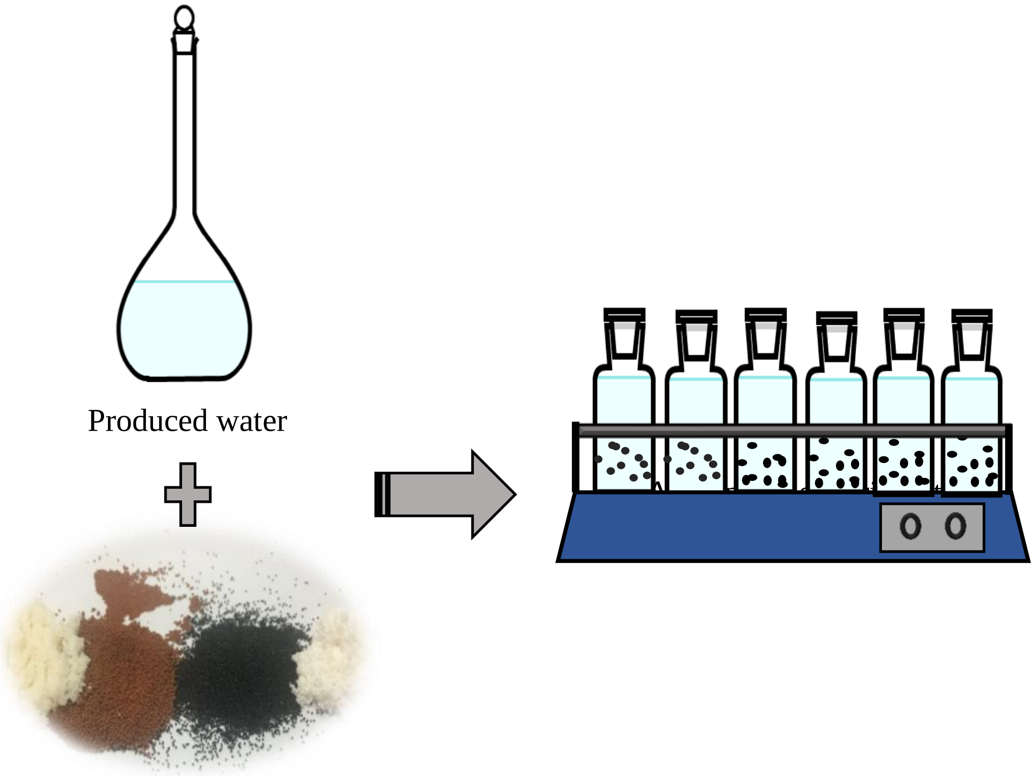

Figure 7. Schematic diagram of brief experimental procedure.

The amount of oil adsorbed on the synthetic resin was calculated according to equation 7 where q_e (mg/g) is the adsorption capacity, C_0 and C_e (mg/L) are the initial and equilibrium liquid phase concentrations of dissolved oil particles respectively, and V (L) is the volume of the solution and m(g) is the mass of the dry synthetic resin.

$$qe = \frac{(C_0 - C_e)xV}{m} \tag{7}$$

Percentage removals were calculated using equation 8:

$$\text{Percentage removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{8}$$

1.6.3.1 Effect of resin dosage

The effect of resin dosage experiment was carried out in the manner explained above by varying the resin dosage from 0.125 to 2 g for each synthetic resin while other parameters were kept constant. After the run was complete, the bottles were kept aside for 5 to 7 minutes to allow the resins to settle to the bottom of the containers. The treated water was then separated from the resins and placed in glass vials for total organic carbon (TOC) analysis. From this experiment, the best performing mass dosage for each resin was selected as the constant mass dosage to perform the rest of the experiments.

1.6.3.2 Effect of contact time

For this experimental procedure, contact time was the varied parameter. Mass dosage, volume, pH and temperature remained constant. The procedure mentioned above was followed; however, samples were taken at different time intervals ranging from 15 minutes to 8 hours. From preliminary experiments, resins L493 and AF 5 reached equilibrium after 8 hours, while XAD 7 reached equilibrium after 1 hour and IRA 958 took 4 hours to reach equilibrium.

1.6.3.3 Effect of initial oil concentration

For this part of the experiment, initial oil concentration was varied while the rest of the parameters were kept constant. A stock solution of concentration around 30 mg/L was prepared and diluted with D.I. water to approximate initial concentrations that include 4, 10, 12, 17 and 24 mg/L. A similar procedure as above was followed after which samples were taken for TOC analysis.

1.6.3.4 Effect of pH

The last parameter studied was the pH of the solution. The pH of the solution prior to alteration was 6.7. In order to vary the pH, 0.5 N NaOH and 0.5 N H_2SO_4 were used and the pH meter was used to identify the pH of the solution. The range of pH variation was from 2 to 10. The pH was measured using a pH bench meter (Orion Versa Star Pro) supplied by ThermoFisher Scientific (USA).

1.6.4 Regeneration experiments

Prior to the regeneration experiments, it is important to ensure that the resins are saturated with the contaminants to be removed. An adsorption experiment was carried out by adding generous amounts of resins to 100 ml of synthetic produced water and were agitated for 8 hours. The resins were filtered and removed to dry at room temperature overnight.

The regeneration experiments comprised of four different solvents to act as regenerant agents. Two organic solvents, Ethanol and Methanol, NaOH and distilled water heated to 60 °C. 1 M NaOH was prepared by dissolving 40 g of NaOH in 1 L of distilled water. Same operating conditions discussed above were carried out for this experiment; 50 ml of the regenerant agent was introduced into the glass bottle along with a fixed mass of dried saturated resins. The glass bottles were placed on the orbital shaker and agitated for 8 hours. The same process was repeated for the organic solvents.

Regeneration using distilled water required the use of a hot plate to heat the water to the desired temperature. A thermometer was placed in the glassware to measure the temperature of the water and to ensure the temperature of the water remains constant throughout the experiment as shown in figure 8. After the desired temperature was reached, resins were introduced into the flask and were stirred using a magnetic stirrer for one hour.

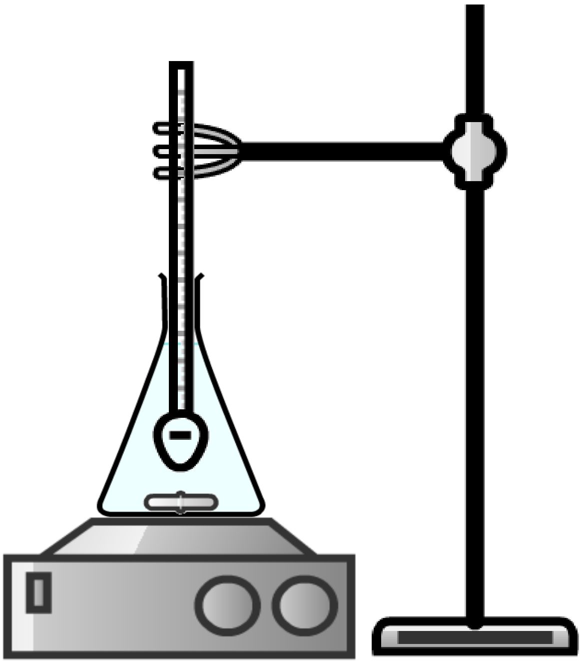

Figure 8. Desorption experimental setup using deionized water heated to 65 °C.

Following the regeneration experiments, another adsorption cycle was conducted. After each regeneration run, resins were filtered and dried at room temperature overnight. Fixed amounts of resins were measured out using the mass balance and introduced into the glass bottles along with 50 ml of synthetic produced water and were agitated for 8 hours. After the adsorption run was complete, samples were taken for TOC testing.

The effectiveness of the regeneration solvent was assessed by regeneration efficiency. The regeneration efficiency (RE) is defined as the percentage of original adsorption capacity resorted post the regeneration step and is represented as follows:

$$RE, after\ nth\ cycle = \frac{adsorption\ capacity\ after\ regeneration}{adsorption\ capacity\ of\ clean\ resin} x100 \tag{9}$$

1.6.5 TOC analysis of produced water

It is important to measure the total organic carbon (TOC) prior and after the batch experiments to be able to assess the adsorption process of oils onto synthetic resins. After each stock solution preparation, three samples were taken for TOC analysis and the average value was reported. The device used in analyzing the TOC is a Formacs TOC/TN analyzer by Skalar Analyzer (Breda, The Netherlands). Firstly, the sample is injected into the high temperature combustion furnace where total carbons (TC) are converted to carbon dioxide at temperature of 850 °C by catalytic oxidation (Pt catalyst). The formed carbon dioxide is then dispersed into the carrier gas and the concentration is measured by a non-dispersive infrared detector (NDIR). Then, the total inorganic carbons (TIC) are measured by injecting the sample into a reactor containing acid (H_3PO_4) converting TIC into carbon dioxide. The concentration of the resulting CO_2 is then determined by the NDIR. Finally, TOC is calculated by subtracting TIC from TC.

Two standard stock solutions are prepared, TC and IC stock solutions. TC stock is prepared by dissolving 2.128g of potassium hydrogen phthalate in carbon free water and diluted to 1000 ml. The solution is mixed well and stored at 4 °C. IC stock is prepared by dissolving 4.418 g of Sodium Carbonate and then 3.5 g of Sodium hydrogen carbonate and diluted to 1000 ml. The solution is well mixed and stored at 4 °C. The preparation of stock solution is based on the description in EPA methods 415.1 and 9060A.

1.6.6 Synthetic resins characterization

In order to have a realistic vision of the surface of the resins, SEM images were generated with the SEM, Nova Nanosem 450 (Field Electron and Ion, USA. This will also give an idea of how the surface of the resins look like. In addition, FTIR analysis was performed before and after the adsorption treatment to see if any visible changes to the structure of the resin will be observed. The machine used is the FTIR, spectrum 400 (PerkinELmer, USA),). Lastly, in order to validate the results of the regeneration experiments and to provide further support to the resulting data, the organic elemental analyzer (Flash 2000, USA) was used to compare the carbon content at resin’s fresh state and after regeneration.

