

OIL REMOVAL FROM PRODUCED WATER USING NATURAL MATERIALS

by

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Dedication

In the name of Allah Almighty, the foundation and source of all knowledge and information, I dedicate this attempt of mine to

My father, who in his existence and death is a steady resource of strength,

My mother, whose regular prayer is my archangel,

My loving brother,

My teachers,

And

My tremendously supportive advisor.

Abstract

The oil and gas industry has had to deal with a massive amount of waste water as a bi-product of the exploration of oil and gas. This waste water referred to as produced water (PW) and the amount of PW increases with the well operation time and may increase to approximately 80%. The discharge of PW may lead to severe pollution of surface, soil and under-ground water. Oil-field-produced water contains organic and inorganic compounds. One commonly used technique to remove oil from PW is adsorption. In this work, pomegranate peel powder (PPP) is used as a low cost adsorbent for the removal of crude oil from simulated produced water (SPW) and real PW from oil and gas wells. Pomegranate peels (agricultural waste) were dried, crushed and washed with double distilled water and dried again. Characterized for surface morphology, elemental composition, functional groups and surface area using analytical equipment like SEM, EDS, FTIR, and BET isotherm respectively. EDS spectroscopy showed that the major elemental constituent in the bio-sorbent was carbon (up to 78%). However, oxygen, calcium, silicon and potassium were also observed in small quantities. Oil was removed from laboratory-produced water in a batch process at standard atmospheric conditions. The effect of contact time, adsorbent dosage, pH as well as temperature on the removal efficiency of oil was investigated. The optimum parameters for oil removal were: pH = 9.5, pomegranate = 2.33 g/L, contact time = 40.0 minutes and adsorption temperature = 55.0 °C. The results showed that as the adsorbent dosage, pH and salinity of SPW are increased, the removal efficiency increased. The adsorption of crude oil by PPP was found to follow the Langmuir adsorption isotherm with an adsorption capacity of 555 mg/g. The adsorption kinetic of crude oil is best described by the pseudo-second-order kinetic model with a rate constant of 3.75×10^{-4} g/mg.min. These results render PPP an excellent adsorbent for the removal of oil from produced water with an oil removal efficiency exceeding 92% in 50 min.

Search Terms: *Produced Water, Pomegranate Peel, Bio-sorbent, Equilibrium Isotherms, Kinetic Model, Organic and Inorganic Pollutants.*

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Nomenclature

ABFs	Aerated Biological Filters
B_D	Free Energy of Adsorption Per Mole of Adsorbete
BET	Brunauer-Emmett-Teller
BFW	Boiler Feed Water
BOD	Biological Oxygen Demand
Bq	Becquerels
BTEX	Benzene, Toluene, Ethyl-benzene and Xylene
C_e	Equilibrium Concentration
C_f	Final Oil Concentration
C_i	Initial Oil Concentration
COD	Chemical Oxidation Demand
D-R	Dubinin-Radushkevich
EDS	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
k	Equilibrium Constant for Langmuir Adsorption Isotherm
k_1	Rate Constant for Pseudo First Order Reaction
k_2	Rate Constant for Pseudo Second Order Reaction
k_f	Constant Freundlich Adsorption Isotherm
k_t	Constant for Temkin Adsorption Isotherm
MMA	Methyl Methacrylate
MVR	Mechanical Vapor Recompression
NORM	Naturally Occurring Radioactive Material
NPD	Naphthalene, Phenantherene, Dibenzothiophene
OTSG	Once Through Steam Generators
PAHs	Poly-aromatic Hydrocarbons
PPP	Pomegranate Peel Powder
PW	Produced Water
q	Adsorption Capacity
q_e	Equilibrium Adsorption Capacity
q_m	Saturation Monolayer Adsorption capacity
q_t	Instantaneous Adsorption Capacity
Q_t	Oil Adsorbed at Given Time
R^2	Regression Coefficient

R _L	Separation Factor
SBRs	Sequencing Batch Reactors
SEM	Scanning Electron Microscope
SPW	Simulated Produced Water
TDS	Total Dissolved Salts
TPH	Total Petroleum Hydrocarbons

CHAPTER 1

INTRODUCTION

1.1. Background

Oil and natural gas are well-known around the world. The oil and gas industry has had to deal with a massive amount of waste water as a bi-product of the exploration of oil and gas. This waste water is referred to as produced water (PW) and the amount of PW increases with the well operation time and may increase to approximately 80% [1]. The discharge of PW may lead to severe pollution of surface, soil and underground water. After treatment, a fraction of the produced water is re-injected into the well and some of it is disposed of in river or sea water. Oil-well produced water contains organic and inorganic compounds [2]. The disposal of produced water in this era of high technology is very uneconomical [3]. Reaching EPA produced water discharge requirements is very difficult, as only 60% of offshore platforms in the Gulf of Mexico can obtain such quality, especially when it comes to removal of dissolved oil components which may exceed the concentration of the dispersed phase. Thus, it is necessary to improve technologies which can help in meeting the required environmental regulations at a lower cost [4].

Alkalis, surfactants and polymers (residual chemicals) are accountable for the stability of oil droplets, the decrease in interfacial tension of the oil water and the zeta potential of the surface of the oil droplets. The stable oil droplets from the produced water are removed by using system which consists of flocculation, coagulation and de-emulsification tanks. First the de-emulsifying surfactants are added in the de-emulsification tank which leads to the destabilization of oil droplets. Afterwards a coagulant is introduced in the coagulation tank. All the coagulated oil droplets are transformed to small lumps by addition of flocculent [5].

This literature review summarizes the characteristics of produced water and distinguishes possible procedures for treating produced water.

1.2. Produced Water

1.2.1. Sources of Produced Water

A large quantity of water is required by the oil and gas exploration and production processes. The oil and gas industry is a combination of industries: oil, coal-bed methane and conventional non-associated gas producers. The aqueous effluent from such process operations is the largest volume stream in the oil and gas operation and exploration processes. Different types of fluids such as saline-water, oil and gas are held down by rocks in the sub-surfaces. The hydrocarbon compounds are saturated with saline water and then captured in the rocks. Due to the density difference, the hydrocarbons with lower density travelled to capture locations in rocks [6]. This led the displacement of saline water. At certain thermodynamic conditions, saline water and hydrocarbons are absorbed by the rocks. Saline water comes from lower side, above and the flow within hydrocarbon zone. There is another type of water that comes with saline water referred to as “connate water” or “formation water” [6]. Formation water is the water which is produced during the production activities by the injection of fluids and additives. Saline water with hydro-carbons extracted from the rocks when it reaches the surface is referred to as produced water [6]. A typical oil and gas reservoir has been shown in Figure 1 [7].

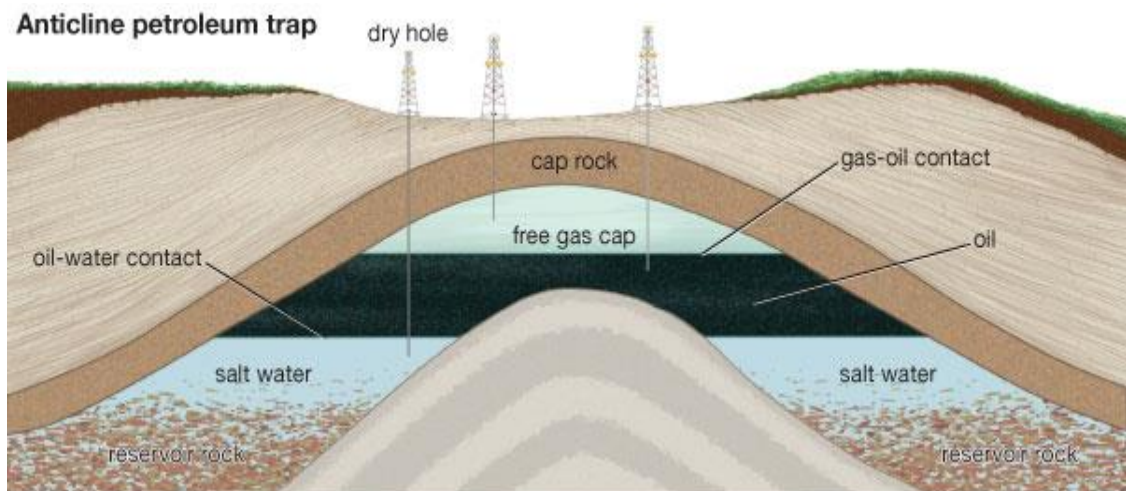


Figure 1 Typical Oil and Gas Reservoir [7].

Additional water is injected during oil and gas production operations to maintain the pressure in the reservoir and to enhance efficiency and recovery levels. Formation and injected water comes to the top surface with different mixtures of hydrocarbons. After

extraction, different processes are followed in order to separate hydrocarbons from the produced fluid [8].

1.2.2. Properties of Produced Water

Produced water contains different concentrations of organic and inorganic substances (see Table 1). Geological location, rock formation, lifetime of reservoir and type of hydrocarbon compounds being produced define the physical and chemical properties shown by produced water [6]. The characteristics of produced water are defined by the nature of the rock formations from which it is extracted, as well as by the conditions and chemicals used in process facilities. Based on different sources, the composition of produced water can be different by orders of magnitude. The composition of organic compounds in PW is qualitatively the same as the oil and gas production well. The main compounds present in produced water includes crude oil constituents (occurring in dispersed and dissolved phases), formation minerals (in dissolved form), some chemical compounds required in production activities, production solids (metal scales, corrosion products, waxes, bacteria, solids by formation, and asphaltenes) and gases (only in the dissolved phase) [9].

1.2.2.1. Dispersed and dissolved oil compounds.

Oil is a mixture of hydrocarbons including

- Polyaromatic hydrocarbons (PAHs).
- Benzene, toluene, ethylbenzene, and xylenes (BTEX).
- Naphthalene, phenanthrene, dibenzothiophene (NPD).
- Phenols.

Due to the polar characteristics of water and its unique properties, it cannot dissolve all hydrocarbons, which is why the major portion of the oil is dispersed in water [8]. The fraction of oil, whether it will be dissolved or suspended in produced water, is a function of oil to water ratio, constituents of oil, mixture pH, salinity, oil/produced water temperature, TDS (total dissolved solid), amount and type of chemicals which are used in the oilfield and the properties of different stable compounds (e.g. waxes, asphaltenes and fine solids) [9].

Dissolved oil: Water-soluble compounds are the main polar constituents of the hydrocarbon mixture present in produced water. Distribution of these polar compounds is between the low and medium carbon chains/ranges. Organic acids which may be dissolved in PW are propionic and formic acids [10].

Table 1. Oil-field produced water parameters [2,11]

Parameter	Values	Metals/ Heavy metal	Values (mg/L)
Density (kg/m³)	1014–1140	Calcium	13–25800
Surface Tension (dynes/cm)	43–78	Sodium	132–97000
TOC (mg/L)	0–1500	Potassium	24–4300
COD (mg/L)	1220	Magnesium	8–6000
TSS (mg/L)	1.2–1000	Iron	<0.1–100
pH	4.3–10	Aluminum	310–410
Total oil (IR; mg/L)	2–565	Boron	5–95
Volatile (BTX; mg/L)	0.39–35	Barium	1.3–650
Base/ neutrals (mg/L)	<140	Cadmium	<0.005–0.2
Total non-volatile oil and grease by GLC/MS base (g/L)	275	Chromium	0.02–1.1
Chloride (mg/L)	80–200,000	Copper	<0.002–1.5
Bicarbonate (mg/L)	77–3990	Lithium	3–50
Sulfate (mg/L)	<2–1650	Manganese	<0.004–175
Ammonical nitrogen (mg/L)	10–300	Lead	0.002–8.8
Sulfite (mg/L)	10	Strontium	0.02–1000
Total polar (mg/L)	9.7–600	Titanium Zinc	<0.01–0.7
Higher acids (mg/L) Phenols (mg/L)	<1–63 0.009–23	Arsenic	0.01–35 <0.005–0.3
VFA's (volatile fatty acids) (mg/L)	2–4900	Mercury Silver	<0.001– 0.002 <0.001–0.15
		Beryllium	<0.001- 0.004

The solubility of organic compounds increases with a rise in pH and temperature of produced water. Pressure has a positive effect on the concentration of dissolved organic compound to some extent. The relative ratio of carbon is changed with

temperature within the PW [10]. Salinity does not have any significant effect on the dissolved organic compounds in produced water [10]. The oil solubility in produced water may vary with oil type, amount of water produced, technique used and age of well/production [12].

The removal of toxic compounds like aromatics from water by available techniques is highly inefficient. By increasing the alkalinity of constituents, it has been found that the concentration of naphthalene, phenanthrene, and dibenzothiophene decreases, and due to this, alkyl homologous and alkylated phenols of C1–C3 also decrease [13]. The solubility of some cyclic compounds, such as BTEX (benzene, toluene, ethylbenzene, and xylenes) and phenols, is very high in produced water [8]. The soluble hydrocarbon compounds in produced water are aliphatic phenols, hydrocarbons and carboxylic acid and the hydrocarbons with lower molecular weight [12].

Dispersed oil: Dispersed oil has oil droplets mixed and suspended in oil well PW. The properties which govern the quantity of oil in the dispersed phase are mainly surface tension, oil density, oil/water interfacial tension and the amount of oil precipitation [12]. Some insolubles like PAHs and heavier alkyl phenols may also present in dispersed oil in produced water [8]. PAHs and C6–C9 alkylated phenols are the main components of dispersed oil in PW [8].

1.2.2.2. Inorganic Compounds/Minerals.

Dissolved inorganic compounds are mostly heavy metals, radioactive materials, anions and cations [2].

Cations and anions: Produced water contains cations and anions and have similar patterns of fraction for different metals [14]. Cations include Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , and Fe^{2+} , and anions include Cl^- , SO_4^{2-} , CO_3^{2-} , and HCO_3^- . The chemistry of the produced water depends on the amount of these ions present in the produced water. Properties such as buffering capacity, salinity, and scale potential are also governed by these ions in produced water [9].

Salinity: Salinity is a characteristic of produced water and can be attributed to dissolved sodium ions, chloride ions and to some extent to calcium, potassium, and

magnesium ions. The salt concentration in PW varies from a few mg/L to about 1000–350,000mg/L [1,10]. Produced water has a lesser amount of sulfates than seawater. Oil production wells where seawater is used for EOR (enhance oil recovery) have high sulfate concentration [1].

1.2.2.3. Heavy metals.

The concentration of heavy metals in produced water varies with the oil well formation geology and its age [12]. Heavy metals which are present as traces in produced water may include lead, chromium, silver, mercury, cadmium, nickel, zinc, and copper [9]

1.2.2.4. Naturally occurring radioactive materials (NORM).

Radioactivity appears in scales due to the presence of radioactive ions, mainly radium, through scales that are co-precipitated from PW. Barium sulfate is one of the most abundant scales co-precipitated [12]. Radium-226 and Radium-228 are two plentifully-occurring NORMs in produced water [15]. There is a strong correlation between the concentrations of radium isotopes and barium isotopes [15]. The produced water from the North Sea has a Ra-226 concentration between 0.3-16 Bq/L, and Ra-228 concentrations between 1.3-21 Bq/L (becquerels per liter) [16].

1.2.2.5. Additive chemical in oil and gas productions.

During the oil and gas operation certain chemicals are added in the oil-well to prevent and treat operational troubles. These chemicals are known as production chemical components. Production chemical components are categorized as treatment chemicals and production treatment chemicals. The treatment chemicals are used for gas production treating, stimulation and processing while the production treating chemicals used are emulsion breakers, biocides, scale and corrosion inhibitors antifoam and water treatment chemicals [12]. Charged and polar molecules such as linear alkyl-benzen-sulfonate (LAS), alkyl-dimethyl-benzenyl-ammonium, 2-alkyl-1-ethylamine-2-imidazoline, 2-alkyl-1-[N-ethyl-alkyl-amide]-2-imidazolines, and a-di-[alkyl-dimethyl-ammonium-ethyl]ether have been detected in the produced water of oil fields in the North Sea [1]. The concentration of production chemicals in produced water is as low as 0.1ppm [6].