CHAPTER 4: RESULTS AND DISCUSSION

This chapter contains the results of performing the experiment explained in chapter 3. The results presented here include SEM, EDX and FTIR characterization of synthetic resins. In addition, the TOC analysis data will act as means of evaluating the adsorption efficiency of synthetic resins, and results are reported as percentage removals of TOC. It is to be noted that the value of TOC reported is the combination of organic carbon originating from gasoline and the surfactant used. For precision and accuracy test, the relative standard deviation method was used. As for adsorption modeling, five isotherms were selected. Two commonly and widely used isotherms, Langmuir and Freundlich isotherms. The DR model was selected to provide in insight into the type of adsorption mechanism. The Flory – Huggins isotherm was selected to be able to calculate the Gibbs free energy to determine the spontaneity of the adsorption process. Lastly, the Toth isotherm was selected because it is a useful model to describe heterogenous adsorption systems. To model adsorption kinetics, three models were employed including pseudo-first and pseudo-second order models and intraparticle diffusion model. The results of the regeneration experiment are included and each regenerant agent will be evaluated according to their regeneration efficiency (RE).

1.7 Synthetic resins characterization

1.7.1 SEM and EDX characterization

The chemical structure of the selected resins was analyzed by energy dispersive X-ray spectroscopy (EDX) using Nova Nanosem 450 (Field Electron and Ion, USA) and are presented in Figure 9 along with the percentage weight of each element present as shown in Table 6. Data generated by EDX analysis comprises of a spectrum with peaks that correspond to all different elements present in the resin. As can be observed, the carbon and oxygen peaks are present in all four spectrums due to the organic

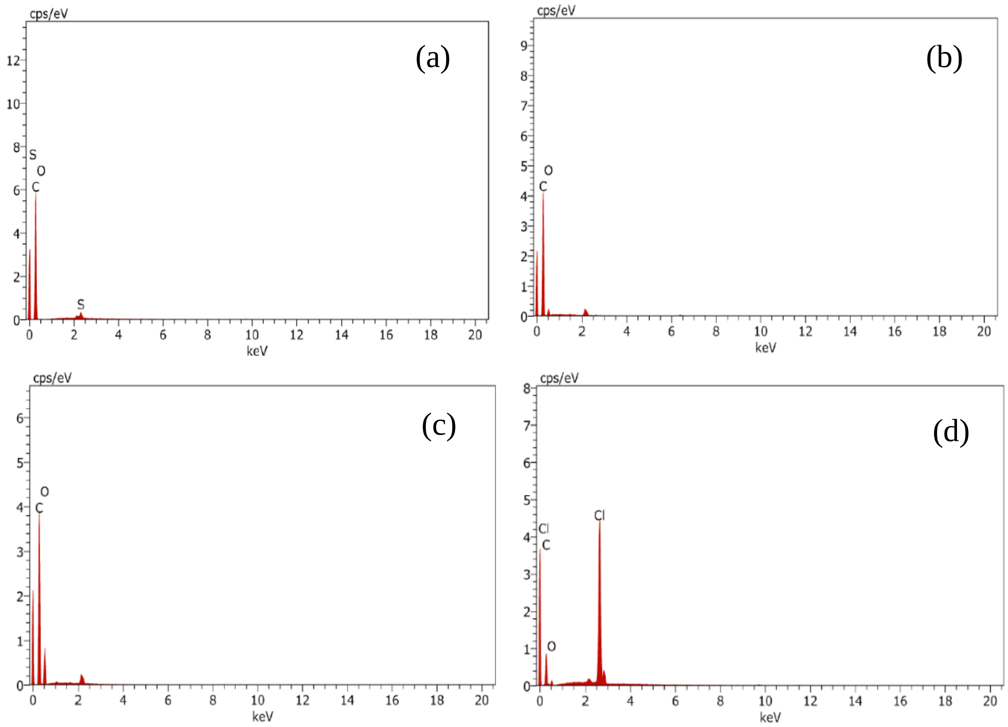

Figure 9. EDX spectrum for (a)AF 5 (b)L493 (c)XAD 7 (d)IRA 958.

compound structure of the resins. An additional peak was found in AF 5 resin that corresponds to the presence of sulfur in the resin matrix. Also, the existence of chloride atoms is confirmed by the additional peak present in the IRA 958 spectrum. The purity

Table 6. Percentage Weight of Each Element Present in Tested Synthetic Resins.

Element	AF 5	L 493	IRA 958	XAD 7
C	99.27 %	94.62 %	83.02 %	86.31 %
O	0.34 %	5.38 %	3.77 %	13.69 %
S	0.39 %	-	-	-
Cl	-	-	13.22 %	

of synthetic resins can be confirmed by the absence of other unwanted elements that may act as barriers in the adsorption process.The scanning electron microscopy (SEM) images of the synthetic resins in Figure 10 reveal spherical shapes. With the same level of scale bar for all insert images

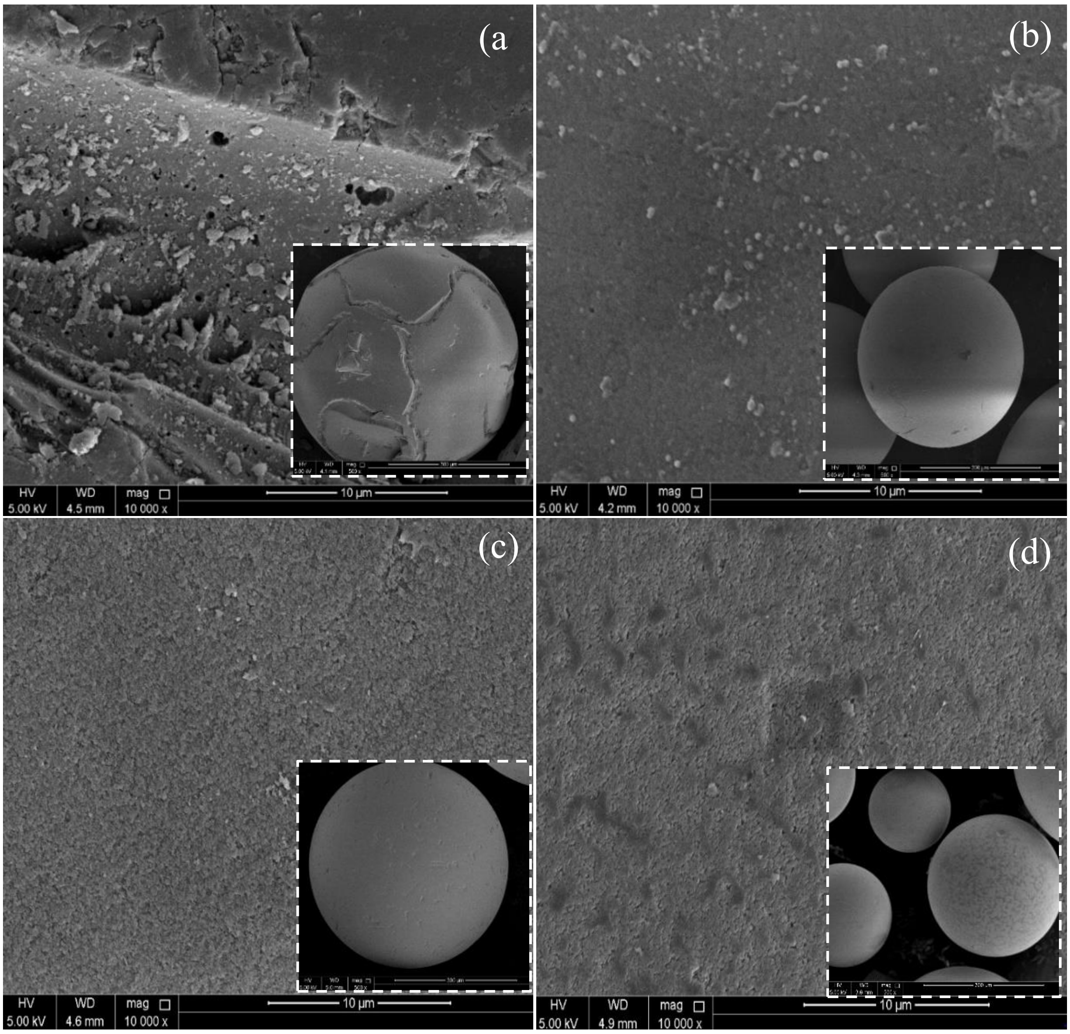

Figure 10. Surface characterization using SEM imaging. (a) AF 5, (b) IRA 958, (c) L493, (d) XAD 7.

(300 µm), it is noted that the size of the spherical beads that pertain to XAD 7 is the smallest; hence, XAD 7 has the smallest BET surface area (see Table 5). Furthermore, the enlarged images with a scale bar of 10 µm show that all resins possess smooth surfaces except for AF 5 resin. AF 5 possesses a crinkled surface with lines that are engraved into the resin producing a wider surface area for adsorption; thus, exhibiting the highest BET surface area among all tested resins.

1.7.2 FTIR analysis

FTIR spectroscopy has been frequently used to detect vibrational frequency changes in synthetic resins. This analysis offers important information on the nature of the bonds present and helps in identification of various functionalities on the resin structure. The FTIR analysis of AF 5 before and after adsorption of oil is presented in Figure 11. There is no drastic change in the synthetic resin structure prior and post treatment. This confirms the nature of the adsorption process which is of physical nature. The existence of aromatic rings is usually determined from the C – H and C=C-C vibrations. By observing the spectrum in Figure 11a, two small peaks are shown at frequencies of 2287 and 2037 cm^{-1} which is an indication of Methyne (C – H) stretch or an aromatic C – H stretch. The C – H set of vibrations can be virtually seen in all organic compounds. A noticeable change between the two spectra is the disappearance of the peak at 2921.14 cm^{-1}, could be due to a C – H stretch, which is most likely due to surface coverage by adsorbed contaminants.

Figure 11. FTIR spectra before (a) and after (b) adsorption of oil onto AF 5

Two prominent peaks can be observed from the FTIR analysis results presented in Figure 12. The peak at 3331.55 cm^{-1} is attributed to the O – H stretch of the hydroxyl group. The presence of this group could be due to moisture or OH groups found on the surface of the resin. The broadness of the peak is the result of hydrogen bonding. The stronger the bond, the broader the peak. A slight shift of this peak is observed after adsorption resulting in a stretch at 3346.76 cm^{-1}. The second prominent peak at 1635.27 cm^{-1} is the result of C=C stretch coming an alkene. After adsorption, a third peak was observed at 1092.97 cm^{-1} due to O – H stretch of adsorbed phenols.