1.2.2.6. Solids in produced water.

Production solids are different multiple solids such as corrosion products, formation solids, products formed by scaling, bacterial solids, asphaltenes and thick waxes. The sulfate bacterial reduction in PW is accountable for sulfides such as polysulfides and hydrogen sulfide [17]. Some of the microorganisms may be alive as there are diverse toxic chemicals present in produced water. Biological analysis has revealed that the concentration of microorganisms is between 50–100 cells of microorganisms per mL, and these include a majority of aerobic microorganisms (Gram-positive bacteria) [18]. Bacteria can clog or cause corrosion of equipment and pipelines [6]. Inorganic solids such as SiO_2 , Fe_2O_3 , Fe_3O_4 , and BaSO_4 are found in suspended form in produced water [19].

1.2.2.7. Dissolved gases.

The most dissolved gases encountered in produced water are O_2 , H_2S , and CO_2 [9].

1.3. Ways to manage/deal with produced water

The properties of produced water depend on the location of oil-well and vary with time. Differences in climates, regulatory rules and type of infrastructure available depicts the way the produced water will be handled. Therefore, different locations may have several treatment technologies. There are different technologies available that can be employed at one specific location [20]. Therefore, the produced water management option selected at a particular site may vary depending on the following conditions of produced water [20]:

- Physical and chemical properties.
- Volume produced and flow rate.
- Desired end use or disposition.
- Disposal and treatment options permitted by state regulations.
- Technical and economic feasibility.
- Availability of suitable infrastructure for disposal.
- Acceptance of companies.
- Cost involved.

Some of the possible options available for the management of produced water are:

- Injection of PW into the same oil well from which the oil is produced, or injection into another formation [21].
- Treatment leading to discharge of produced water (after meeting discharge regulations) [21].
- Reuse of produced water after treatment in the same oil and gas operation [21].
- Consumption (after treatment) by irrigation [22], cattle and animal consumption, and as drinking water [23].

1.4. Technologies for treatment of produced water

The treatment of produced water is the best option to manage produced water because the treated water is harmless and gives valuable products that can be reused in various applications. Some methods used for treatment of produced water are enlisted in Figure 2. The common objectives of treating produced water are as follows [20]:

- Removal of grease and dispersed oil.
- Removal of organic compounds (soluble).
- Disinfection.
- Removal of suspended solids [2].
- Elimination of dissolved gas.
- Desalination (i.e., exclusion of dissolved salts).
- Softening (i.e., removal of excess water hardness) [2].
- Removal of NORM [15].

1.4.1. Physical treatment

1.4.1.1. Adsorption

Activated carbon has porous sites which adhere to the organic matter present in produced water. A wet air oxidation process is used for the regeneration of activated carbon [9]. BTEX compounds are soluble in water and activated carbon is capable of removing them. Organoclay is helpful in eliminating unsolvable hydrocarbon compounds that contribute to oil and gas measurement and total petroleum

hydrocarbons (TPH). To produce organoclay, a thorough mixing of sodium montmorillonite clay is done with a cationic quaternary amine salt. On using activated carbon along with organoclay, it has been observed that the hydrocarbon concentration falls lower than the international standards of water quality [24]. Copolymer beads are produced by suspension polymerization based on methyl methacrylate (MMA) and divinyl-benzene (DVB). These copolymers are capable of reducing the oil content of PW to around 84.9% [25].

Zeolites are frequently deployed as ion-exchange resins. In this study, it was anticipated that hydrophobic zeolite pellets could be used in a fixed bed to adsorb dissolved organic compounds mixed in the produced water [9]. Another suggestion for removing soluble organic compounds was to use a resin-filled adsorption column [26]. Regeneration can be done by acid backwash and solvents. Adsorption efficiency varies with pH, suspended oil concentration, temperature, organic metal complex, low heavy metal concentration, dissolved contaminants like organic chemicals, and salinity [9].

Suspended particles plug into the media responsible for the reduction in efficiency of separation. At the same time, regeneration produces a lot of waste from the adsorbers, which also adds the difficulty in using these techniques [2]. Janks and Cadena [27] suggested to use “tailored” zeolites which can remove BTEX from PW full of minerals. They were prepared by the adsorption of neutralized amines onto the natural zeolites. The predicted efficiency of the process was between 70–85% [2,27].

Biosorption with eggshells has been found to remove almost 100% of oil from produced water with 194 mg/L by using just 1.8 g eggshell/L [28]. Barley straw, which is an agricultural byproduct, was modified with a cationic surfactant and hexadecylpyridinium chloride monohydrate (CPC) and used as an adsorbent to remove oil from oily waste water [29]. An adsorbent made from dry banana peels was used to remove 194 mg/L of oil in just 35 minutes. The maximum dosage per liter of produced water was 267 mg of banana peels [30].

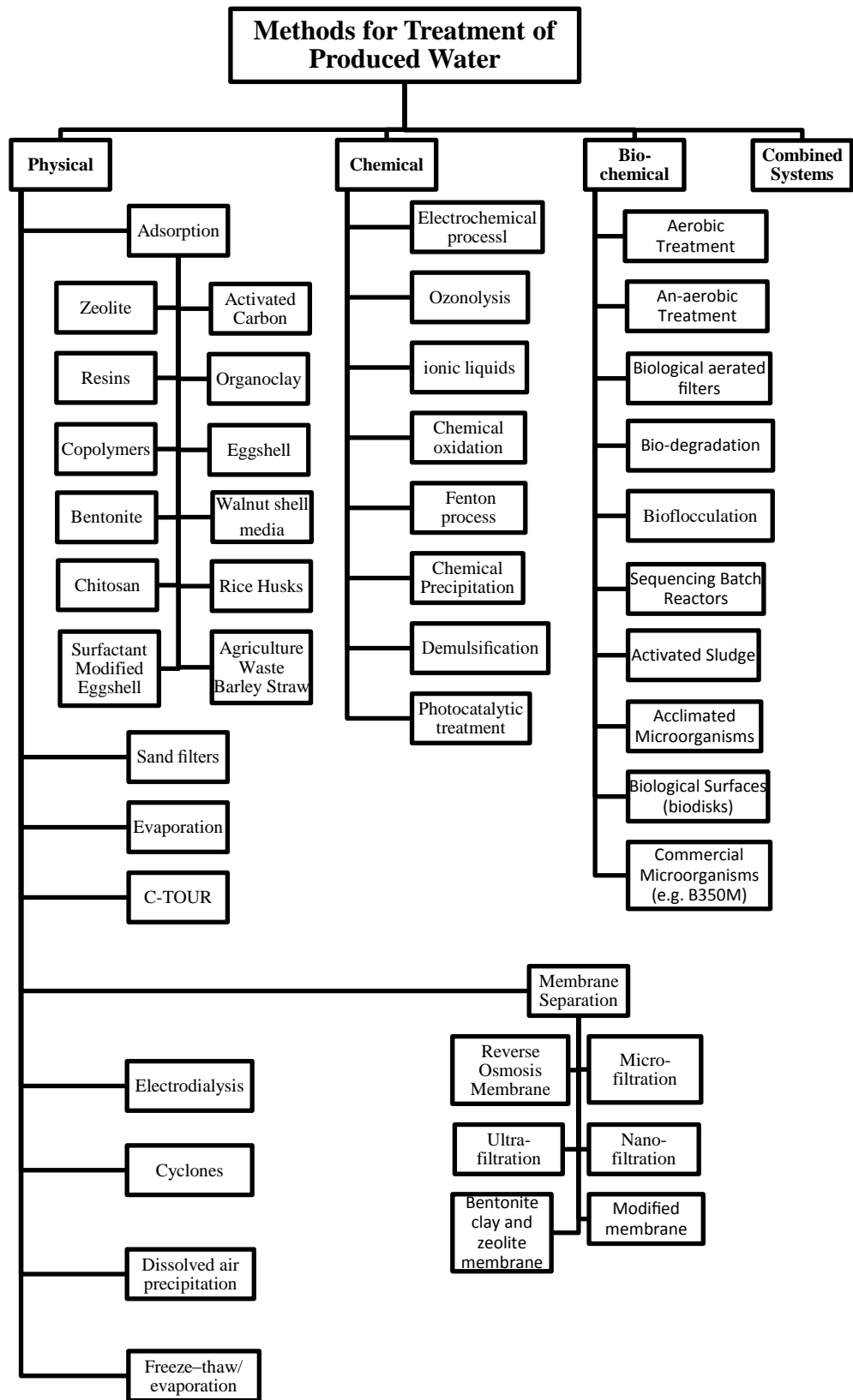


Figure 2. Methods of oil-well-produced water treatment.

The PET fibers surfaces were customized from oleophilic to hydrophilic for the utilization in grafted process with $-OH$, $-COOH$ and $-NH$ compound groups. Oil-field produced water was examined and treated with modified fibers. Analysis of treated produced water showed that it has $O\&G < 2.4$ mg/L and $SS < 2$ mg/L. The waste matter was cleaned extraordinarily as it is cleaned by using admired walnut medium, the effluent produced is fit and recommended to use for water injection or water flood in process of enhanced oil recovery [31]. Figure 3 shows a schematic of adsorption.

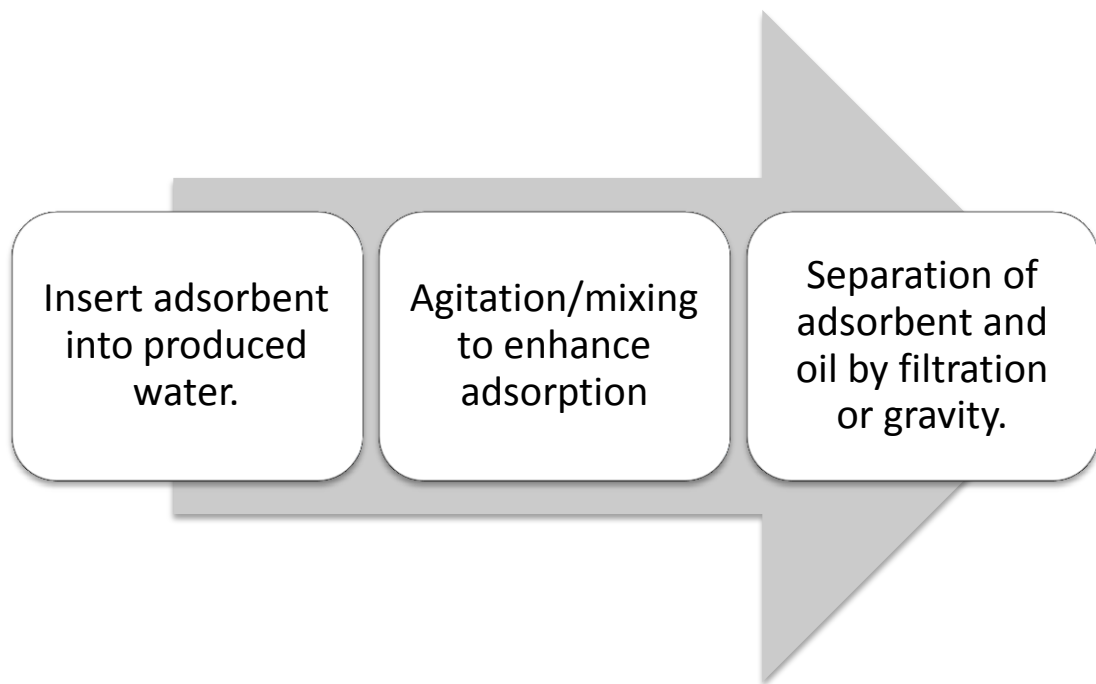


Figure 3. Schematics of adsorption process.

Adsorption process by different sorbents consisting of polymeric resins and Crudersorb technology, the offshore produced water was treated to decrease oil concentration levels to lower than 29ppm [2]. Crudersorb is able to eliminate suspended as well as dispersed oil droplets whereas the resin removes aliphatic carboxylic acids, dissolved hydrocarbons, phenolic compounds, and aromatic carboxylic acids [32].

1.4.1.2. Sand filters.

For the removal of metals from produced water, a process with a three-step pretreatment leading to filtration was proposed. The system consists of the following [33]:

- Maintain pH: Enhance the oxidation reaction.
- Aeration: Raise the oxygen level for oxidation.
- Solid removal: Use a gravity settling tank to have retention time for the settling of precipitated solids.
- Filtration: Use sand filtration to remove solids that could not settle.

From the results, it can be inferred that iron removal could be more than 90% [2,33].

1.4.1.3. Cyclone Separators.

Hydrocyclones, which belong to the category of the enhanced gravity separators, are used to separate oil from produced water. Hydrocyclones use centrifugal force to separate both phases. The typical hydrocyclone sections include a cylindrical swirl chamber, concentric reducing section, fine tapered section and a cylindrical tail. Hydrocyclone is shown in Figure 4. Oil droplets with larger diameters are separated into cone sections while the smaller particles are separated into tapered sections. These separators are capable of removing oil droplets as big as 5-15 microns [34].

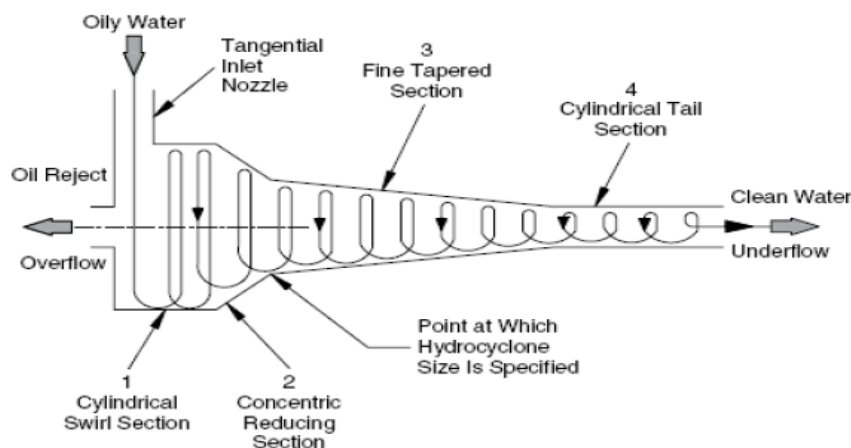


Figure 4. Hydrocyclone as an Oil Water Separator [34]

A compact floatation unit (a design of Epcon) is a three-phase separator capable of separating water, oil and gas. This separation works on the principle of centrifugal

force and gas floatation. Bottoms have treated water and top products are gases. This three-phase separator has an efficiency of up to 50–70% [35]. Compact systems having small and light accessories are also available for onshore services [9].

1.4.1.4. Evaporation methods of separation.

In 1989, Bertness [36] proposed an evaporative method for oil water separation by using direct contact of steam with saline water. Falling film evaporators and vapor compression evaporators are mainly used in evaporative methods. There is no chemical sludge produced in these methods because there is no chemical or physical treatment. They also have low capital investment, maintenance and operational costs [2]. Feed water introduced to once-through steam generators (OTSG) can be obtained from evaporative methods which improves OTSG efficiency and reliability [37]. High impurity levels of solid salts in sludge and water inhibits the reuse [38].

Waste water distillation was proposed by Becker [39]. He used two proprietary new designed (PND) systems which recover 95% of the energy consumed to distill water. First, a mechanical vapor recompression (MVR) system is used to recycle the produced water into distilled water. Second, the waste steam is used to achieve the same. The cost of energy is more than 95% of the operating cost of distillation in typical commercial applications. Therefore, the planned PNDS decreases the total operating cost by 90% [2].

1.4.1.5. C-TOUR PROCESS.

C-Tour, a patented technology of the AS company, is a liquid-liquid extraction process. Liquid condensate is deployed to take out liquid for the soluble constituents in produced water. The condensate also removes dispersed oil by coalescing with small oil droplets. The C-Tour process includes [35]:

- Taking a suitable condensate stream from production.
- Injecting condensate as liquid into the produced water.
- Mixing leading to dispersion of the condensate into the water.
- Giving reasonable contact time to mixtures.
- Separating the contaminated condensate from the water in a separation process.

- Cycling the condensate, containing contaminants, back into the production stream.

In field trials of the C-Tour process, high removal efficiencies for dispersed oil were observed. For 2–3 ring PAHs and NPD the efficiency was 70%, for C6 and C6 phenols was approximately 60%, and for C4–C5 phenols 20% [35].

1.4.1.6. Dissolved Air Precipitation (DAP).

Dissolved air precipitation generates bubbles for use in columns of solvent sublation. The use of solvent sublation is to separate bubbles by non-foaming adsorption. Air from a packed column separator (480–820kPa and saturated into water) was depressurized into the water column by a throttling valve. This resulted in the precipitation of air and formed bubbles of 60–100mm in diameter [40].

1.4.1.7. Freeze–thaw/evaporation

The freeze thaw/evaporation process utilizes naturally-occurring temperature swings to alternately freeze and thaw produced water. This process agglomerates the dissolved solids and produces a large quantity of dirt-free water [41].

1.4.1.8. Electrolysis Technique

Salts dissolved in water are present in the form of ions. These cations and anions are attracted when electrodes with an opposite charge are dipped in water. In electro-dialysis, different membranes are fixed between a pair of electrodes that allow either cations or anions to pass through them. For produced water reclamation with low concentrations of TDS, this method is appropriate [21].

1.4.2. Chemical Treatment

1.4.2.1. Precipitation with Chemicals.

Suspended and colloidal constituents from the produced water can be removed by coagulants and flocculants. An inorganic mixed metal is a poly-nuclear polymer, FMA (Fe, Mg, and Al) is with properties of coagulation scale inhibition and de-oiling. This can remove suspended particles from produced water with concentration levels of 50–400mg/L. Suspended solids and oil can be removed up to approximately 92% and 97%, respectively [35]. Similarly, heavy metals can also be removed by using spillsorb, lime and calcite. The suspended solid removal efficiency of lime is higher

than others and it is an economical chemical as well. Treatment of produced water from oil and gas fields to remove arsenic, hydrocarbons and mercury has been done with flocculants, oxidant and ferric ions.

1.4.2.2. Chemical oxidation process.

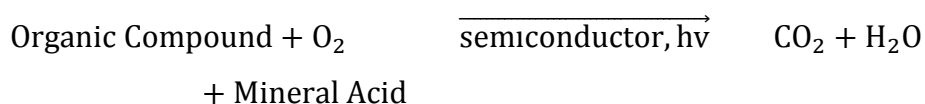
Refractory chemicals present in wastewater are decomposed by a process of chemical oxidation which uses a catalyst, oxidant, and irradiation [42].

1.4.2.3. Electrochemical process.

In a laboratory experimental setup of a pilot scale plant, the COD and BOD of produced water can be reduced to 10% in just 6 minutes. This laboratory unit is fixed with double anodes, one with noble metal content crystal (large surface), and a cathode of an active metal like graphite or iron. Electrochemical processes result in oxidization of the produced Mn^{2+} ions and coagulation of organic pollutants which also include bacteria [43].

1.4.2.4. Photocatalytic treatment.

Photo catalytic decomposition of water on TiO_2 electrodes is a method used for pollutant removal. The process is as follows:



For oilfield-produced water treatment, a photo catalytic reaction was performed in a reactor with 60 mL clarified produced water at a high pH. The required amount of photocatalyst- TiO_2 was added. The suspension was heated up to 298 K and illuminated using mercury lamp of 250 W at a high pressure. As a result, the toxicity of the produced water was decreased [44].

1.4.2.5. Fenton treatment process.

The Fenton oxidation adsorption process is carried out in two steps: flocculation followed by settlement. The COD of produced water was reduced from 93.1 mg/L to 5 mg/L and oil was reduced to traces of 100mg/L from a large amount of 2634 mg/L. The poly-ferric sulfate flocculent was used with a settling time of 30 minutes. In this process, the pH value was 3–4 with 30% H_2O_2 . The Fe^{3+} to H_2O mass ratio was

maintained at 4% and an oxidation time of 120 minute was given for the emulsion. Active carbon dosed was 4000–5000 mg/L with a specific adsorption time of 120 minutes [45].

1.4.2.6. Treatment with ozone.

Ozonolysis was proposed by Morrow et al. [46] for the treatment of oil-well-produced water by the decomposition of dissolved hydrocarbons through ozone. Sono-chemical oxidation is capable of decomposing some organic compounds such as BTEX. These methods are not usually used on a large scale because chemical oxidation products cannot be removed efficiently and up to the required value [42].

1.4.2.7. Ionic liquids.

Ionic liquids are the polar organic compounds at room temperature which show a tendency towards the organic contaminants present in produced water. In experiments, ionic liquids were used in the removal of specific hydrocarbons in produced water. These experiments showed that separation is easy but the regeneration of ionic liquid is low as it is soluble in water [47].

1.4.2.8. Separation by Demulsifiers.

Alkali, surfactants, and polymer chemicals were used to separate oil from produced water. In the alkali/surfactant/polymer (ASP), chemicals are added into produced water during the production processes. Surfactants reduce oil-water interfacial tension and zeta potential on the surface of tiny oil droplets [5].

1.4.3. Bio-chemical Methods

Biological treatment uses aerobic and anaerobic microorganisms for the decomposition of the organic constituents of the produced water. The main systems used for the biological treatment are trickling filters, activated sludge systems, sequencing batch reactors (SBRs), chemostat reactors, lagoons and biological aerated filters (ABFs). Sources of the microorganisms for the treatment are:

- Naturally-occurring microorganisms.
- Commercial microorganisms.
- Specific groups of microorganisms.
- Acclimated sewage sludge.

The most common method for treating wastewater is the activated sludge system. Oil skimmers are used at the upstream of the activated sludge system. The aeration tanks used have naturally occurring microbial growth. The activated sludge system can remove 98-99% of petroleum hydrocarbons at the residence time of 20 days [48].

1.4.4. Combination of different systems

Different physical and chemical methods can be applied at the same time in an optimized sequence. To convert produced water into drinking water, different pretreatments (physical/chemical) for reverse osmosis were proposed such as clarification, air floatation, softening, and filtration [49].

Produced water can be treated up to standards of boiler feed water (BFW) by using optimized pretreatment and unique separation (OPUS). OPUS is a combination of physical and chemical treatment technology process units such as degasification, chemical softening, filtration, ion-exchange treatment, cartridge filtration and reverse osmosis [50]. In Figure 5, a combination of processes for treatment of oil production wastewater is shown.

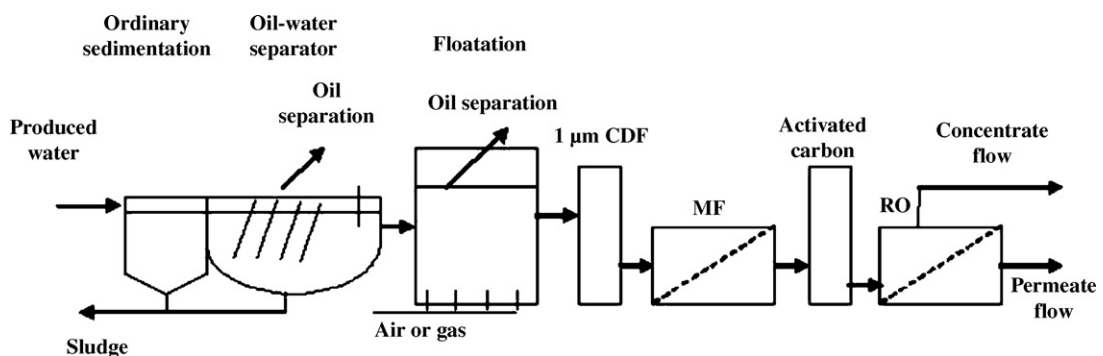


Figure 5. Proposed combination of processes for treatment of oil production wastewater [51].

1.4.5. Surfactant Treatment of Produced Water

Surfactants are the compounds that decrease the interfacial tension between two liquids or a liquid and a solid. Surfactants have seven requirements to enhance oil water separation:

1. At a specific required dosage a surfactant must hit all the oil molecules.

2. Surfactant molecules must have thorough mixing and retention time to penetrate into the produced water.
3. Orientation of the surfactant molecules must be in such a way that hydrophilic groups must be in the water phase and lipophilic groups must be in the oil phase (see Figure 6).
4. In order to lessen the cohesive strength of the oil film, the surfactant must decrease the oil-water interfacial tension in produced water.
5. Generation of small droplets must be done with thorough mixing to obtain a high interfacial surface area.
6. The oil droplets must be dispersed throughout the column.
7. The oil droplets must be skimmed after entrainment.

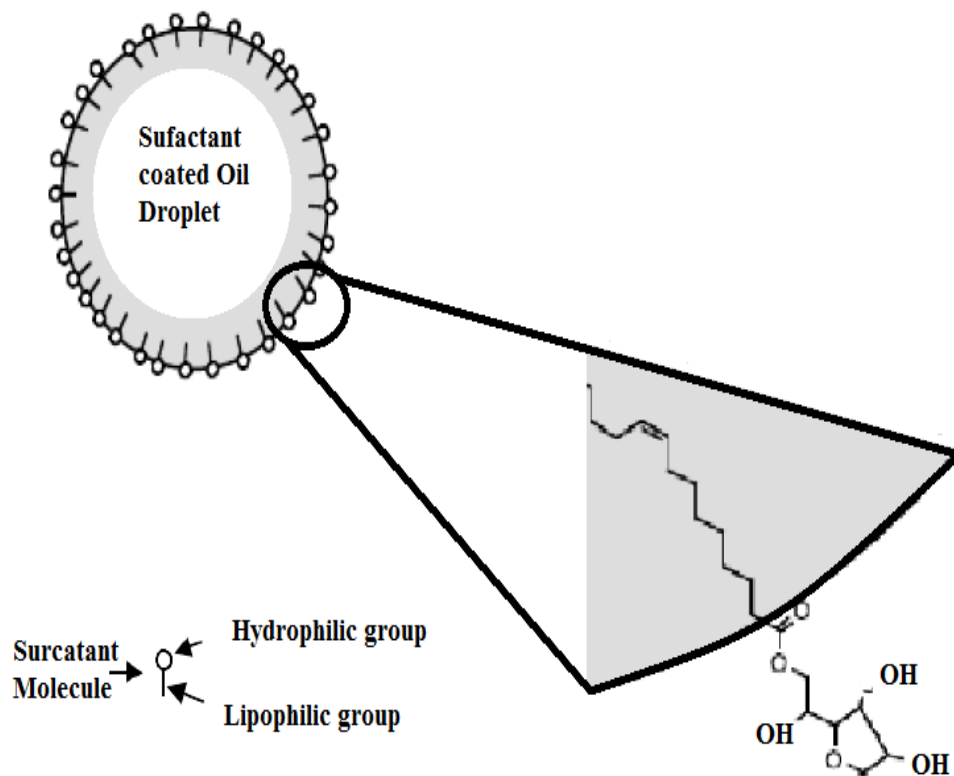


Figure 6. Accumulation of surfactant around the oil-water interface makes the oil entrain and become separate from water

1.5. Adsorption

In 1881, the word "adsorption" was introduced by German physicist Heinrich Kayser (1853-1940) [52]. It is a surface-based binding process involving the adhesion of any substance (gas/liquid/dissolved solids), molecules, atoms or ions on the surface

of the other substance. An adsorbed substance is referred to as an adsorbate (organic compound or metal) and the substance on which the adsorbate adsorbs is called the adsorbent. A thin film is formed on the adsorbent by the adsorbate. Figure 7 explains the steps involved in adsorption mechanism.

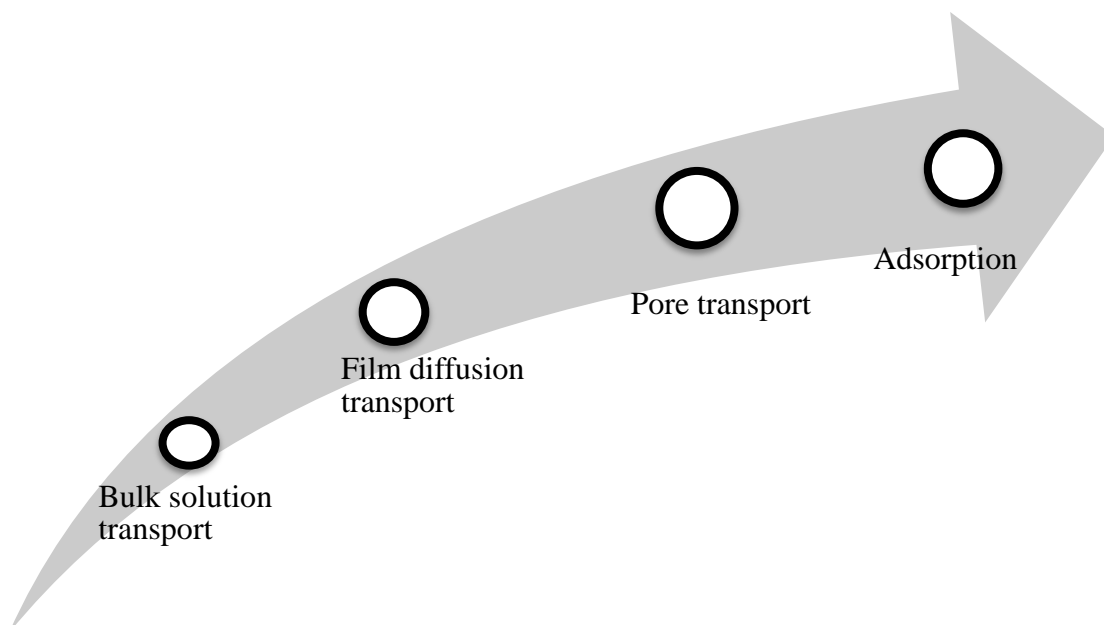


Figure 7. Steps involved in the dynamics of adsorption.

Adsorption sites are the sites on the surface of the adsorbent available for the adsorbate to adsorb. Adsorption may be on the surface of the adsorbent or within the pores (micro, meso or macro). Micro-pore surface area is larger than meso-pore and macro-pore surface area. Therefore, the adsorption capacity of the micro-pore surface area is considered very high compared to the adsorption capability of the meso-pore and macro-pore surface area [53].

1.5.1. Adsorption isotherm

An adsorption isotherm provides a relation between total mass of adsorbed adsorbate per unit mass of sorbent and concentration at constant ambient conditions. In order to develop adsorption isotherms, adsorption experiments are performed. Langmuir adsorption isotherm and Freundlich adsorption isotherm are the most common isotherms which are used for adsorption studies [54]. In the present study, an adsorption study was performed for pomegranate peel powder (PPP). The adsorption models were applied to calculate the sorption capacity of PPP sorbent.

Adsorption equilibrium is typically explained by the Isotherm Equations. The parameters of isotherms describe the surface properties and affinity at a constant

temperature and pH. In this study, different adsorption isotherm models were applied to manipulate the sorption capacity. The adsorption capacities were calculated using the relation below:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where, C_i is the initial oil concentration, C_e is equilibrium oil concentration, V is the volume of the produced water solution used and m is the mass of PPP adsorbent.

In process design, the adsorption study plays a vital role and also helps to find the uptake rate and capacity. The most commonly-used adsorption models are the Langmuir, Freundlich, Temkin and D-R models. The Langmuir and Freundlich models explain the behaviour of oil adsorption on the adsorbent and the remaining ionic concentration in the solution.

1.5.1.1. The Langmuir Isotherm.

The Langmuir adsorption model explains that monolayer adsorption occurs consistently on the active site of the sorbent surface, and once the active sites are covered by the sorbate, the adsorption process will stop. The Langmuir adsorption isotherm is given as:

$$q_e = \frac{q_m k C_e}{1 + k C_e} \quad (2)$$

where,

C_e = Equilibrium concentration (mg/L),

q_e = Amount of the substance adsorbed at equilibrium per amount of the adsorbent (mg/g)

q_m = Saturation monolayer adsorption capacity (mg/g),

k = Equilibrium adsorption constant (l/mg).

There are two assumptions which are taken in the Langmuir isotherm. The first is that maximum adsorption of the adsorbate takes place only at monolayer sites (homogeneous saturated) on the surface of the adsorbent. The second is that the energy of the adsorption will remain unchanged [55].

1.5.1.2. *The Freundlich Isotherm.*

The Freundlich model is an empirical expression and one of the most primitive models. The Freundlich model is based on heterogeneous surface and adsorption heat. The Freundlich adsorption isotherm is an empirical relation. This model was designed to explain the multilayer adsorption and may be best fit to the highly heterogeneous bio-sorbent surfaces. The model is given as:

$$q_e = k_f C_e^{1/n} \quad (3)$$

where,

C_e = Equilibrium concentration (mg/L)

q_e = Amount adsorbed at equilibrium per amount of the adsorbent (mg/g)

k_f = Freundlich constants (related to capacity and intensity of adsorption)
(mg/g)

n = Freundlich constants (related to capacity and intensity of adsorption)
(g/L)[54].