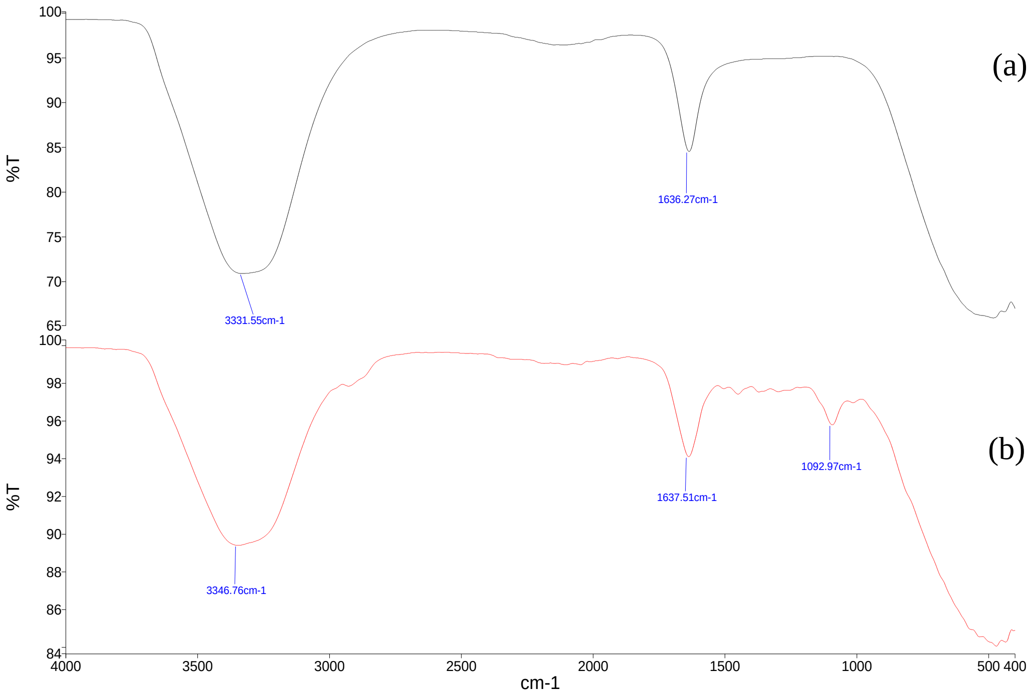

Figure 12. FTIR spectra before (a) and after (b) adsorption of oil onto L 493

FTIR analysis results for XAD 7 resin are presented in Figure 13. The prominent changes between the two spectra are the presence of the OH peak at 3343.78 cm^{-1} after adsorption due to moisture and the O – H stretch at 1147.9 cm^{-1} due to the OH bend of an adsorbed phenol group. Also, the noticeable disappearance of unsaturated C=C peaks due to surface coverage.

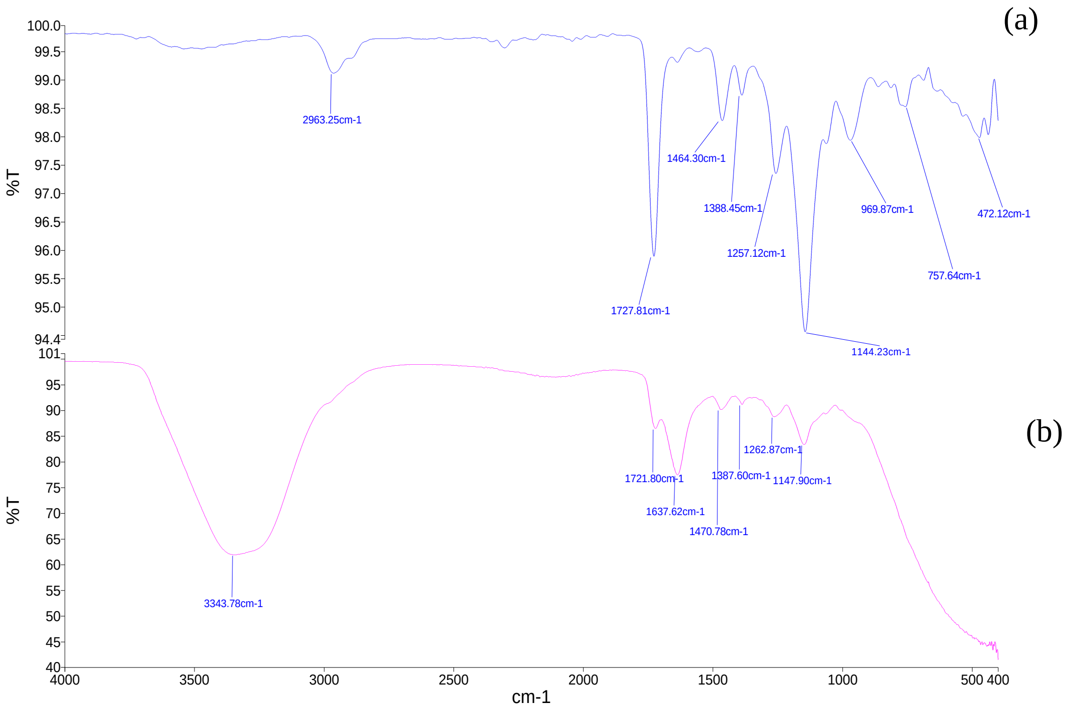

Figure 13. FTIR spectra before (a) and after (b) adsorption of oil onto XAD 7

The FTIR spectra for IRA 958 are shown is Figure 14. The results show an O – H stretch at 3338.46 cm^{-1} before adsorption and 3337.66 cm^{-1} after adsorption. Other prominent peaks are due to unsaturated C=C stretch at 1634.61 and 1479.97 cm^{-1}. It is observed that there is no change in the spectra before and after the adsorption process. This shows that no adsorption occurred onto the resin. A more detailed analysis is provided in section 4.2 (Adsorption studies).

Figure 14. FTIR spectra before (a) and after (b) adsorption of oil onto IRA 958

1.8 Adsorption studies

1.8.1 Effect of adsorbent dosage

In order to determine the optimum resin dosage, the mass of each resin was varied from 0.125 to 2 g while maintaining other parameters such as pH of 6.7, room temperature and initial oil concentration (28 ppm) constant. The results are presented in Figure 15. By observing the graph, it is clear that the three resins, namely XAD 7, L492 and AF 5 behaved similarly with similar percentage removals. The graph shows

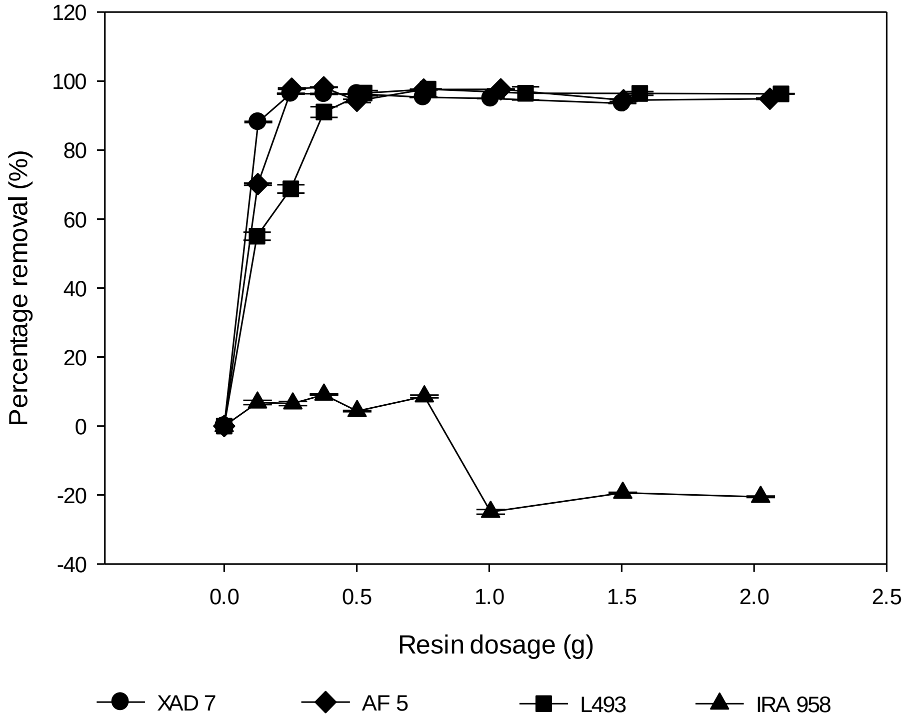

Figure 15. Effect of resin dosage on the adsorption of oils at neutral pH, temperature 25 °C and contact time 24 hours

that initially increasing the adsorbent dosages,enhances the adsorption efficiency of oil. Towards the end; however, it is noted that there is a slight decrease in percentage removals which is attributed to the fact that adsorption is a surface phenomenon where oil particles are adsorbed at the surface of the adsorbent. High mass dosages will cause resins to agglomerate in turn, reducing surface areas that should have been accessible to oil particles. Thus, lower percentage removals are obtained. XAD 7 exhibits the highest percentage removal at 0.5 g for 96.3 % after which the percentage removal starts to decrease. A similar phenomenon is also observed by Uslu et al. [97] for the removal of Lactic acid using XAD 7. Their reported results state that the percentage removals decreased with an increase in XAD 7 dosage reaching optimum removal at 2.5 g which is lower than the optimum mass dosage reported in this study. The working concentrations of target contaminants of this study are substantially lower than the study reported in turn, lower optimum mass dosage will be required. L 493 displays a gradual increase in percentage removal reaching peak removal of 96.5% at 1.5 g after which no further increase is attained. AF 5 displayed a peak percentage removal of 97.5 % at 0.75 g followed by a slight decrease reaching 94% removal at 2 g.