1.5.1.3. *Dubinin-Radushkevich Adsorption Isotherm.*

The Dubinin-Radushkevich (D-R) model is used to classify the mechanism and the energy of sorption. The D-R model also provides a means of distinguishing between chemisorption and physisorption. The D-R adsorption isotherm gives excellent results of equilibrium data for the adsorption of organic compounds in the gas phase on a porous solid. It is not commonly applied to adsorption in the liquid phase [56]. Mathematically it is expressed as:

$$q = q_e \exp(-B_D(RT \ln(1 + \frac{1}{C_e}))^2) \quad (4)$$

where,

q_e = Equilibrium adsorption capacity (mg/g),

B_D = Free energy of adsorption per mole of adsorbate,

C_e = Equilibrium concentration (mg/L).

1.5.1.4. Temkin Adsorption Isotherm.

The Temkin equation was initially proposed to study the adsorption capacities of hydrogen on platinum electrodes in acidic solutions. The assumption taken during the derivation of the Temkin isotherm is that the diminishing in the strength of heat of sorption as a function of temperature is linear instead of logarithmic as implicit in the Freundlich equation. The linear form of the Temkin isotherm is as follows:

$$q_e = B \log k_t + B \log C_e \quad (5)$$

In this equation B and k_t are constants of the Temkin isotherm. $B=RT/b$, T is the temperature in Kelvin, r is the universal gas constant and 1/b is the absorption potential of the adsorbent.

1.6. Adsorbents

Adsorption was analysed and considered to be the most efficient and successful technique to eliminate matter from waste water [57]. Activated carbon is the most extensively used adsorbent. However, there is a major disadvantage of using activated carbon, which is that it has a high initial and regeneration cost [58,59]. Lately, a lot of natural adsorbents have been urbanized for the elimination of oil from produced water [28, 30, 60-69]. These comprise egg-shells [62] modified Barley straw [65], banana peel [30] and surface-modified ball media filtration fibers [31]. A synopsis of the adsorbents used for oil removal from aqueous solution is mentioned in Table 2.

1.7. Kinetic Studies of Adsorption

The dynamics of adsorption is the very important phenomenon that explains the uptake rate which describes the interaction time at surroundings of solid-liquid interface. Basically, the kinetic study elaborates data regarding the pathway and time to achieve equilibrium. Moreover, it absolutely depends on the inherent characteristics and performance of material. However the obtrude environment (operating parameters) of process also affects kinetics [70]. To examine the sorption kinetics, the most common pseudo first- and second-order kinetic models were applied in this study.

Table 2 Oil adsorption capacities of different adsorbents.

Adsorbent	Emulsified oil studied	Sorption capacity (g/g)	Reference
Banana pseudo-stem fibres	Palm oil	0.169	[60]
Raw banana peel (RBP)	Crude oil	0.726	[30]
Bentonite	Crude oil	0.4933	[61]
Powdered activated carbon (PAC)	Mineral oil	0.322	
Deposited carbon (DC)	Mineral oil	0.374	
Surface modified eggshell (SMES)	Crude oil	0.121	[62]
Raw eggshell	Crude oil	0.107	[28]
Treated vegetable fibre	Mineral oil	0.52	[65]
Natural feathers	Crude oil	0.65	[65]
	Standard mineral oil	0.56	[65]
Yellow horn shell residues	Cooking oil	0.42	[63]
Yellow horn shell residues (Treated)	Cooking oil	0.61	[63]
Chitosan powder	Palm oil mills effluent	3.42	[64]
Chitosan flake	Palm oil mills effluent	1.97	[64]
Bentonite organoclay	Valcool (cutting oil)	0.14	[65]
Acetylated rice straw	Machine oil	24.0	[66]
Acetylated sugarcane bagasse	Machine oil	18.8	[67]
Natural wool fibers (NWF)	Real oily wastewater (motor oils)	5.56	[68]
Recycled wool-based nonwoven material (RWNM)	Real oily wastewater (motor oils)	5.48	
Sepiolite	Real oily wastewater (motor oils)	0.19	
Expanded vermiculite	Standard mineral oil (SMO)	0.0150	[69]
	Canola oil (CO)	0.0463	
	Kutwell 45	0.0110	
	Refinery effluent (RE)	0.00809	
Hydrophobized vermiculite	Standard mineral oil	0.0230	[69]
	Canola oil (CO)	0.00612	
	Kutwell 45	0.00670	
	Refinery effluent (RE)	0.00270	
Modified barley straw (BMBS)	Canola oil (CO)	0.613	[65]
	Standard mineral oil (SMO)	0.584	
This study	Crude Oil	0.556	

1.7.1. Pseudo First Order Model.

The pseudo first order model (Lagergen Model) [71,72] explains the sorption at the interface of liquid and solid. This expression is as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (6)$$

The solved linear form is as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

To get the value of the rate constant k_1 plot a graph between $\ln(q_e - q_t)$ and t which gives a linear curve equation which ultimately gives k_1 from the slope [73], [74].

1.7.2. Pseudo Second Order Model.

The pseudo second order rate equation is expressed as follows:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

For the pseudo second order, k_2 is the rate constant of adsorption [75,76] and is articulated in $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$. The linear form of the pseudo second order rate equation can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where, the adsorption capacity at equilibrium is represented as q_e (mg/g of sorbent), the instantaneous adsorption capacity is represented as q_t (mg/g of sorbent), T is time in minutes, k_1 is the rate constant of the pseudo first order reaction (min^{-1}) which can be calculated from the slope, and k_2 is the rate constant for the pseudo second order reaction ($\text{g}^{-1}\cdot\text{min}^{-1}$). The value of k_2 can be inferred from the y-intercept of the graph between t/q_t and t .

1.8. Objectives

The objective of this work is to investigate the effectiveness of natural material pomegranate peel powder (PPP) towards the removal of hydrocarbons and crude oil from Produced Water. Furthermore, this work aim at determining the optimum parameters (pH, salinity, temperature, amount of adsorbent etc.) for treating produced water by PPP. The adsorption capacity, the adsorption kinetics as well as adsorbent regeneration will be also studied.

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1. Materials

Pomegranate peels were obtained from a local market in Dubai, UAE. Crude oil was obtained from the Abu Dhabi National Oil Company (ADNOC), UAE. All chemicals used were of analytical grade. The solvent used was n-Hexane (95% pure, J.T. baker). The water used in all experiments was double distilled water (Water Still Aquatron A4000D, UK). A fluidized bed dryer (Sherwood Scientific, UK) was used for drying pomegranate peels. A precise vacuum oven (Model WOV-30, DAIHAN Scientific Co. Ltd., Korea) fitted with a vacuum pump (Model G-50DA, Ulvac Kiko, Japan) was used to dry the sorbent in powdered form. Agitation of the sample was done by using a fuzzy control system which is a digital reciprocating shaker (Model SHR-2D, DAIHAN Scientific, Korea). The temperature was controlled using a Hotplate Stirrer (Model MSH-20D, DIHAN Scientific Company, Korea). A mechanical shaker was used for comprehensive mixing of the emulsion. The oil was analyzed using spectrophotometer (HACH DR-5000) at wavelength 450 nm [11]. The pH was measured using a pH meter (3320, JENWAY Ltd., UK). The pH adjustment of all the solutions was done using either 0.1M HCl or 0.1M NaOH. Classification of the particles was done by separating them into different sizes (500-50 microns) using sieves (Stainless steel; Aperture 150-500 micro meter; Pascal Engineering Company, UK). The topography images and chemical composition were obtained using a scanning electron microscope with energy dispersive spectroscopy (SEM: TESCAN VEGA.3-LMU, USA). Fourier transform infrared spectroscopy (Bomem MB-3000 FT-IR equipped with ZnSe optics and a DTGS detector) was used to obtain spectra for the pomegranate peel powder before and after treatment.

2.2. Method

2.2.1. Bio-Sorbent Preparation

Pomegranate peel was washed assiduously with doubled distilled water and then dried in air for 24 hours. The pomegranate peel was ground to particle sizes between 2-3 mm and was extra dehydrated by means of a fluidized bed drier at 60 °C.

In order to remove the hydrophobic soluble organic matter and colored pigments, the tattered peel was then refluxed for 2 hours in n-hexane. The n-hexane-treated pomegranate peel was then washed carefully with doubled distilled water and dried in a fluidized bed dryer. A chopper was used to gain fine pomegranate peel powder which was then sieved all the way through a 500-150 micron sieve. Finally, the fine particles of pomegranate peel were washed with double distilled water and dried in a vacuum oven at 80 °C for 24 hours. The manufactured PPP was stored in air tight sealed glass containers.

2.2.2. Batch adsorption experiments

Simulated produced water (SPW) solution was prepared with oil concentration of 200 ppm. To avoid phase separation the solution was continuously stirred at 1200 rpm. The equilibrium time was determined using eight samples of 150 mL SPW solution with oil concentrations of 200 ppm and 1.5 g of PPP sited in 250 ml conical flasks. The solutions were stirred using a mechanical shaker at 140 rpm for different time intervals at normal atmospheric conditions and an initial pH of 9.5. Then, the bio-sorbent was separated from the sorbate. The oil content remaining in the treated water was extracted using 150 ml of n-hexane solvent. The absorbance of the n-hexane extract at wavelength = 450 nm was then recorded using a Hack spectrophotometer. The amount of oil removed by the PPP was predicted from a calibration curve [11]. In order to avoid error in oil measurement in water a blank test to measure the oil removal efficiency by using n-Hexane was carried out. The oil removal efficiency using n-Hexane was found to be 90 %. Analogous experiments were done using SPW of 400 ppm, 600 ppm, 800 ppm, 1000 ppm, 1200 ppm, 1400 and 1600 ppm.

A calibration curve (Figure 8) was plotted to determine the initial and final concentration of oil in the sample.

The amount of oil adsorbed on the surface of the bio-sorbent was calculated from the difference between the initial and residual oil concentrations given below:

$$Q_t = \frac{V_s(C_i - C_t)}{m} \quad (10)$$

where,

Q_t = Oil adsorbed (mg oil/g bio-sorbent) at a given time.

V_s = Volume of sample solution (L).

C_i = Initial concentration (mg/ L).

C_f = Final concentration (mg/L).

m = Weight of dry bio-sorbent (g).

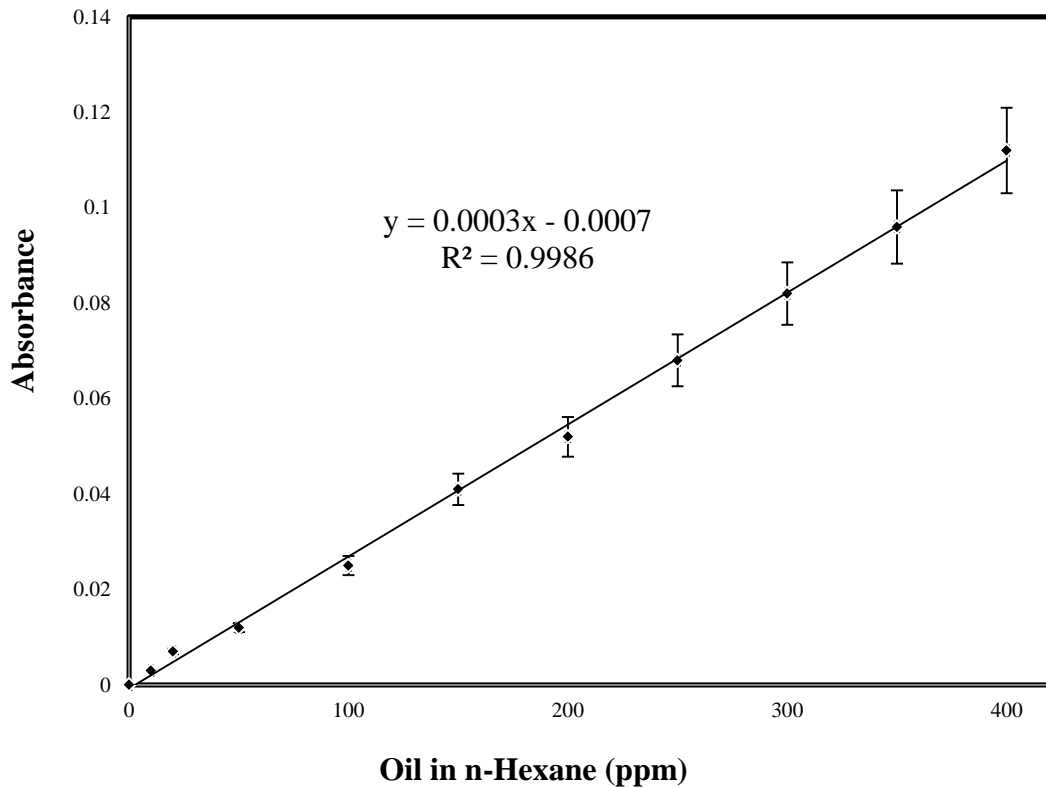


Figure 8. Absorbance of oil in n-Hexane, spectrophotometer HACH DR-5000 and wavelength of 450 nm

A control experiment (without bio-sorbent) for measuring any loss in oil concentration during the experiment was carried out. The same solution and equipment was used in the absence of the pomegranate peel powder. However, there was no change observed in the oil concentration after the control experiment.

The adsorption capacity of PPP was determined by fitting the experimental data to the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models. A linear regression curve fitting on Microsoft Excel was performed using a

regression method of least-square. Goodness of fit of the experimental data was found by the coefficient of determination, R^2 , which is defined as [77]:

$$R^2 = \frac{\sum_1^n (Y_m - Y_a)^2}{\{ \sum_1^n (Y_m - Y_a)^2 + \sum_1^n (Y_e - Y_m)^2 \}} \quad (11)$$

where n is the total number of data points; Y_a , Y_e and Y_m are the values (averaged) of experimental data, experimental data points (individual) and the expected value (from the linear model), respectively.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Characterization of PPP

3.1.1. Characterization of the PPP by FT-IR

Each spectrum of the FT-IR of PPP before as well as after extraction of n-hexane extraction is shown in Figure 9. A strong absorption band is shown by both spectra at 3436 cm^{-1} for the OH stretching mode. The $-\text{CH}_2-$ bond stretching was associated with the absorption band at 2918 cm^{-1} and the weak absorption band at 2845 cm^{-1} was assigned for the $-\text{CH}-$ bond of methylene group. To the C=O stretching vibration of carboxylic acid, the peak at 1734 cm^{-1} was assigned. At 1628 cm^{-1} , a strong absorption band appears corresponding to the stretching vibration frequency of carboxylic acid with intermolecular hydrogen bonds [78,79]. Aromatic hydrocarbon rings can be related to the C=C deformation mode which appears at 1530 cm^{-1} and 1440 cm^{-1} . Only in the natural PPP do these two bands appear. Presumably due to the extraction of this aromatic hydrocarbon by this solvent, however, both bands are lacking in the n-hexane-extracted PPP. Moreover, several absorptions bands representing C-O stretching modes, presumably of phenols, appear between 1384 cm^{-1} and 872 cm^{-1} [79]. In n-hexane extracted PPP, however, those absorptions bands are much less pronounced. Hence, a strong suggestion can be made based on these results that the efficient extraction of the majority of the phenolic components was made by n-hexane.

3.1.2. Surface area measurements

The surface areas of PPP have been measured by using NOVA quanta-chrome instrument version 11.02. The BET (Brunauer-Emmet-Teller) multipoint method has been employed for the determination of surface area using nitrogen gas. The surface areas of PPP is $5.2\text{ m}^2/\text{g}$.

3.1.3. Characterization of the PPP by SEM

Using SEM, as Figure 10 indicates, the physical morphology of the n-hexane-extracted PPP surfaces was determined before and after crude oil adsorption. Figure 9a shows that the PPP loaded with oil lacks these pores and cavities, whereas the oil-

free PPP has clear cavities and pores (Figure 10b). Energy dispersive X-ray spectrometry (EDS) analysis further strengthened this finding, which clearly shows that in comparison to the PPP oil-free samples, the carbon peak in the PPP oil-loaded samples is larger.

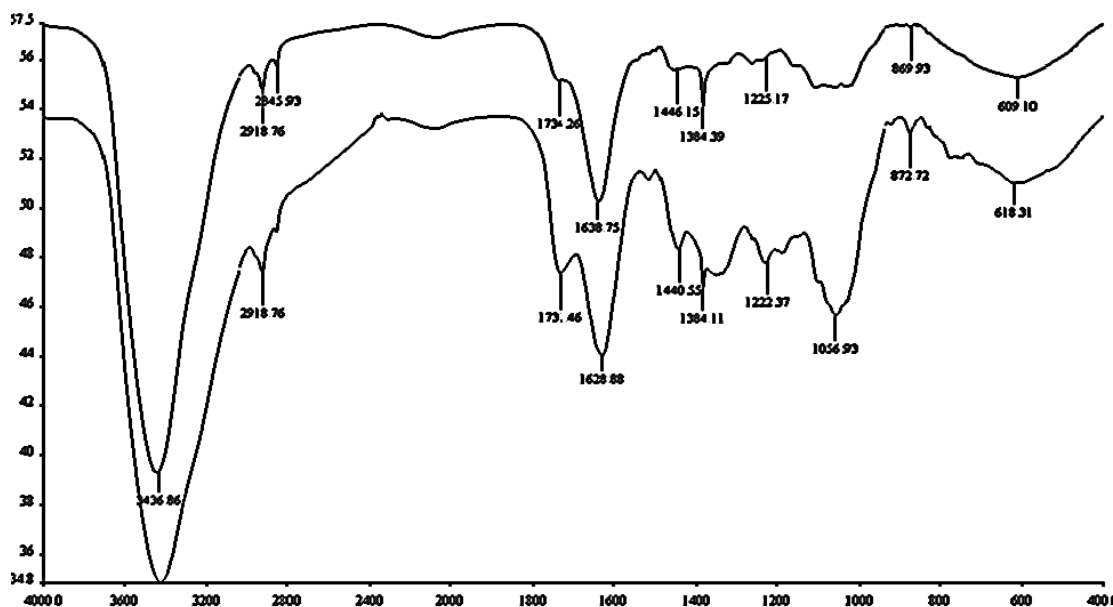


Figure 9. FTIR Spectra of PPP (a) treated with n-hexane (after reflux for 2 h) and (b) without treatment.

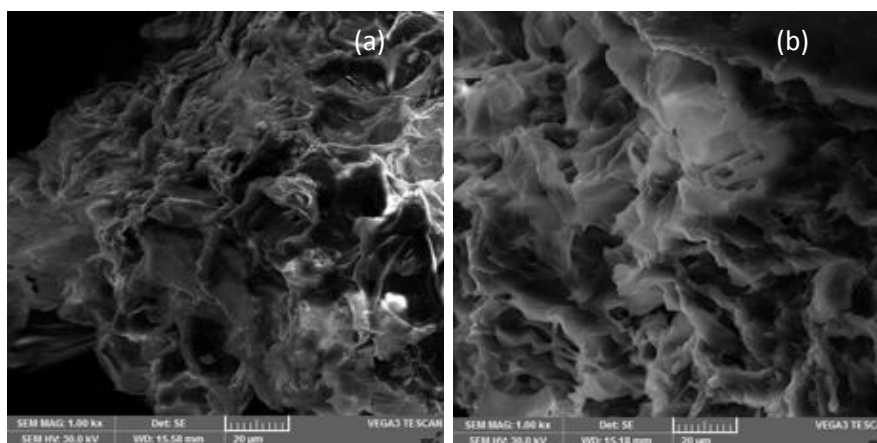


Figure 10. SEM of PPP (a) before and (b) after adsorption.

3.2. Effect of Operating Parameters

Oil removal efficiency is affected by the variation in the temperature, pH, salinity and PPP dosage. The effect of pH, salinity, temperature and PPP dosage on

oil removal efficiency was investigated. The initial pH of the SPW varied between 0.1-13.7. The experimental conditions for this experiment were PPP loading of 10 g/L, oil content of 300 mg/L and contact time of 50 minutes. Likewise, the salinity was varied from 0 mg/L to 2000 mg/L by using NaCl and adjusting the initial pH to 9.5. Moreover, the temperature effect on sorption was studied by varying the solution temperature in the range of 25-70 °C at a constant initial pH of 9.5. Finally, the bio-sorbent dosage was varied from 0.33 g/L to 2.64 g/L.

3.2.1. Effect of Contact Time

Figure 11 is related to the investigation of the effect of contact time on the removal efficiency of crude oil by n-hexane-extracted PPP. A close look at this figure shows 50 minutes to be the optimum contact time for the adsorption of oil by PPP. Moreover, it can be seen in the figure that the oil removal efficiency decreases as the initial oil concentration increases at a given contact time. In specific terms, the oil removal efficiency decreased from 95% to 76% as the initial oil concentration increased from 200 to 1600 ppm at 60 minutes contact time. One explanation for this finding is the following: at high initial oil concentrations, the extent of surface coverage increases, leading to the observed saturation of the surface which gives rise to the observed decrease in removal efficiency.

3.2.2. Effect of pH

Among the parameters that control the adsorption process is pH. The surface properties of bio-sorbent as well as its binding sites are both affected by the concentration of proton or hydroxide ions in solution [80]. Hence it can be expected that pH will play a vital role in the removal of crude oil by PPP. This work covers the investigation of the effect of pH on the removal of crude oil by PPP at 50 minutes contact time, 300 ppm initial concentration of oil, and PPP dose of 10.0 g/L. Figure 12 is a presentation of this data. A decrease in the removal efficiency as the pH increased from 0.100 to 3.50 can be seen in this figure. However, a sharp increase in the removal efficiency of crude oil by PPP accompanies a further increase in pH from 4 ± 0.2 to 10 ± 0.2 . The high efficiencies at pH=0.1 can be attributed to the electrostatic attractions between the protonated binding sites on the surface of PPP and oil molecules are very high, thus leading to the observed high efficiency at this pH [81].

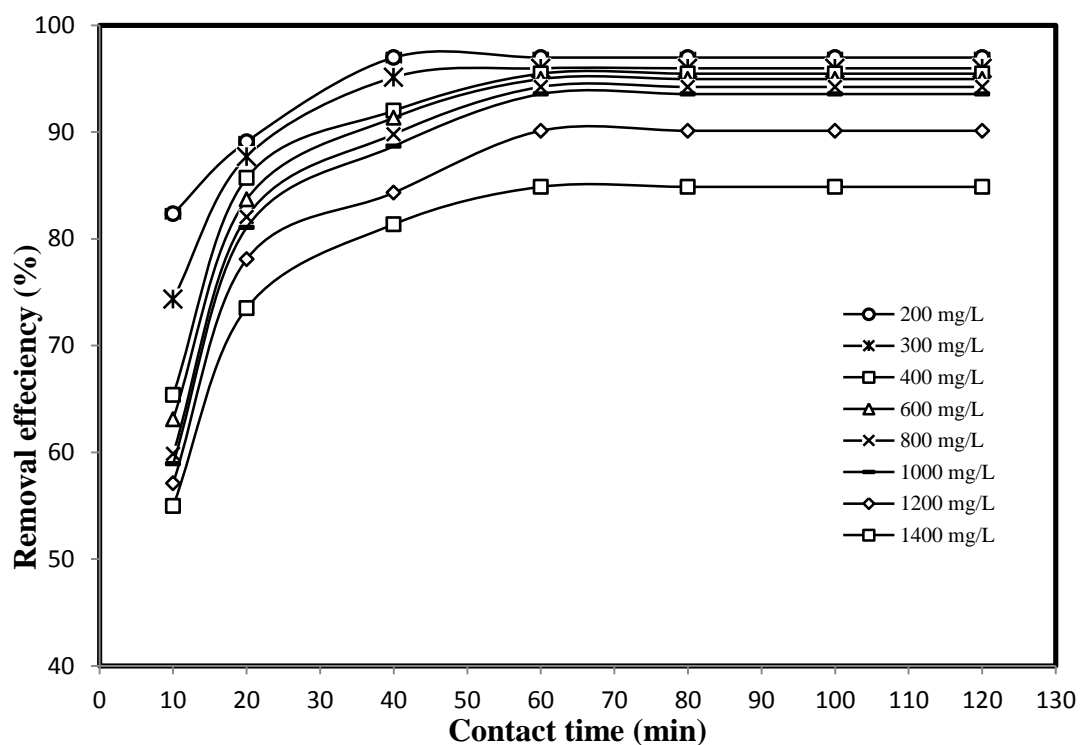


Figure 11. Effect of contact time and initial oil concentration on oil removal efficiency by PPP. Initial pH: 9.5 ± 0.2 , temperature: 25 ± 2 °C, adsorbent dosage 10.0 g/L, and standards deviation: 1.0.

Furthermore, the decrease in the efficiency of oil removal at pH between 0.100 to 3.50 which could be due to the availability of proton ions in the solution competing with the oil molecules at this interval. Two factors can be deemed responsible for the sharp increase in the efficiency of oil removal above a pH of 4. First, presumably, is the production of flocs of oil due to the oil water getting destabilized at a high pH [64]. This resulted in larger oil droplet size and coalescence of oil, enabling larger efficiency. A second factor can be the increasing hydrophobicity of the bio-sorbent surface as the pH value rises [29]. The oil adsorption efficiency reduced slightly at pH 12 ± 0.2 , which could be credited to a rise in oil emulsion stability resulting in a reduced contact area between PPP and oil droplets [29]. Inspection of Figure 12 reveals that the optimum pH is 9.5.

3.2.3. Effect of salinity

A set of adsorption experiments was performed studying crude oil removal from SPW at NaCl concentrations of 0 to 2000 mg/L. The salinity study was performed at an initial oil concentration of 300 mg/L, initial pH of 9.5 ± 0.2 , 50 minutes of contact time, 140 rpm of shaker stirring and a bio-sorbent dose of 10.0 g/L. The increase in

the oil removal efficiency along with the increase in salinity is shown in Figure 13. At the highest salinity, 96% of the oil was removed. The solubility of oil in SPW declines as the concentration of NaCl in the SPW increases, leading to an increased oil uptake [82].

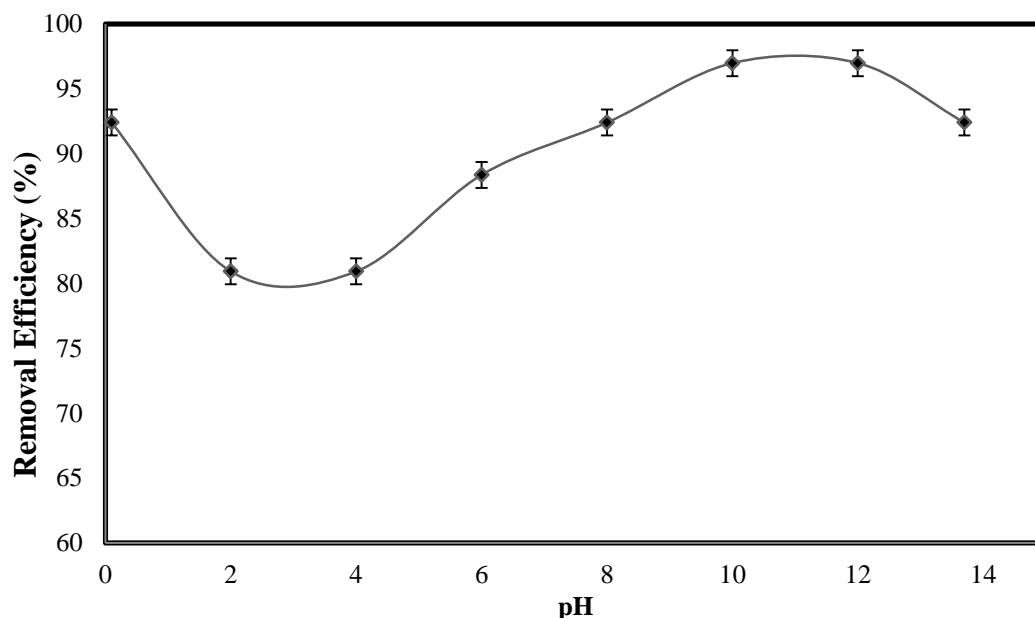


Figure 12. Effect of pH on adsorption of crude oil. Initial oil concentration is 300 mg/L, temperature is 25 ± 2 °C, adsorbent dose is 10.0 g/L, contact time is 50 min and shaking/stirring speed is 140 rpm.

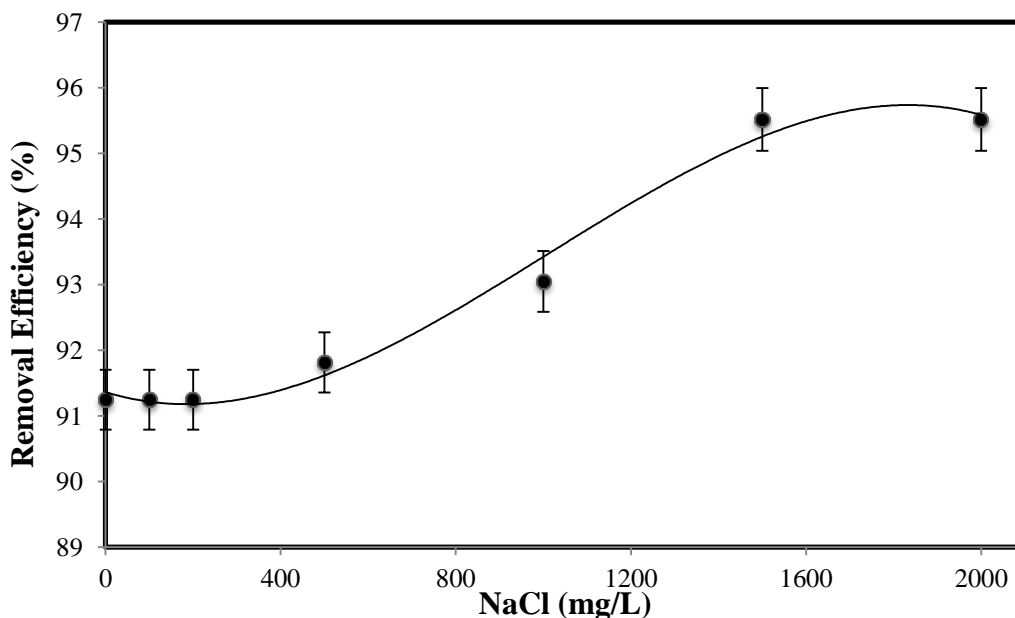


Figure 13. Effect of salinity on crude oil removal efficiency. Initial oil concentration is 300 mg/L, initial pH is 9.5 ± 0.2 , temperature is 25 ± 2 °C, adsorbent dose is 10.0 g/L, contact time is 50 minutes, and shaking/stirring speed is 140 rpm.

3.2.4. Effect of temperature

One of the most important factors which may have a significant impact on the removal of oil from produced water is temperature. The effect of temperature on the oil sorption was studied in this work. Experiments were conducted at temperatures between 25 and 70°C. The study of temperature was executed at an initial oil concentration of 300 mg/L, initial pH 9.5 ± 0.2 , 50 minutes of contact time, 140 rpm of shaker stirring and a bio-sorbent dose of 10.0 g/L. Figure 14 shows that the oil removal efficiency increased by four percent (92 to 96%) by increasing the temperature from 25 to 55 °C. However, when the temperature is raised beyond 60 °C, a decrease in oil removal efficiency was observed. The rise in the oil removal efficiency up to 55 °C is caused by the drop in the surface tension of oil and water emulsion. Moreover, the oil uptake of the bio-sorbent improves as the viscosity of the oil diminishes [63]. The viscosity of oil is inversely proportional to the oil penetration rate into the interior surfaces of the biosorbent [83].