IRA 958 behaved in a different manner with only 8.6% removal. It is noted that the separation mechanism of IRA 958 is heavily influenced by its polymer structure. IRA 958 is an anion exchange resin with quaternary ammonium as its functional group. The hydrophobic interactions between the aromatic rings in the hydrocarbon mixture and polystyrene-based resins play a key role in the adsorption of hydrocarbons. In the case of IRA 958 a polyacrylic resin with quaternary ammonium group these types of interactions are substantially minimized and therefore, less removal is obtained [82]. Resin IRA 958 showed poor percentage removals throughout the variation of the resin dosage. The highest percentage removal was obtained at 0.375 g followed by a substantial decrease in removal where percentage removals went below 0 reaching negative values indicating that organic compounds may have leached into the solution, therefore, increasing the TOC value. The determined optimum mass for each resin was then used to carry out the rest for of the experimental study

1.8.2 Effect of initial oil concentration

The effect of initial concentration of dissolved oils on the adsorption capacity of XAD 7, L493, AF 5 and IRA 958 has been investigated by varying the initial concentration of oil from 3 to 27 mgl/L. Other parameters were kept constant such as a neutral pH, room temperature of 25 °C, contact time of 24 hours and mass of resin 0.25 g, 1.5 g, 0.75g and 0.375 g for XAD 7, L493, AF 5 and IRA 958 respectively. The

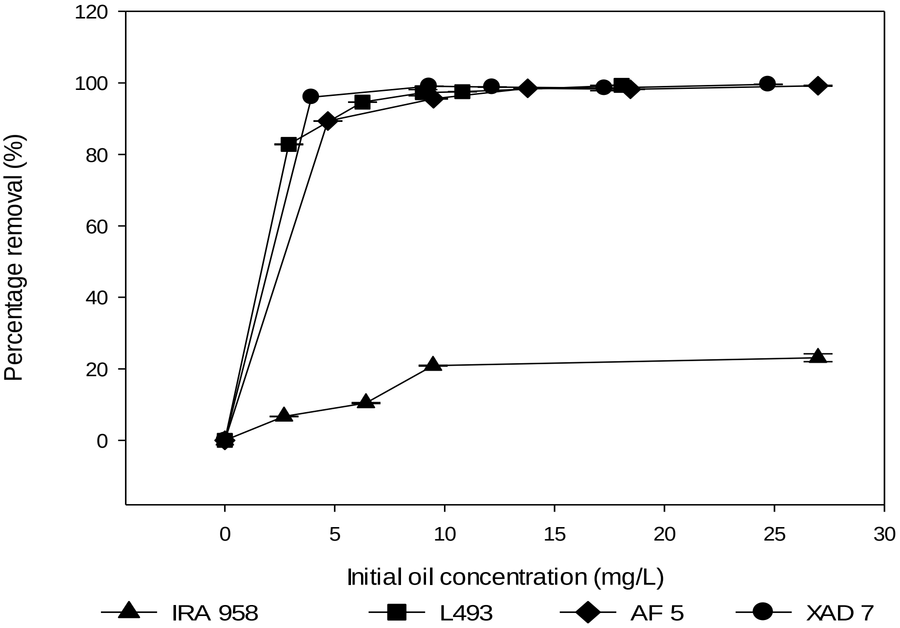

Figure 16. Effect of initial oil concentration on the adsorption of oils at temperature 25 C, contact time 24 hours and neutral pH

results are presented in Figure 16. As can be observed, initially percentage removals increase with increasing the initial oil concentration due to the increase in the concentration gradient between the bulk solution phase and the solid phase. In other words, the higher the concentration introduced into the system, the higher the uptake will be in turn, the higher the percentage removal. Thus, this data demonstrate that the adsorption process is controlled by the diffusive mass transport of oil particles onto the active sites. A published study by Makhathini et al. depict the same behavior but with a polystyrenic resin for the removal of BTEX compounds. Scarce information is found in the literature regarding this particular studied parameter for synthetic resins for the removal of oil from water. However, there are studies reported with AC for removal of oil form water. The same trend as in this present study is observed placing current findings in perspective.

1.8.3 Effect of pH

The pH effect on the adsorption of oils onto three resins of different polarity L493, XAD 7 and IRA 958 has been studied for the pH range of 2 to 10. The pH of the aqueous solution should act as a key parameter that controls the adsorption of oils onto the synthetic resins. However, this is not the case as can be seen in Figure 17. The change in pH had no effect on the adsorption process; the percentage removals for all three resins remained almost constant throughout the pH variations. A similar finding has been reported by Liu et al. where the effect of pH has also been examined for the adsorption of trihalomethanes on L 493 [84]. Their results also displayed no change in percentage removals while varying the pH. This proves that the additional H^+ or OH^- ions do not cause any changes in the adsorption mechanism. A similar case is also observed in the literature for IRA 958 where pH has no influence on the adsorption of hydrocarbons on strong base anionic exchangers [98]. Furthermore, Gogoi et al.

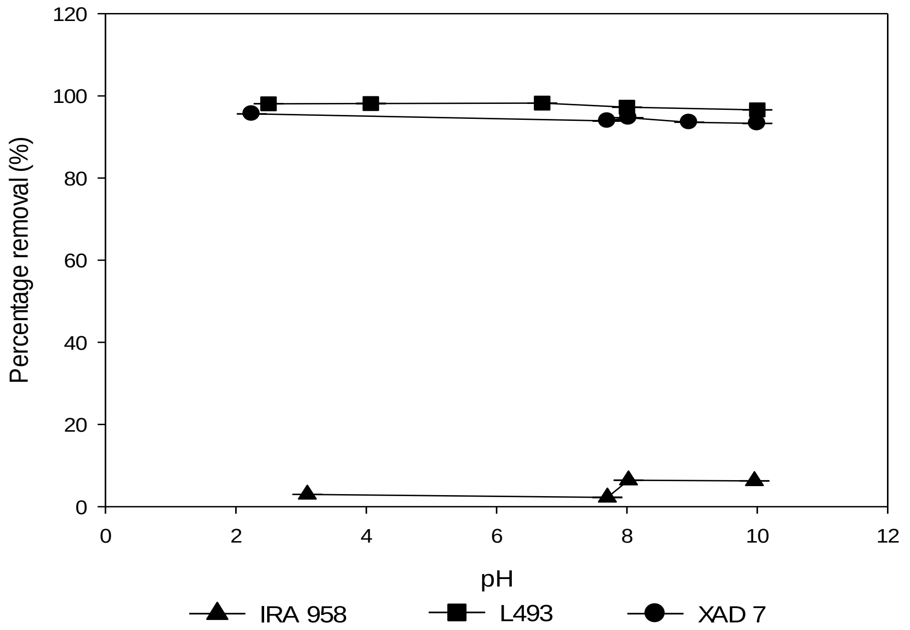

Figure 17. Effect of pH on the adsorption of oils at temperature 25 °C, contact time 24 hours and initial oil concentration of 28 mg/L

reported a similar finding when assessing the adsorption efficiency onto XAD 7 while varying the pH [33]. The results of the reported study validate the results of this present study where the variation in pH had no or marginal effect on the adsorption process.

1.9 Adsorption isotherms

Equilibrium studies are crucial in the design of adsorption system as they determine theoretically the maximum adsorption capacity that can be achieved during the treatment process. In order to determine the adsorption coefficients of the adsorption isotherm models, the parameters were obtained using the non-linear regression method by employing Marquardt-Levenberg algorithm a method of finding the minimum function that is a sum of squares of nonlinear functions [99]. The solver add-on in Excel was also used to optimize the coefficient values by non-linear regression. The solver method allows the user to test multiple error functions to further optimize the approach. All methods were then compared based on R^2 values and the one with a higher R^2 value was selected. The parameters are presented in Table 7 and the experimental data along with the five equilibrium isotherms for the best performing resins (XAD7, L493 and AF 5) are depicted in Figures 18 through 20.

Based on the calculated constants, AF 5 exhibited the highest maximum adsorption capacity (q_m) of 13.35 mg/g followed by XAD 7 with a value of 11.86 mg/g. This is due to the fact that AF 5 has the highest surface area among tested resins and that has a crucial effect on the adsorption capacity.

The experimental data obtained from the adsorption of oils onto XAD 7 was best described by the Freundlich isotherm among all adsorption processes with R^2 of 0.9811. Thus, this model is very suitable in describing the adsorption process on XAD 7 for the studied concentration range. This model cannot predict the level of saturation of oil particles on the surface of the resin; therefore, it is predicted that surface coverage goes to infinity from a mathematical point of view. However, an insight can be gained on the favorability of the adsorption process through the term 1/n. The numerical value obtained for the term 1/n is 0.77 which is less than 1 indicating that the adsorption is favorable.

Looking at Table 7, R^2 values pertaining to the Flory Huggins model are relatively higher effectively describing the adsorption process on all three resins. The Gibbs free energy was calculated for the adsorption process on XAD 7, L493 and AF 5 and were determined to be -9.77, -6.07 and -7.47 kJ/mol respectively. The negative values indicate that the adsorption process is spontaneous.

Both resins XAD 7 and AF 5 adequately obey the RD model; however, this model does not describe the adsorption process on L493 resin. The attained parameters are then used to calculate the mean free energy ($E = 1/\sqrt{2k_{ad}}$) and were found to be 1.127, 0.138 and 3.494 kJ/mol for XAD 7, L 493 and Af 5 respectively. According to Srivastas et al. the magnitude of the mean free energy provides an insight on the type of the adsorption mechanism [100]. Values of E less than 8 kJ/mol indicate that the adsorption process is physical of nature. Values between 8 and 16 kJ/mol are chemical in nature. The calculated E values in this experimental study are less than 8 suggesting that the adsorption processes on the three synthetic resins are controlled by physical adsorption. In the case of nonfunctionalized resins Optipore L493 and Lewatit AF 5, the adsorption process is governed by the Van der Waals interactions between the aromatic rings between the gasoline molecules and phenyl ring on the resin matrix [36]

Table 7. Isotherm Parameters for Models Used.

Isotherm model	Parameter	XAD 7	L 493	AF 5
Langmuir	Qm (mg/g)	11.86	9.51	13.35
	B (L/mg)	0.15	0.19	3.16
	R^2	0.9808	0.905	0.6361
Freundlich	Kf (L^n $mg^{1/n}$/g)	3.82	2.93	7.34
	n	1.29	2.91	4.05
	R^2	0.9811	0.8360	0.7992
Toth	K_T	4.46	2.96	12.22
	a_T	0	0	0.25
	t	2.84	1.5	1.04
	R^2	0.9449	0.923	0.6604
Flory-Huggins	K_{fh}	51.62	11.57	18.88
	n_{FH}	0.77	0.52	0.25
	R^2	0.9218	0.896	0.8647
Dubinin	q_s	11.60	14.28	12.27
Radishkevich	K_{ad}	0.39	26.38	0.04
	R^2	0.9168	0.698	0.9741

Generally, the dominant determinant of adsorption capacity is the surface area with respect to pore size [38]. By observing the maximum adsorption capacities obtained by fitting the isotherm models (Table 6), AF 5 exhibited the highest adsorption capacity among all tested resins. This is attributed to the fact that AF 5 has the highest surface area allowing more room for oil uptake. Although L493 has a higher surface area than XAD 7, the adsorption capacity of XAD 7 was higher than that of L493. This shows that the chemical structure of the synthetic resin plays a major role in the adsorption process. XAD 7 is an acrylic ester which is relatively a more hydrophilic structure and possesses intermediate polarity. The oil/water mixture contains polar aromatic compounds which are more readily adsorbed onto XAD 7 despite the fact that it has a lower surface area than L493. Also, XAD 7 reached equilibrium faster than the rest of the resins by a substantial amount of time which further proves that adsorbent polarity plays a key role in the adsorption process.

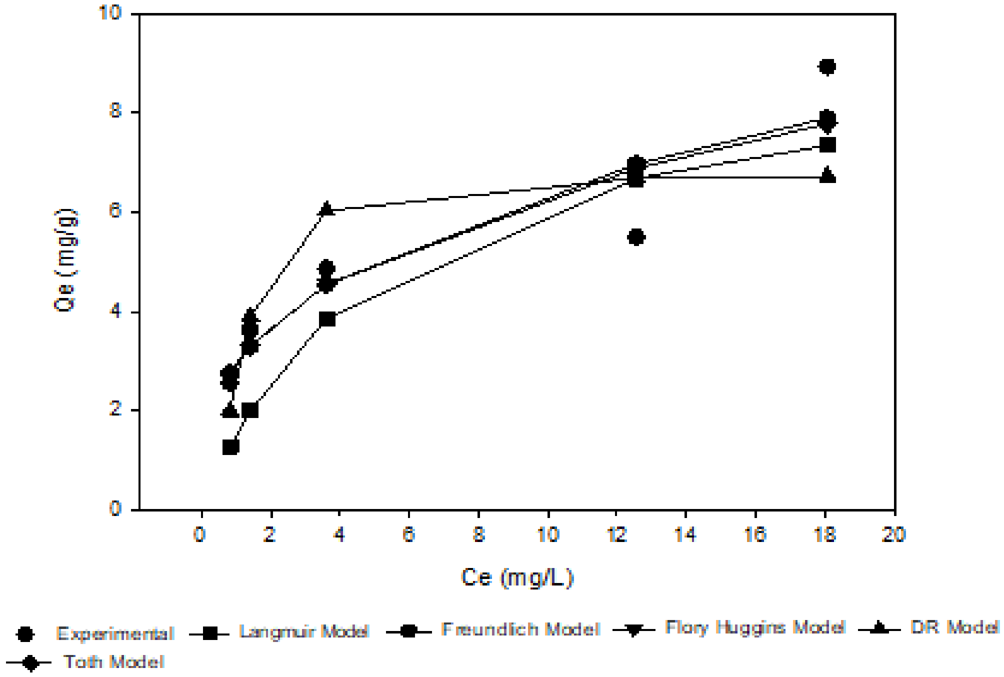

Figure 18. Fitted adsorption isotherms for the adsorption process onto L493 at neutral pH, temperature 25 C and initial oil concentration of 28 mg/L.

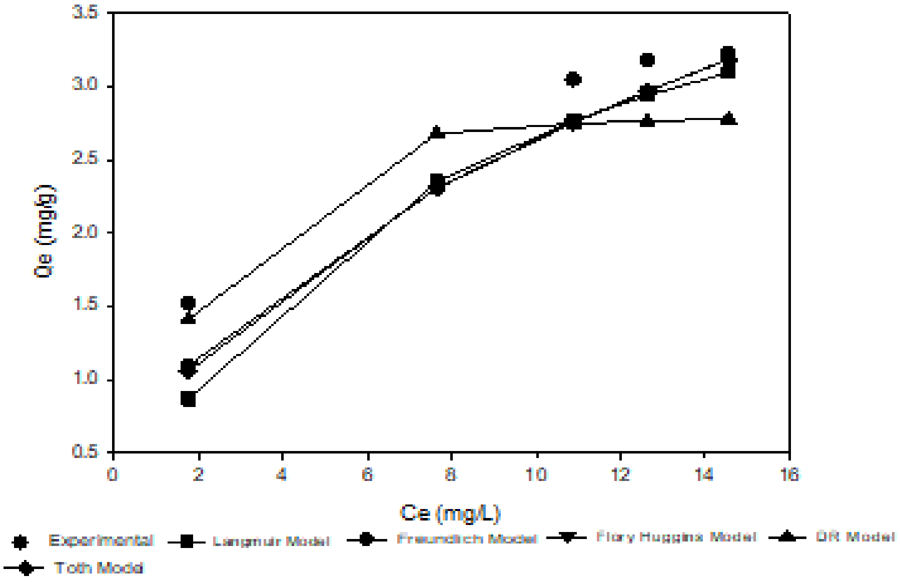

Figure 19. Fitted adsorption isotherms for the adsorption process onto AF 5 at neutral pH, temperature 25 C and initial oil concentration of 28 mg/.

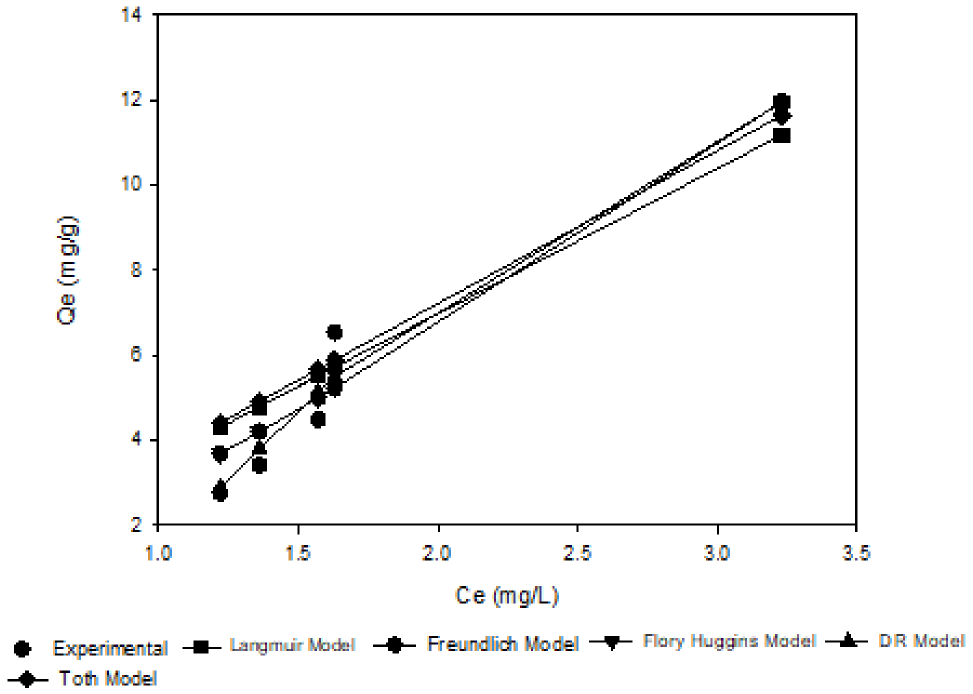

Figure 20. Fitted adsorption isotherms for the adsorption process onto XAD 7 at neutral pH, temperature 25 C and initial oil concentration of 28 mg/.

1.10 Kinetic studies

For industrial applications, it is important to determine the rate at which the contaminants are removed by the adsorbents. Batch experiments were carried out to study the effect of contact time to be able to determine the time at which equilibrium is reached for each resin. The equilibrium contact time refers to the time frame required for the adsorption process to reach equilibrium. Equilibrium is reached when the rate of adsorption of contaminants from the solution onto the surface of the adsorbent equals to the rate of desorption from the adsorbent surface to the solution after which no more adsorption occurs. It was observed from Figure 21 that almost all resins displayed a rapid adsorption process initially followed by a gradual decrease in speed until equilibrium was reached. This is attributed to the large number of available vacant sites for adsorption during the first stage of the process. As can be seen, throughout the middle stage, adsorption decreases progressively as more vacant sites become occupied. Finally, adsorption reaches the last stage where vacant sites are blocked, and equilibrium is reached. Adsorption impedes due to the repulsive forces between organic compounds adsorbed on the solid surface and the ones in the liquid phase. Among all synthetic resins, XAD 7 exhibited the fastest adsorption kinetics for equilibrium was reached after 1 hour after which no more adsorption occurred. A similar finding has been reported by Freitas et al. for the adsorption of di-2-pyridyl ketone salicyloylhydrazone on XAD 7 [101]. Uslu et al. reported a different equilibrium contact time for the adsorption of Lactic acid on XAD 7 where equilibrium was reached after 90 minutes [97]. As for Optipore L493 and Lewatit AF 5, equilibrium reached after 8 hours for both resins. It is difficult to precisely identify the equilibrium contact time for IRA 958.

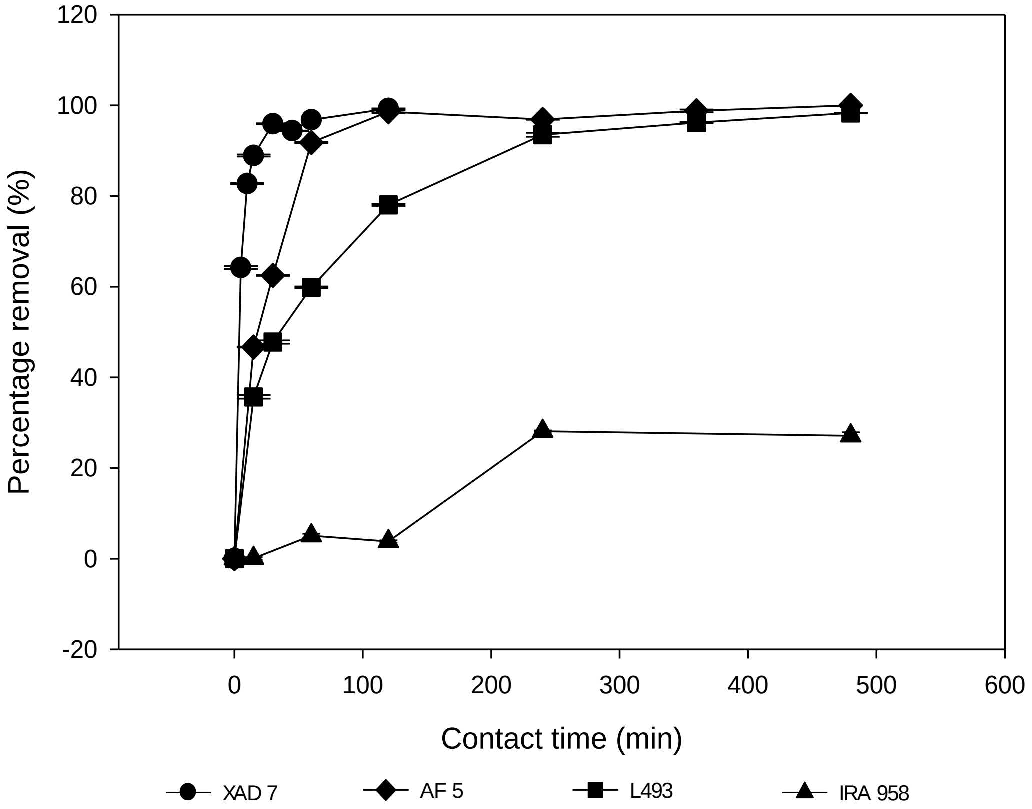

Figure 21. Effect of contact time for each resin at 25 °C, neutral pH and initial concentration of 28 mg/L.