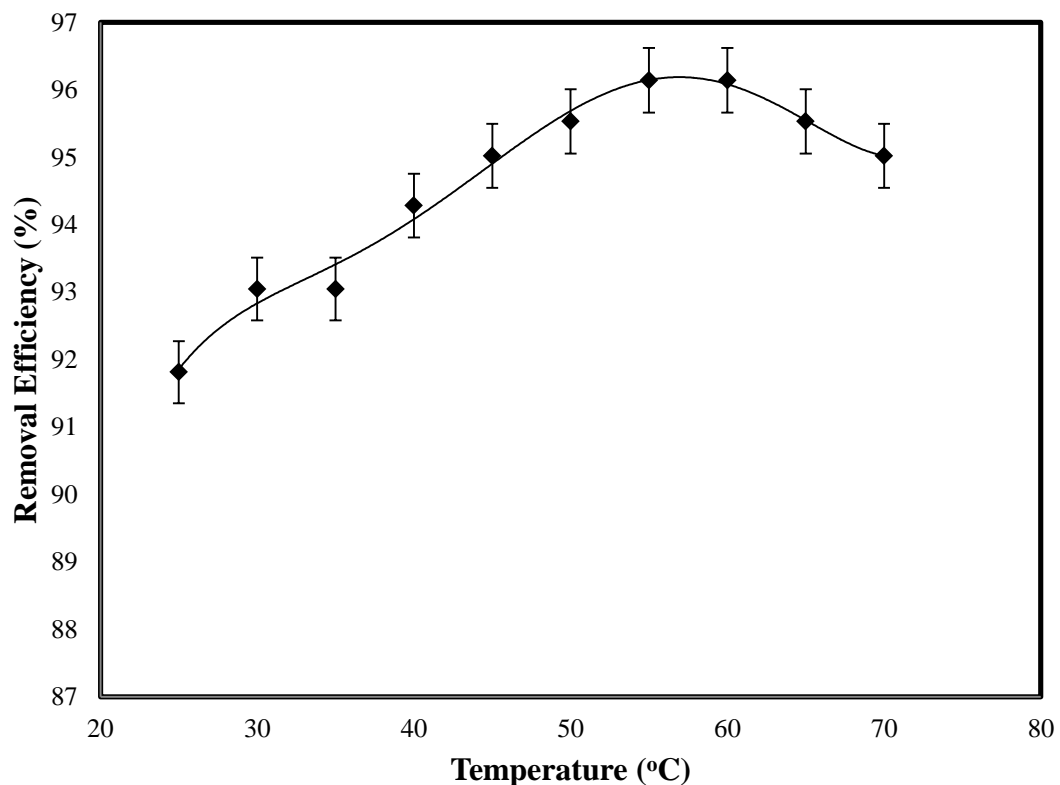


Figure 14. Effect of temperature on crude oil removal efficiency. Initial oil concentration is 300 mg/L, initial pH is 9.5 ± 0.2 , temperature is 25 ± 2 °C, adsorbent dose is 10.0 g/L, contact time is 50 minutes, and shaking/stirring speed is 140 rpm.

The adsorbate molecules are in random Brownian motion in the liquid phase and effective collisions are responsible for getting them adsorbed when they are close to the sorbent. In fact, raising the temperature increases the velocities or the movement of the molecules. This rise in the Brownian motion leads to an instability of the oil molecules and increases interaction between the sorbent and the oil particles. Thus, with temperature, the oil removal efficiency improves. The reduction in the oil removal efficiency after 60°C indicates that the exothermic process controls the rate of adsorption. Therefore, increase in the adsorption shows that the rate of adsorption is controlled by kinetics of adsorption process. Less efficiency at higher temperature may also be attributed to the loss of some organic compounds by vaporization.

3.2.5. Effect of bio-sorbent concentration

The relation between bio-sorbent dosage and crude oil removal efficiency can be seen in Figure 15. When the bio-sorbent dose was raised from 0.050 to 2.325 g per liter of the solution, the oil removal efficiency increased from 70.8 to 95.5%. Also, 2.325 g/L of produced water was deemed the optimum quantity of bio-sorbent. Owing to the rise in number of available sites for adsorption, the removal efficiency was improved.

3.3. Sorption Studies

The adsorption isotherm provides a relation between the total mass of adsorbed adsorbate per unit mass of sorbent and concentration at constant ambient conditions. In order to develop adsorption isotherms, adsorption experiments were performed. Langmuir adsorption isotherm and Freundlich adsorption isotherm are the most common isotherms which are used for adsorption studies [54]. An adsorption study was performed for pomegranate peel powder (PPP). The adsorption models were applied to calculate the sorption capacity of the PPP sorbent. Adsorption equilibrium is typically explained by the isotherm equations.

The parameters of isotherms describe the surface properties and affinity at a constant temperature and pH. In process design, the adsorption study plays a vital role and also helps to find the uptake rate and capacity. Langmuir and Freundlich models explain the behavior of oil adsorption on the adsorbent and remaining ionic concentration in the solution.

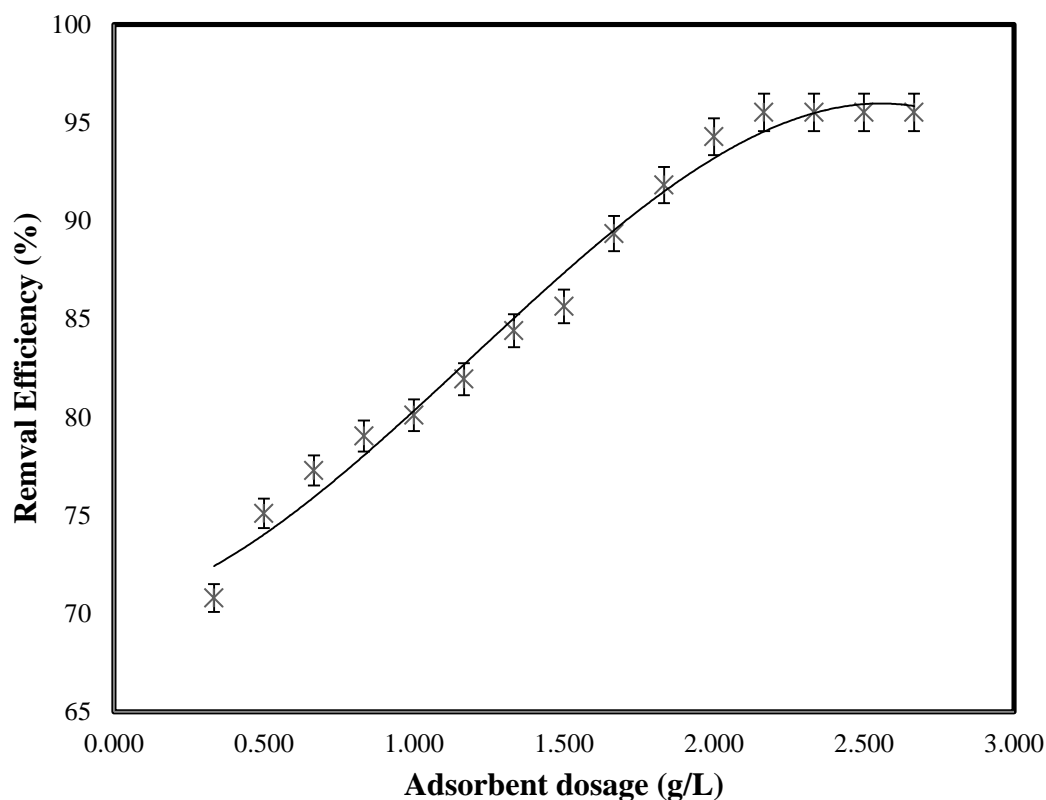


Figure 15. Effect of adsorbent dosage on the removal efficiency of oil. Initial oil concentration is 300 mg/L, initial pH is 9.5 ± 0.2 , temperature is 25 ± 2 °C, contact time is 50 minutes, and shaking/stirring speed is 140 rpm.

3.3.1. Adsorption isotherms models

A correlation to find total mass of adsorbed adsorbate per unit mass of sorbent at constant ambient conditions is provided by the adsorption isotherm. Adsorption experiments were conducted in order to develop adsorption isotherms. The quantity of adsorbent needed to be kept constant in these experiments, whereas variations were introduced in the initial concentration of the adsorbate. The Langmuir and Freundlich adsorption isotherm are the most common isotherms used in adsorption studies [83].

The equilibrium data were correlated using Langmuir (Eq. 1), Freundlich (Eq. 2), D-R Isotherm (Eq. 4) and Temkin (Eq. 6) isotherms, where, q_e is the amount of the substance adsorbed at equilibrium per amount of adsorbent; q_m is the saturation monolayer adsorption capacity, C_e is the equilibrium concentration, k is the Langmuir adsorption equilibrium constant, k_f and n are the Freundlich constants, B_D is the free energy of adsorption per mole of adsorbate, and B is the Temkin equilibrium adsorption constant.

The Langmuir isotherm linear plot gave a regression coefficient (R^2) of 0.989, the Freundlich isotherm gave 0.915 and the Temkin gave 0.961. Clearly, the better fit is offered by the Langmuir isotherm.

A summary of the absorption capacity of different bio adsorbents under various conditions was given by Table 2. PPP displayed an adsorption capacity which was comparable with most adsorbents used. Table 3 summarizes the adsorption parameters of the different isotherms employed to fit the adsorption isotherm.

3.3.1.1. Langmuir Adsorption Model.

The Langmuir adsorption model predicts that monolayer adsorption occurs consistently on the active site of the sorbent surface, and once the active sites are covered by the sorbate the adsorption process will stop [55]. Using a linear mathematical expression for the Langmuir model, a graph can be obtained by plotting C_e/q_e vs C_e , as given below:

$$\frac{C_e}{q_e} = \frac{1}{kq_m} + \frac{C_e}{q_m} \quad (12)$$

where q_m is the maximum capacity calculated from the slope, q_e is the maximum capacity after equilibrium is achieved (experimental value), k is the binding energy constant which is associated with net enthalpy or energy of adsorption (calculated from the y-intercept and q_m) and C_e is the concentration at equilibrium.

The Langmuir adsorption isotherm of oil by PPP is shown in Figure 16. The capacity of bio-sorption, Q_L , and the Langmuir constant, k , were manipulated by the plotting the linear regression and tabulated in Table 3. The coefficient of determination, R^2 , for the oil is 0.989, which confirms that the bio-sorption of the oil on the pomegranate peel powder is explained by the Langmuir model and the biosorption data is a good fit to the mono-layer Langmuir model. From the equilibrium condition it can be inferred that all the accessible active sites for the adsorption were roofed/saturated by the atoms, ions or molecules of the adsorbate. The equilibrium condition may also suggest that the adsorption rate of the adsorbate molecules has become equal to the desorption rate of the adsorbate molecules.

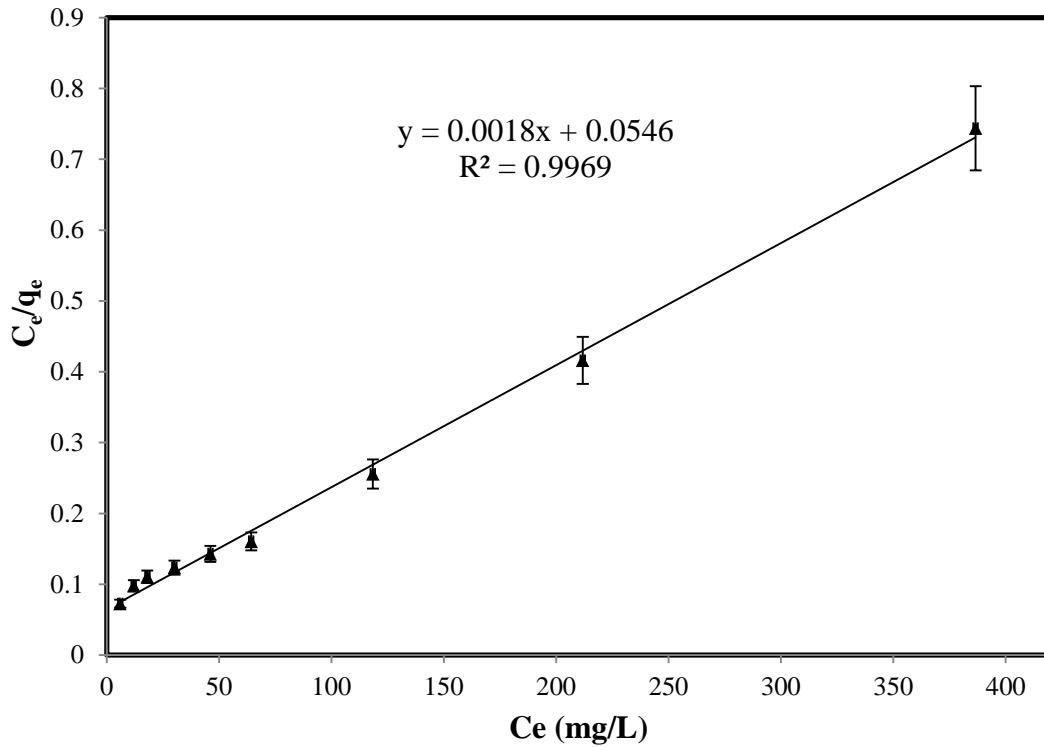


Figure 16. Langmuir adsorption isotherm for adsorption of oil on PPP. Initial pH: 9.5 ± 0.2 ; temperature: 25 ± 2 °C; adsorbent dose: 2.325 g/L; adsorbent particle size: 150-500 micron; contact time: 50 minutes; shaker RPM: 140.

The utmost adsorption capacity or uptake of the oil by PPP was 555.56 mg/g as given in Table 3. The dimensionless constant separation factor, R_L , is the vital trait of the Langmuir isotherm and can be articulated as,

$$R_L = \frac{1}{1 + bC_0} \quad (13)$$

The value of R_L defines the attributes of the Langmuir isotherm. The R_L value indicates favorability ($0 < R_L < 1$), un-favorability ($R_L > 1$), linearity ($R_L = 1$) or irreversibility ($R_L = 0$) of the isotherm. Figure 17 shows that for initial oil concentrations ranging from 20 to 1600 ppm, all the values for R_L stretch out from 0.0186 up to 0.6026. The R_L values from the experimental results illustrate that the adsorption of oil onto the surface of the PPP takes place. Consequently, it can be affirmed that PPP is a good sorbent which favors adsorption.

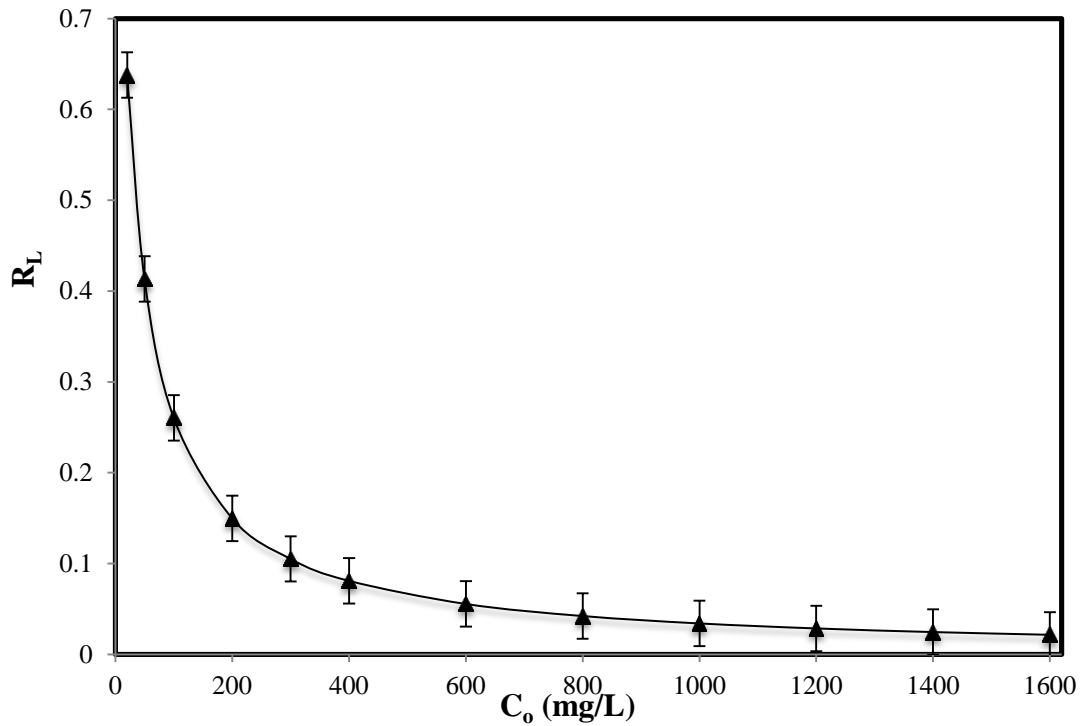


Figure 17. The calculated separation factor R_L against the oil initial concentration C_o (mg/L).

Table 3 Equilibrium adsorption parameters of four isotherms for the removal of oil from produced water using PPP.