The results show fluctuations at the beginning after which IRA 958 exhibited maximum adsorption after 4 hours after which no further adsorption was observed. XAD 7 was able to reach equilibrium faster than other resins due to the fact that XAD 7 is an acrylic ester allowing it to expand 20% more than styrene resins (L493 and AF 5). This expansion causes an increase in the porosity of XAD 7 beads; thus, allowing it to attain equilibrium faster [102].

Evaluation of the kinetic mechanism of adsorption of dissolved oil compounds onto XAD 7, L493 and AF 5 synthetic resins was performed using three kinetic models: pseudo-first order, pseudo-second order and intraparticle diffusion models.

Lagergren's first order rate equation which is also referred to as pseudo-first order model is one of the most commonly used models for adsorption kinetic studies. This model is based on the assumption that the rate of the adsorption process is directly proportional to the number of unoccupied sites by the solutes [103]. This model is given by the form of equation 10 [104].

$$\ln(Q_e - Q_t) = lnQ_e - K_1 t \tag{10}$$

A graph of ln (Qe-Qt) as a function of time is plotted for all three synthetic resins at room temperature, pH of 6.7 and a resin dosage of 0.25 g, 0.75 g and 1.5 g for XAD 7, AF 5 and L493 respectively is shown in Figure 22 (a). The constants k_1 and Qe were calculated by obtaining equation of line. The constants are summarized and presented in Table 8.

The experimental data did not fit well with the pseudo-first-order model expect with resin L493 where the correlation constant R^2 was calculated and determined to be 0.984. A high R^2 value indicates that the adsorption of dissolved oil particles on L493 follows pseudo-first-order model. In contrast to the adsorption of dissolved oil contaminants on XAD 7 and AF 5 where R^2 values are relatively low implying that they do not follow pseudo-first-order model.

Pseudo-second-order model previously known as Ho's second-order rate equation is also a commonly used kinetic model. It is commonly employed to distinguish kinetic equations on the basis of adsorption capacity from concentration of solution [105]. A linearized plot of t/Qt as a function of time is presented in Figure 22 (b). The experimental data are well-fitted with this model for all three resins with R^2 extremely close to unity indicating that the adsorption system strongly follows pseudo-second-order kinetic model. This model is given by equation 11.

$$\frac{t}{q_t} = \frac{1}{k_2^2 q_e^e} + \frac{t}{q_e} \tag{11}$$

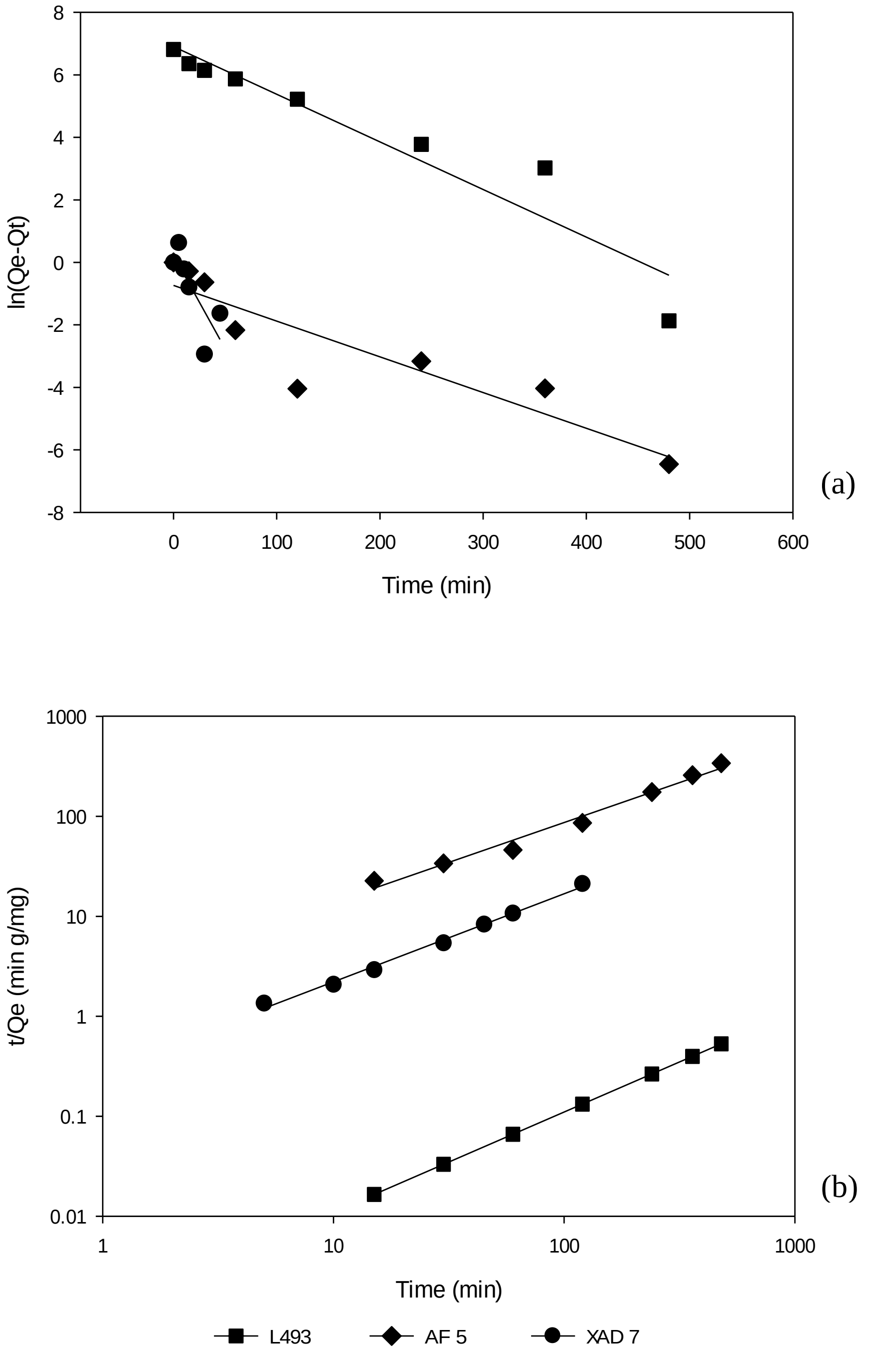

Figure 22. Pseudo-first (a) and second order (b) kintetics at 25 C and, pH 6.7 and initial concentration of 28 mg/L.

1.10.1 Intraparticle diffusion model

In order to have an insight into the rate controlling steps affecting the adsorption process and the mechanism, the intraparticle diffusion model proposed by Weber and Morris was employed [106]. The model is given by equation 12 where the constant C provides an indication on the thickness of the boundary layer and k_i is the intraparticle diffusion rate constant. The constants are evaluated by plotting qt verses time$^{0.5}$ shown in Figure 23 and are presented in Table 7.

$$q_t = k_i t^{0.5} + C \qquad (12)$$

As can be seen from Figure 23, the plot does not show a linear relationship over the entire time frame. The model exhibits three stages where each stage represents a different sorption mechanism. The first portion illustrates boundary layer diffusion where oil compounds diffuse through the boundary layer to the external surface of the resin. The first stage depicts instantaneous adsorption which explains the sharp rise in uptake seen in Figure 23. The second stage is slower than the first representing a gradual adsorption process controlled by intraparticle diffusion. Finally, the last stage involves the equilibrium step where internal diffusion occurs within the pores of the resin resulting in a slow adsorption rate. As can be viewed in Figure 23, the multi-phase behavior suggests that the adsorption process proceeds by intraparticle diffusion in addition to surface film diffusion.

It can be concluded that the adsorption of dissolved oil particles on all three resins strongly follows pseudo-second-order due to R^2 values that are extremely close to one. Conversely, it was observed that not all resins obeyed the pseudo-first-order model. The adsorption of oil on L493 was the only process that followed pseudo-first-order with R^2 value of 0.984. However, the case is not the same for adsorption onto

XAD 7 and AF 5 where R^2 values are comparatively low. A summary of the determined constants is presented in Table 8.

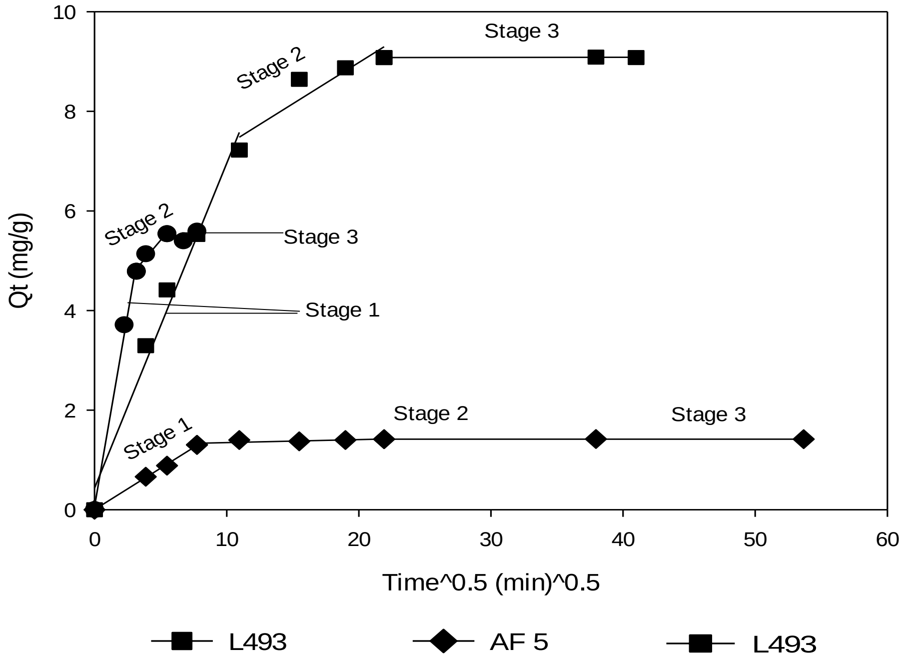

Figure 23. Intraparticle diffusion model at 25 °C, pH 6.7 and initial concentration of 28 mg/L.

Table 8. Pseudo first-order Model Parameters for The Adsorption of Dissolved Oils at Temperature 25 °C, C0 28 Mg/L and Ph 6.7.

Pseudo-first-order	Qe (mg/g)	k1 (1/min)	R^2
L 493	6.919	0.0104	0.984
XAD 7	1.250	0.0598	0.619
AF 5	0.4804	0.0114	0.823

Table 9. Pseudo Second-Order Model Parameters for The Adsorption of Dissolved Oils at Temperature 25 °C, C0 28 Mg/L and Ph 6.7.

Pseudo-second-order	Qe (mg/g)	k_2 (g/mg min)	R^2
L 493	909.1	0	0.999
XAD 7	5.763	0.286	0.999
AF 5	1.489	0.227	0.998

Table 10. Intraparticle Diffusion Model Parameters for The Adsorption of Dissolved Oils at Temperature 25 °C, C0 28 Mg/L and Ph 6.7.

Intraparticle diffusion	k_i (mg/g $min^{0.5}$)	C (mg/g)	R^2
L 493	0.1324	4.844	0.619
XAD 7	0.634	1.665	0.717
AF 5	0.0096	1.0638	0.324

1.11 Regeneration

The overall economics of synthetic resins is tightly linked to its reuse during regeneration. As such, the objective of the adsorbent regeneration is to desorb the contaminants and restore the original adsorption capacity. The effectiveness of solvent regeneration is measured by the regeneration efficiency. The regeneration ability of the synthetic resins was evaluated using four regenerants which include: 1 M NaOH, methanol, ethanol and water heated to 65 °C.

Resin L493 generally shows potential for reusability as the lowest RE value obtained is around 80 % with ethanol as the regenerant. It is also noted that RE using NaOH reached above a 100 % indicating the formation of new active sites. As can be

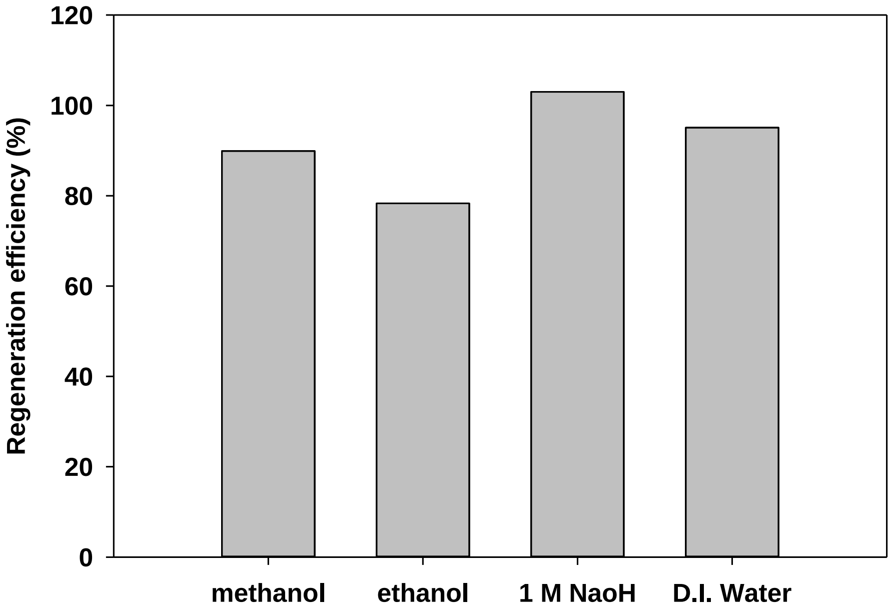

Figure 24. Regeneration efficiency of four solvents onto L493 at ambient temperature (except D.I. water at 65 C°) and pressure

seen in Figure 24, NaOH is the most efficient desorbing agent among all solvents followed by D.I. water with RE value of 95.10 %. A similar finding was reported in the literature by Liu et al. where NaOH was used to regenerate L 493 and a RE of 98 % was obtained [84].

By looking at Figure 25, it is noted that both solvents methanol and D.I. water achieve high desorption capabilities with RE values of 100 % and 95.8 % respectively. Methanolregenerated AF 5 resin completely by restoring its original adsorption capacity. However, ethanol and NaOH did not show positive results showing relatively low RE values of 74 % and 65 % respectively.

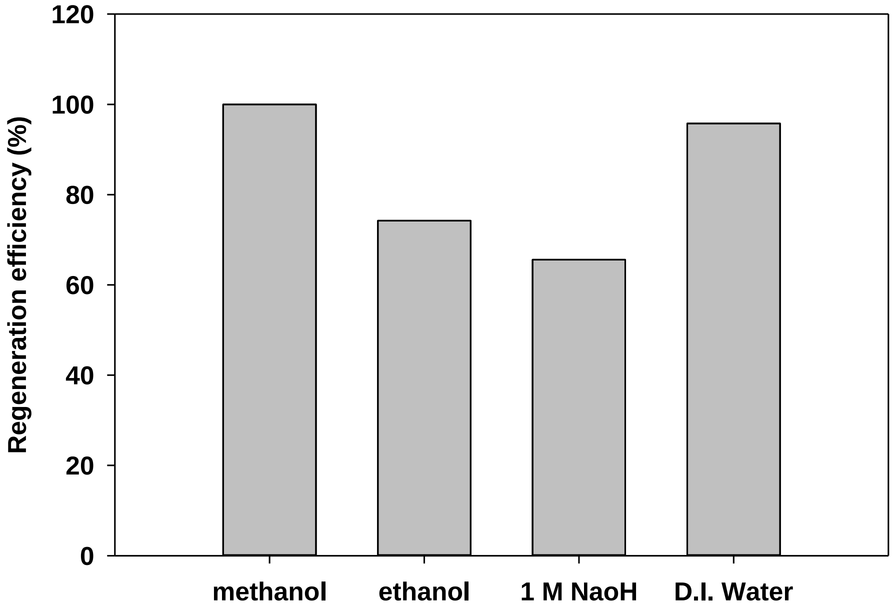

Figure 25. Regeneration efficiency of four solvents onto AF 5 at ambient temperature (except D.I. water at 65 C°) and pressure.

Among all three resins, XAD 7 showed the best candidate for regeneration and reusability. Almost all solvents were able to completely desorb the contaminants from XAD 7 restoring its original adsorption capacity, results illustrated in Figure 26. RE values of 100 % is achieved with both organic solvents. NaOH also exhibited good regeneration capabilities with RE value of 85.6 %; nonetheless, regeneration is better achieved using methanol or ethanol. Similar results were obtained D.I. water at 65 °C was also tested as a regenerant agent; however, XAD 7 behaved in an expected way. It was discovered that XAD 7 cannot withstand water at high temperatures for the water turned cloudy (see Figure 27) indicating that XAD 7 might have melted during the regeneration process. Since this behavior has not been observed with other resins, the main reason behind it is that XAD 7 is an acrylic ester thus, hydrogen bonding can be formed through their oxygen atoms with hydrogen atoms of water molecules making them soluble in water.

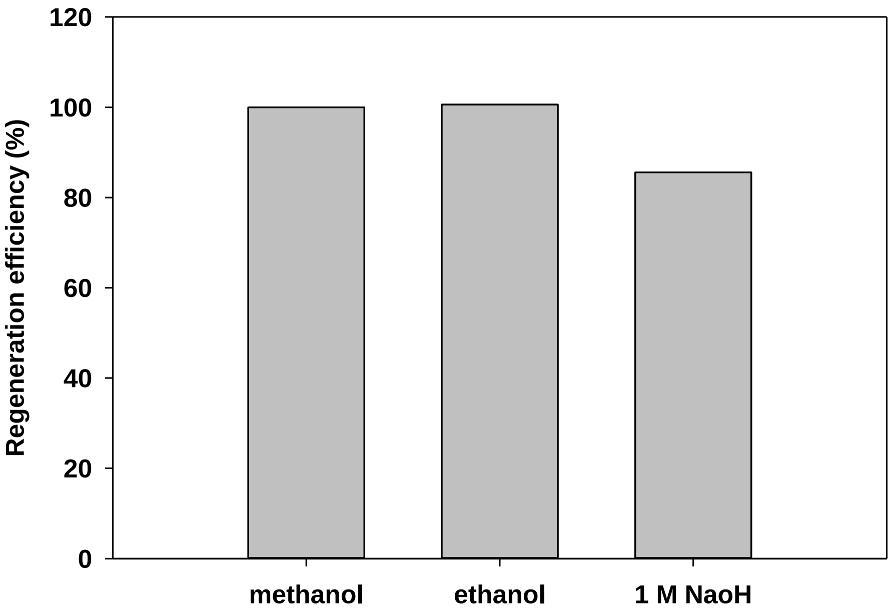

Figure 26. Regeneration efficiency of four solvents onto XAD 7 at ambient temperature (except D.I. water at 65 C°) and pressure.

Also, since this phenomenon has not been observed at ambient temperature during the adsorption process, it is apparent that the elevated temperature accelerated the melting process.