Isotherm model	Parameters	Values
Langmuir	q_m (mg/g)	555.56
	k (L/mg)	0.0284
	R^2	0.989
Freundlich	k_f (mg/g)	5.1454
	n	2.1299
	R^2	0.9151
Dubinin	q_m (mg/g)	13.867
	B_D	0.0026
	R^2	0.8917
Temkin	B (L/g)	279.64
	k_t	0.282866
	R^2	0.9606

3.3.1.2. *Freundlich Adsorption Model.*

The Freundlich model is an empirical expression and one of the most primitive models. The Freundlich model is based on heterogeneous surface and adsorption heat. For calculation of the parameters following linearised Freundlich mathematical expression (plot the graph between $\ln(q_e)$ vs $\ln(C_e)$) was used:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (14)$$

where q_e is the maximum capacity after equilibrium is achieved (experimental value), k_f is the Freundlich constant related to adsorption capacity (calculated from the intercept), $1/n$ represents the adsorption intensity (calculated from the slope), and C_e is the concentration at equilibrium. The favorability of the Freundlich isotherm model is indicated by the value of $1/n$. A lesser value of “ n ” shows that the bonding among adsorbate and adsorbent is stronger. However, the values of “ n ” between 1-10 present a proposal about high-quality adsorption. The values of $n > 1$ denote that the adsorption environment and conditions are favorable [84].

Adsorption behavior was studied using the Freundlich Isotherm model by plotting $\log q_e$ versus $\log C_e$ which revealed the values of the isotherm constants. The Freundlich isotherm plot is shown in Figure 18. k is associated with the adsorption capacity of PPP whereas “ n ” is the measure of the adsorption intensity. Figure 18 shows a straight line with the correlation coefficient (R^2) of 0.9151. All the values for the constants are tabulated in Table 3. The value of “ n ” found after the calculation was 2.1299.

3.3.1.3. *Dubin-Rudoshick (D-R) model.*

The Dubinin-Rudoshick (D-R) model is used to classify the mechanism and the energy of sorption. The D-R model also provides a means of distinguishing between chemisorption and physisorption. The linear form of the D-R model is given below:

$$\ln q = \ln q_m - B_D \mathcal{E}^2 \quad (15)$$

where, q_e is the amount adsorbed per unit mass of adsorbent (mol g^{-1}), q_m is the maximum sorption capacity, \mathcal{E} is the polanyi potential, and B_D is the D-R constant.

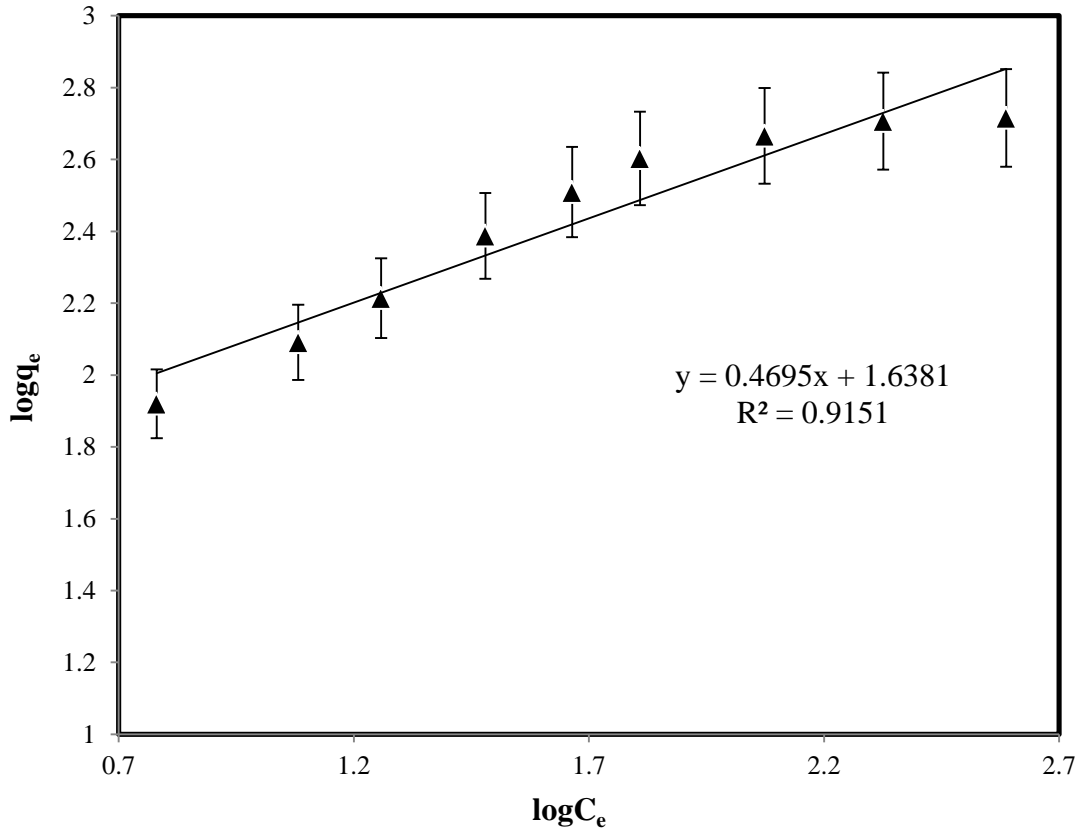


Figure 18. Freundlich adsorption isotherm for adsorption of oil on PPP. Initial pH: 9.5 ± 0.2 ; temperature: 25 ± 2 °C; adsorbent dose: 2.325 g/L; adsorbent particle size: 150-500 micron; contact time: 50 minutes; shaker RPM: 140.

The polanyi potential can be measured by the following relation:

$$\mathcal{E} = RT \ln \left[1 + \left(\frac{1}{C_e} \right) \right] \quad (16)$$

where T is the absolute temperature, R is universal gas constant and C_e is the concentration at equilibrium. The plots of $\ln(q)$ vs \mathcal{E}^2 give a linear relationship. The values of q_m and B_D can be calculated from the intercept and slope of the plots. The adsorption energy (E) can be calculated from the following mathematical expression,

$$E = \frac{I}{\sqrt{-2B_D}} \quad (17)$$

The E values provide information concerning the mechanism of the sorption process. The chemisorption (ion-exchange mechanism) process is confirmed if the E value lies in the range of 8-16 kJ/mol, while the physisorption mechanism is indicated by values of E lower than 8 kJ/mol.

The plot for the D-R isotherm model is shown in Figure 19. The regression coefficient R^2 is 0.8917 which is less than the Langmuir and Freundlich isotherm models which are 0.989 and 0.9151. Therefore the equilibrium data did not fit well as compared to the Langmuir and Freundlich isotherm models.

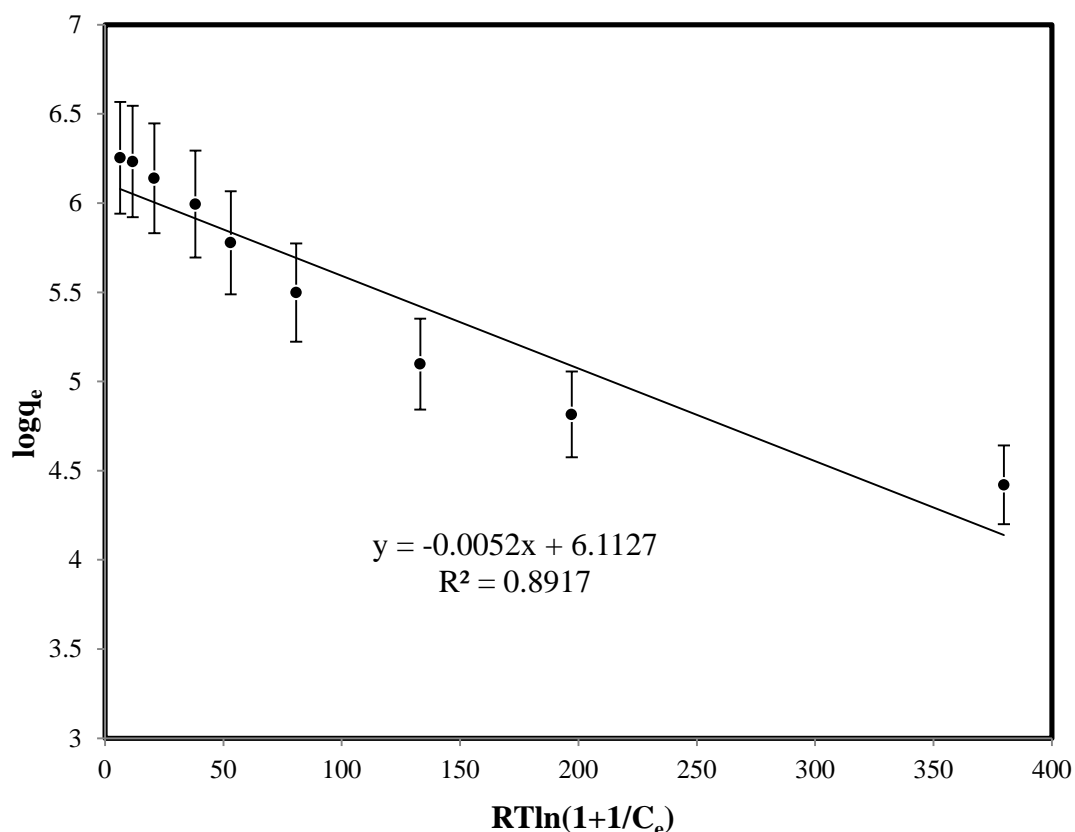


Figure 19. Dubinin-Radushkevich adsorption isotherm for adsorption of oil on PPP. Initial pH: 9.5 ± 0.2 ; temperature: 25 ± 2 °C; adsorbent dose: 2.325 g/L; adsorbent particle size: 150-500 micron; contact time: 50 minutes; shaker RPM: 140.

3.3.1.4. Temkin Adsorption Isotherm.

The Temkin isotherm equation was originally proposed to explain the adsorption capacities of hydrogen on platinum electrodes in acidic solutions. Temkin and Pyzhev [85] observed experimentally that heats of adsorption will frequently decrease rather than increase with increasing coverage. The supposition in use throughout the derivation of the Temkin isotherm is linear behavior of receding in the strength of heat of sorption as a function of temperature. This relation was

logarithmic in the Freundlich equation. The linear form of the Temkin isotherm is as follows:

$$q_e = B \log k_t + B \log C_e \quad (18)$$

In equation 6, B and k_t are the constants of the Temkin adsorption isotherm, where $B=RT/b$, T is the temperature (Kelvin), R is the universal gas constant and $1/b$ is the absorption potential of the adsorbent. Figure 20 shows the Temkin isotherm which is a plot of q_e versus $\log C_e$. The constants of the Temkin adsorption isotherm are calculated from Figure 20 (slope and y-intercept). For the bio-sorption on PPP sorbent, the Temkin adsorption isotherm is appropriate to some degree to the equilibrium statistics ($R^2 = 0.9606$). The regression coefficient for the Temkin isotherm ($R^2 = 0.9606$) is higher than the Dubinin-Radushkevich isotherm ($R^2 = 0.8917$) and Freundlich isotherm ($R^2 = 0.9151$) though it is lower than the Langmuir isotherm ($R^2 = 0.989$). This suggests that the equilibrium data for the bio-sorption of oil onto PPP better fits to the Temkin isotherm model as compared to the Dubinin-Radushkevich and Freundlich adsorption isotherm models. However, the Temkin isotherm model is not really appropriate for the liquid phase adsorption study since liquid phase adsorption is more complex than gas phase adsorption. The complexity in liquid phase adsorption may be due to the agglomerate formation of adsorbed molecules by the high interaction between the solvent molecules and adsorbate [86].

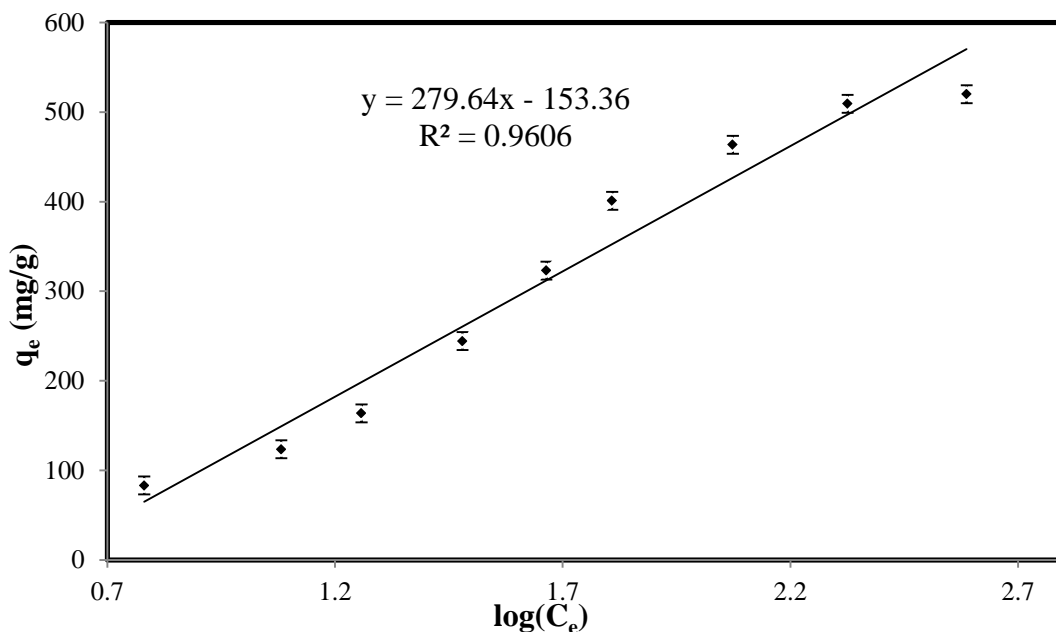


Figure 20. Temkin adsorption isotherm for adsorption of oil on PPP. Initial pH: 9.5 ± 0.2 ; temperature: 25 ± 2 °C; adsorbent dose: 2.325 g/L; adsorbent particle size: 150-500 micron; contact time: 50 minutes; shaker RPM: 140.

3.3.2. Kinetics studies of bio-sorption

Another study was carried out to examine the kinetics of bio-sorption and to reveal the dynamics of sorption of oil onto PPP. In order to estimate the amount of oil adsorbed with time, models were predicted which explain all the kinetics. The information obtained from these predictive models can be scaled up to be used for larger systems. Therefore, to investigate the rate controlling mechanisms of sorption such as chemical reactions or mass transfer, different kinetic models were used. The oil uptake increased by increasing the contact time. However, the oil removed became constant after equilibrium time (see Figure 21). The rate of adsorption of residual oil by PPP was calculated using simple kinetic analysis. Hence, pseudo first order and pseudo second order kinetics were applied to the experimental data of bio-sorption of oil onto PPP.

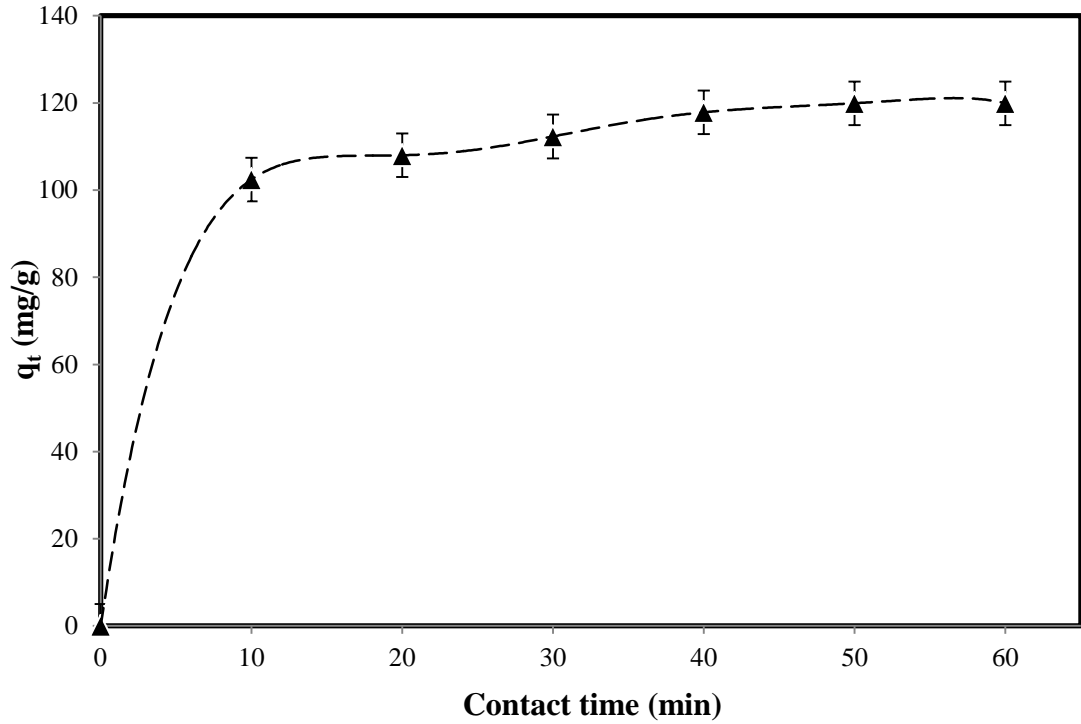


Figure 21. Effect of contact time on adsorption of oil on PPP. Initial pH: 9.5 ± 0.2 ; temperature: 25 ± 2 °C; adsorbent dose: 2.325 g/L; adsorbent particle size: 150-500 micron; contact time: 50 minutes; shaker RPM:140.

3.3.2.1. Pseudo First Order Kinetics.

The pseudo first order kinetics is expressed as,

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (19)$$

where Q_t is the amount of oil adsorbed at a given time and Q_e is the amount of oil adsorbed at equilibrium and k_1 is the bio-sorption rate constant. Integration and rearrangement of Equation 19 gives:

$$\ln(Q_e - Q_t) = -k_1 t + \ln Q_e \quad (20)$$

Figure 22 shows the plot of Equation 20, $\ln(Q_e - Q_t)$ versus t , which is actually a plot of the pseudo first order kinetics. Here the y-intercept is $\ln Q_e$ and the slope of the curve is k_1 .

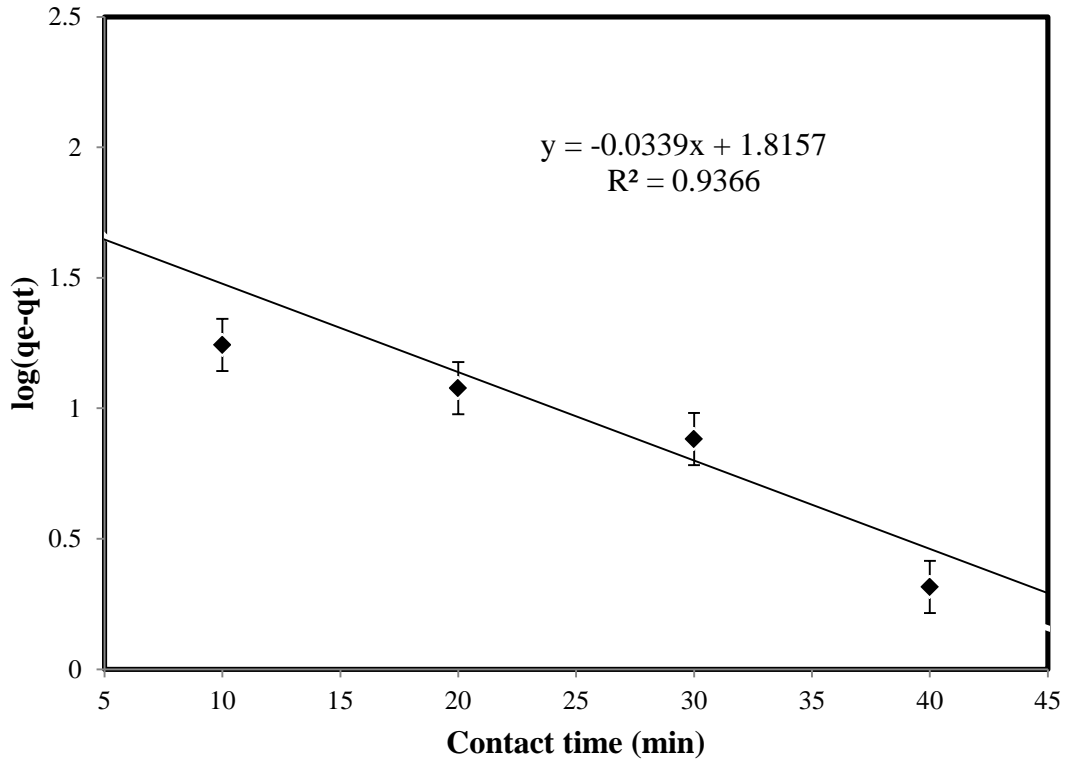


Figure 22. Pseudo-first-order kinetic model for adsorption of oil on PPP. Initial pH: 9.5 ± 0.2 ; temperature: 25 ± 2 °C; adsorbent dose: 2.325 g/L; adsorbent particle size: 150-500 micron; contact time: 50 minutes; shaker RPM: 140.

3.3.2.2. Pseudo Second Order Kinetics.

The pseudo second order kinetics is represented by the following expression

$$\frac{dQ}{dt} = K_2(Q_e - Q_t)^2 \quad (21)$$

After integrating and rearranging we get,

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2(Q_e)^2} \quad (22)$$

Figure 23 shows the plot for Equation 22 as t/Q_e versus t . The regression coefficient, R^2 , shows that the sorption of the oil on PPP follows pseudo second order kinetics. The data obtained by plot of linear relation and calculation has been tabulated in Table 4. Based on the regression coefficients and the calculated Q_e from the graphs for the pseudo first- and second-order kinetic models, it has been observed that the

pseudo second-order kinetic model fit the data very well as compared to the pseudo first-order kinetic model.

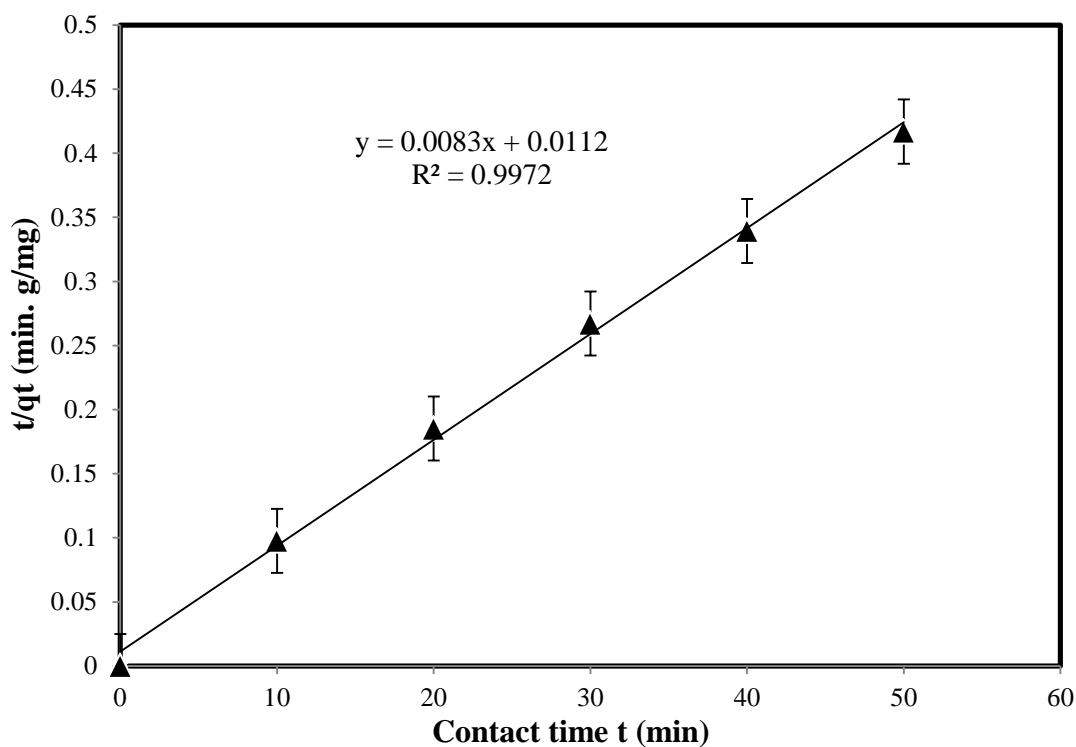


Figure 23 Pseudo-second-order kinetic model for adsorption of oil on PPP. Initial pH: 9.5 ± 0.2 ; temperature: 25 ± 2 °C; adsorbent dose: 2.325 g/L; adsorbent particle size: 150-500 micron; contact time: 50 minutes; shaker RPM: 140.

Table 4 enlists the values of different model parameters such as K_1 , K_2 , $Q_{e(cal)}$, and R^2 . The Q_e obtained from Langmuir isotherm is given in Table 3.

Table 4. Kinetic model parameters for sorption study of oil onto the surface of PPP.

Kinetic model	Parameters	Values
Pseudo-first-order	K_1 (g/mg min)	0.0339
	$Q_{e(cal)}$ (mg/g)	65.4
	R^2	0.9366
Pseudo-second-order	K_2 (g/mg min)	0.000375
	$Q_{e(cal)}$ (mg/g)	588.2
	R^2	0.9903

Inspection of Table 4 reveals that $Q_{e(cal)}$ given by the pseudo second order kinetic model (588.3 mg/g) is more close to the experimental value $Q_{e(cal)}$ (555.6 mg/g) obtained from Langmuir isotherm than that obtained from pseudo first order kinetic model (65.4 mg/g). Also, the R^2 value for the pseudo second order kinetic model (0.9903) is higher than that of pseudo first order kinetic model (0.9366).

3.4. Thermodynamic Studies

The thermodynamic behavior for the biosorption of oil from water can be described by evaluating the thermodynamic parameters. These thermodynamic parameters are the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). These parameters are determined by the following two equations,

$$\Delta G^\circ = -RT \ln K \quad (23)$$

Where,

R = Ideal gas constant (8.314 Jmol⁻¹K⁻¹)

T = Temperature (K)

K = Distribution co-efficient = Q_e/C_e (which may be obtained from Langmuir adsorption isotherm at different temperatures).

ΔG° = Change in Gibbs free energy (J/mol)

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (24)$$

Where,

ΔG° = Change in Gibb's free energy (J/mol)

ΔS° = Change in Entropy (J/mol.K)

ΔH° = Change in Enthalpy (J/mol)

T = Temperature in Kelvin (K)

The change in enthalpy and entropy was determined from the slope and intercept of the plot between $\ln K$ and $1/T$ respectively, as shown in Figure 24. After calculation all the thermodynamic parameters are tabulated in Table 5.

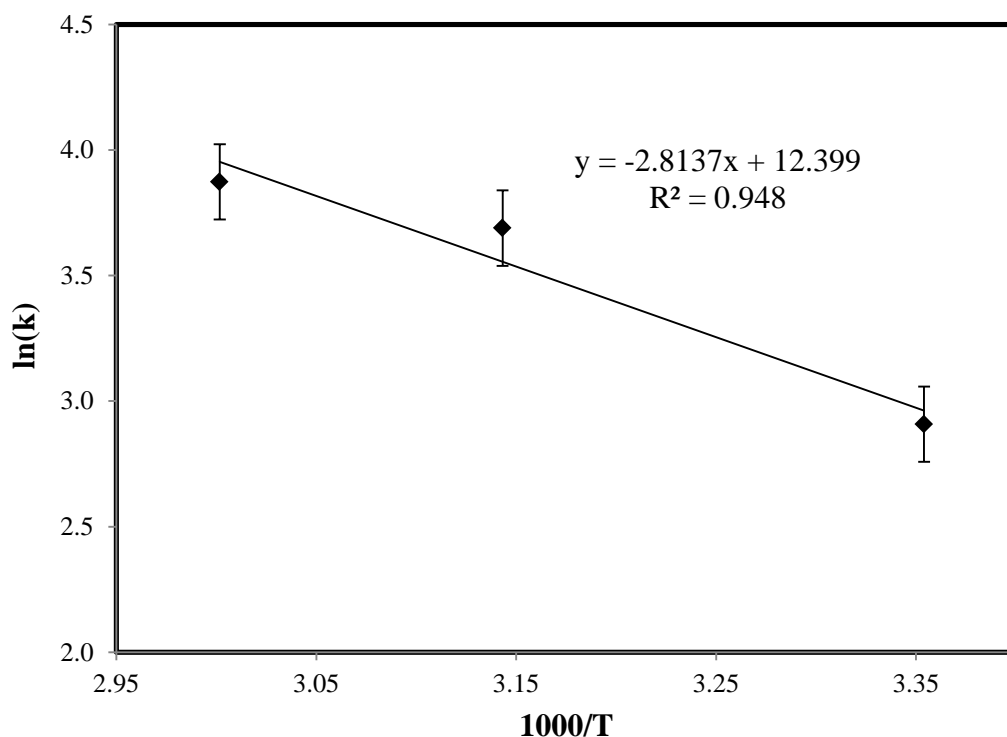


Figure 24 Thermodynamic study for adsorption of oil on PPP. Initial pH: 9.5 ± 0.2 ; temperature: 25 ± 2 , 45 ± 2 and 60 ± 2 °C; adsorbent dose: 2.325 g/L; adsorbent particle size: 150-500 micron; contact time: 50 minutes; shaker RPM: 140.

Table 5 Thermodynamic parameters for the adsorption of oil by PPP.

$\Delta^{\circ}G$ (kJ/mol)			$\Delta^{\circ}H$ (kJ/mol)	$\Delta^{\circ}S$ (kJ/mol.K)
298.15 K	308.15 K	318.15 K	30.235	0.124
-7.208	-6.777	-9.757		

3.5. Desorption

A desorption experiment was carried out on adsorbed crude oil on the surface of PPP by means of n-hexane. The experiment of adsorption-desorption was repeated three times. The n-hexane used was 150 ml for the crude oil to get desorbed from the adsorbent (PPP). The contact time and agitation speed were 50 minutes and 140 rpm, respectively. The amount of oil desorbed from the PPP surface was more than 90%. The adsorption capacity of PPP after used once showed a slight change (89% of the crude oil was adsorbed compared to 94% for the first use). These results indicate that

the PPP adsorbent can be reused without a pronounced change in its adsorption capacity.

3.6. Oil removal from Real Produced Water

The sample of real produced water was obtained from Sharjah National Oil Company (SNOOC), Sharjah. The extraction of oil from this water using n-hexane revealed that its oil content is 230 mg/l. Upon treatment of 150 ml of produced water with 0.350 g of PPP, the removal efficiency of oil is found to be 95.7 ± 1.0 %. This result gives evidence that our proposed method is powerful in treating PW from oil and gas well.

CONCLUSION

In this work, a new promising and efficient natural adsorbent for the removal of oil from produce water was developed. Following conclusions can be drawn from this study:

- The adsorbent was prepared from pomegranate peel (PPP) with optimum adsorption efficiency greater than 92%.
- Batch adsorption experiments for the adsorption of oil from produced water have been carried out by using pomegranate peels powder (PPP). Effect initial pH, contact time, oil initial concentration and adsorbent dose have been studied at temperature of 25 ± 2 °C and orbital shaker RPM of 140 with adsorbent particle size of 150 micron.
- The optimum parameters for oil removal were: pH = 9.5, pomegranate dosage = 2.33 g/L, contact time = 40.0 minutes and adsorption temperature = 55.0 °C.
- The oil removal efficiency by pomegranate peels powder (PPP) was found to increase with increasing the salinity of produced water.
- The results show that the mixing time affects the adsorption characteristics and hence the oil removal efficiency of the respective PPP (pomegranate peels powder).
- Scanning electron microscope (SEM) analysis shows that PPP is highly porous and has cavities responsible for high removal efficiency of oil from synthetic produced water.
- Energy dispersive X-ray spectroscopy (EDS) analysis shows that PPP is composed of variety of elements such as C, Ca, K, P, O and S.
- With the increase in the initial concentration of oil, the removal efficiency of pomegranate peels powder (PPP) decreases.
- Initially by increasing the adsorbent dose, removal efficiency of the oil from produced water increased rapidly up to 92% and then became almost constant. At 92% removal efficiency, the optimum dose is 2.33g/L.
- The removal efficiency of oil by PPP increased with the increase in the pH of adsorbate solution. The optimum pH for oil removal is 9.5.
- The removal rate of oil was rapid in the beginning up to 92% then became constant with time. Equilibrium time for oil removal was 40 min.

- The kinetics of adsorption was found to follow Pseudo-second-order kinetic model with rate constant of 3.75×10^{-4} g/mg.min. This shows that chemical adsorption has major influence in the current adsorption studies.
- The adsorption isotherm for crude oil removal was found to follow Langmuir adsorption isotherm as compared to Freundlich, Dubinin-Redushick and Temkin isotherm models. Maximum adsorption capacity of 555 mg/g for PPP has been obtained by Langmuir model for crude oil removal.
- Batch adsorption studies for oil removal by PPP indicate that PPP is effective and efficient for oil removal and thus it can be significantly used as low cost adsorbent for produced water treatment.
- This newly developed adsorbent was found to be easily regenerated without noticeable change in adsorption capacity.
- These finding render PPP as efficient, cost effective and environmentally friendly adsorbent.

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Vita

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