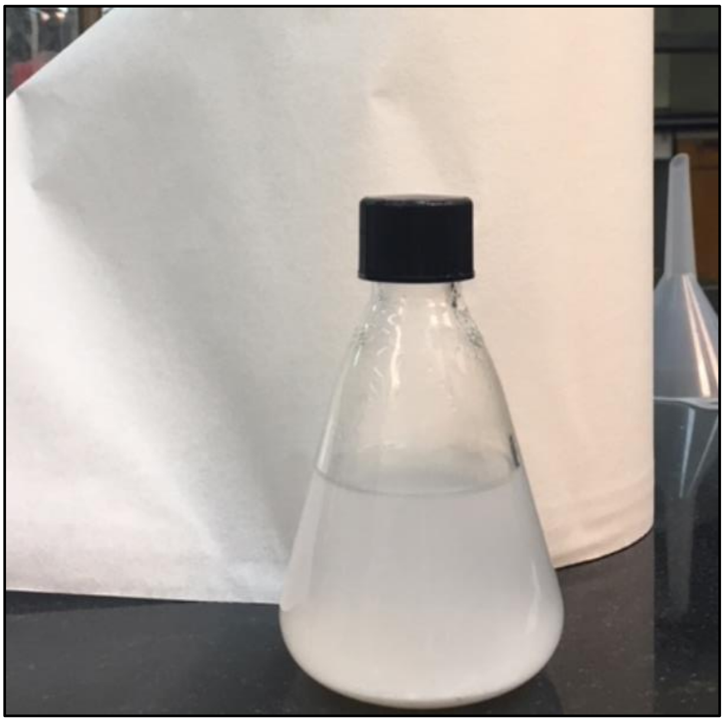

Figure 27. Cloudy solution of XAD 7 melted in water at 65 °C

Ferri et al. performed desorption experiements on XAD 7 with different desorbing agents, acidified ethanol, ethanol and water [67]. The results demonstrated that XAD 7 was regenerated almost completely with ethanol with RE values of 90 %. which is in agreement with the regeneration results obtained in this work.

Generally, the best solvent to use is the solvent that has similar solubility parameters to the contaminants to be removed. Since contaminants removed in this study originate from gasoline, organic solvents are the most viable option as desorbing agents for gasoline can be easily dissolved in ethanol or methanol. Nonetheless, polarity and hydrogen bonding effects should also be taken into consideration.

The ease of regeneration is an indication of weak attraction forces between the surface functional groups of the resin and the contaminants. If the resin is of hydrophobic nature, as is the case of resins L 493 and AF 5, the interaction forces are most likely van der Waals which are weak forces in nature and the concentration gradient is strong enough to overcome the interaction forces for the desorption process to happen. Generally, organic solvents chosen in this study were able to desorb both L493 and AF 5 with methanol completely desorbing AF 5 and XAD 7 was completely regenerated using both solvents. Also, it is noted that methanol performed better than ethanol for both hydrophobic resins. As a chemical, methanol is less expensive than ethanol; however, ethanol is not toxic unlike methanol which is a toxic chemical. For industrial applications, methanol would be preferable since is it cheaper but, handling precautions should be taken into consideration when dealing with this chemical.

For further supporting data, synthetic resins were analyzed using the organic analyzer to assess the carbon content. Since it is difficult to measure the TOC after regeneration with an organic solvent, the percentage of carbon will serve as a basis to see the difference between the carbon content before and after regeneration. The regenerated resins are rinsed thoroughly with deionized water to ensure the removal of methanol or ethanol residues left behind.

Tables 9 through 11 summarize the content of the tested synthetic resins for the three elements carbon, nitrogen and hydrogen at their clean state and after regeneration with organic solvents. Looking at Table 9, the carbon content in L493 increases by 9.6 % after regeneration with methanol and by 34.2 % after regeneration with ethanol.

Since the carbon content was not restored to its original state, resin L 493 was not completely regenerated. This result is in accordance with the RE data regarding this resin mentioned above.

There has been a substantial increase in carbon content in resin AF 5 after regeneration with ethanol with a percentage increase of 78 %. This shows lack of complete regeneration with ethanol whereas regeneration with methanol exhibited complete regeneration with a slight decrease in carbon content could be due to the formation of new pores. Also, Table 10 represents the results obtained for resin XAD 7. Carbon content decreases after regeneration with both organic solvents. Looking at the RE values for XAD 7 after regeneration, the values obtained are slightly above a hundred indicating the formation of new active sites or new pores where more adsorption could occur. Overall, this data serves as a confirmation of what has been reported in the graphs above regarding regeneration with the four desorbing agents.

Table 11. Percentage of Atom Elements in L493 in Clean State and after Regeneration with Methanol and Ethanol

	Percentage of element		
L 493 resin	% C	% N	% H
Clean resin	55.3	0.329	7.12
Regeneration with methanol	60.32	0.63	6.94
Regeneration with ethanol	73.82	0.31	8.88

Table 12. Percentage of Atom Elements in AF 5 in Clean State and after Regeneration with Methanol and Ethanol

	Percentage of element		
AF 5 resin	% C	% N	% H
Clean	54.07	0.10	2.64
Regeneration with methanol	52.65	0.43	2.99
Regeneration with ethanol	96.28	0.26	2.33

Table 13. Percentage Atom Elements in XAD 7 in Clean State and after Regeneration with Methanol and Ethanol

	Percentage of element		
XAD 7 resin	% C	% N	% H
Clean	61.13	0.234	7.69
Regeneration with methanol	54.54	0.282	7.85
Regeneration with ethanol	50.42	0.57	2.64

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

Produced water is considered the largest waste stream in the oil and gas industry. This water contains contaminants of different nature including organic compounds, inorganic compounds, TDS, NORM and chemical additives such as hydrate inhibitors to enhance oil production. Managing large streams produced water is a key issue that needs to be carefully addressed. Managing produced water and treating it to the required water quality depends on its target destination. For this research, the target is to treat produced that can be disposed back into the environment. In order to do that, governmental regulation should be met. Governmental regulations are becoming more stringent with time and that is placing pressure on oil and gas companies to comply with these tight legislations. Meeting strict regulations requires the use of novel and enhanced technologies as opposed to the conventional ones that cannot operate at low levels of concentrations of contaminants. Adsorption, a premier and established water treatment technique, is increasingly receiving attention due to its high efficiency removal, small footprint and simple operating procedures.

In this study, four commercial synthetic resins were tested for the removal of oil from oil in water emulsion. Key parameters studied include resin dosage, contact time, initial oil concentration and pH. Key observations of this part of the study include:

- Resin AF 5 demonstrated highest adsorption capacity
- XAD 7 exhibited fastest adsorption kinetics
- A slight decrease in percentage removal at high mass loadings
- No need for pH alterations prior to treatment

AF 5 showed highest adsorption capacity due to fact that is has the highest surface area among all tested resins. XAD 7 established the fastest kinetics where equilibrium was reached in one hour, whereas L493 and AF 5 reached equilibrium after

8 hours. It was difficult to determine when IRA 958 reached equilibrium since no explicit trend can be seen while testing it. It was observed for all resins that percentage removal starts to decrease at high mass loadings. This implies that there is no need for high amounts of adsorbent mass for the adsorption process and this helps in reducing operating costs. In addition, experimental results indicate that there is no change in percentage removal while varying pH. This shows that no need to use chemicals to alter pH prior to the adsorption process.

The adsorption isotherms revealed that the adsorption of oil onto XAD 7 and L493 was efficiently described by the Freundlich and Toth models respectively. However, the adsorption on AF 5 was best fitted to Dubinin-Radushkevich model. Also, the adsorption kinetics study showed that Pseudo-second order was the best suited model to describe the experimental data.

The study confirmed the feasibility of using synthetic resins as potential adsorbents for the removal of oil from water. The natural next step would be is the assessment of their ability to be recycled and reused. Chemical regeneration was performed using two organic solvents (methanol and ethanol), 1 M NaOH and D.I. water heated to 65 °C. Results show complete regeneration of XAD 7 using both organic solvents. AF 5 was completely regenerated with methanol and D.I. water and L493 was successfully regenerated with NaOH. To further support this data, the results obtained from the organic elemental analyzer further prove that regeneration occurred by assessing the carbon content of each resin at its clean state and after regeneration. It is noted that when complete regeneration occurred the carbon content after regeneration is fairly close to the carbon content of resin at fresh state. Adsorption capacities of synthetic resins during the first and second adsorption cycles are also compared, and it is noticed that XAD 7 and L493 exhibited higher adsorption capacities after regeneration indicating that formation of new active sites.

For future work, other parameters can be assessed. For example, the effect of temperature Should be assessed in order to identify whether synthetic resins have the ability to withstand higher temperatures or not. Salinity and TDS should be tested to see whether contaminants other than organic compounds can interfere with the adsorption process. The ideal next step is to perform column tests for they serve as a better representation of adsorption columns employed in the industry. In addition, the need to assess the number of adsorption/desorption cycles is of utmost importance. This will give a better estimate of the resin's lifetime and that in turn, will aid in enhancing the cost efficiency of the process. Moreover, it is important to develop a plan to deal with the waste by-product generated during regeneration. For example, if organic solvents are used for regeneration, the organic solvent can be separated and recycled back into the system. Finally, because cost is an important feature in research, the development of cost estimates associated with this technology is another future task to consider.

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APPENDIX

Tabulated data of comparison of adsorption capacities for the first and second cycles of adsorption for each resin.

Table 14. Percentage Removals of Synthetic Resins Using Methanol as A Regenerant

Resin	1st adsorption cycle	2nd adsorption cycle	Qe_1 (mg/g)	Qe_2 (mg/g)	RE
L 493	96.50 %	80.00 %	5.528	4.970	89.9
AF 5	94.27 %	89.14 %	1.595	1.601	100
XAD 7	96.82	96.14 %	11.86	11.91	100

Table 15. Percentage Removals Of Synthetic Resins Using Ethanol as A Regenerant

Resin	1st adsorption cycle	2nd adsorption cycle	Qe_1 (mg/g)	Qe_2 (mg/g)	RE
L 493	96.50 %	70.14 %	5.528	4.331	78.34
AF 5	94.27 %	62.23 %	1.595	1.184	74.24
XAD 7	96.82	97.21 %	11.86	11.93	100.61

Table 16. Percentage Removals Of Synthetic Resins Using 1 M Naoh As A Regenerant

Resin	1st adsorption cycle	2nd adsorption cycle	Qe_1 (mg/g)	Qe_2 (mg/g)	RE
L 493	96.50 %	91.25 %	5.528	5.729	103
AF 5	94.27 %	84.86 %	1.595	1.046	65.61
XAD 7	96.82 %	82.19 %	11.86	10.15	85.61

Table 17. Percentage Removals Of Synthetic Resins Using Water At 65 °C

Resin	1st adsorption cycle	2nd adsorption cycle	Qe_1	Qe_2	RE
L 493	96.50 %	96.45 %	5.528	5.526	95.10
AF 5	94.27 %	83.79 %	1.595	1.528	95.79
XAD 7	96.82	-	11.86	-	-