ADSORPTION OF ANIONIC SURFACTANTS FROM SYNTHETIC PRODUCED WATER ON CRUDESORB AND KAOLIN

By

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14917

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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NUR ALIA AQILAH BT ZULKIFLI

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ABSTRACT

Conventional treatment process cannot meet the need for treatment of produced water from surfactant flooding of Enhanced Oil Recovery (EOR) field. In this study, adsorption of surfactants using commercialised adsorbent, CrudeSorb and natural adsorbent, kaolin were investigated to assess the removal of surfactants from synthetic produced water. Adsorbents were first sent for XRD to verify theirs mineralogical and SEM to determine their external morphology texture. In the adsorption test, the adsorbents were exposed to anionic surfactants in produced water and final surfactant concentration of produced water is measures using titration method. The amount of surfactant that was adsorbed was quantified by subtracting the concentration of surfactants after adsorption from the initial concentrations. The surfactant removed was optimized at pH value of 2 for kaolin, and pH12 for CrudeSorb. An increase in of contact time also increases the percentage removal of surfactants from produced water on both CrudeSorb and kaolin. The adsorption activities for both CrudeSorb and kaolin fitted the Langmuir Isotherm with correlation coefficients of 1.00 and 0.9962. The adsorption activities also found to be fitted the pseudo second-order reaction kinetic model at correlations coefficients value of 0.9993 and 0.9923 respectively.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Produced water is by far the largest waste stream by volume associated with oil and gas exploration and production (Ahmadun et al., 2009). Such water is trapped in underground formations and carried to the surface along with oil or gas. The main produced water pollutants are oil and grease, chemical additives, natural compounds (both organic and inorganic) and naturally occurring radioactive materials (Maretto et al., 2014). Organic contaminants in produced water are toxic and corrosive leading to environmental and operational problems (Deriszadeh et al., 2010). Discharging produced water can pollute surface and underground water and soil. On the other hand, because large volume of produced water are being generated, many countries with oilfields which are also generally water-stressed countries, are increasingly efforts to find efficient and cost-effective treatment methods to remove pollutants as a way to supplement their limited fresh water resources (Ahmadun et al., 2009).

In recent years, surfactant flooding is use as a method for the enhanced recovery of oil from partially depleted reservoirs. Surfactant injected helps to mobilize the residual oil that is trapped by capillary forces in oil reservoirs, which many of enhanced oil recovery (EOR) methods rely on reducing the oil-water interfacial tension (IFT) to extremely low values, e.g. 10^{-4} dyne/cm or lower (Curbelo et al., 2007). Due to the use of surfactant in the injected water, produced water from ASP (Alkaline/Surfactant/Polymer) flooding contains some residual chemicals that are difficult to treat than produced water from water flooding (Liu et al., 2005). The surfactants magnitude of contamination being high may prove fatal for aqueous flora and fauna, (Pahphane and Ramirez, 2013). Within this framework, polluted water remediation should be considered a major challenge.

Conventional produced water treatment line up including bulk separator, hydrocyclone, and induced gas flotation (IGF) are only meant to promote oil removal efficiency from produced water rather than treating surfactants. Thus new polishing system need to be evaluated and put in place to ensure the produced water comply with reuse and discharge limits of surfactants from surfactant flooding. The optimization of wastewater purification process requires a development of new operations based on low cost materials, with high pollutant removal efficiency. In addition, compact physical and chemical treatment technologies are preferred in offshore extraction facilities due to space constraints. Therefore smaller size of equipment with high surfactant removal efficiency is promising to be settled in surface facilities of oil production.

Each year there is numerous academic publications in all aspects of adsorption. Adsorption studies using low-cost adsorbent reviewed by Gadd, 1993; Volesky and Holan, 1995; Chang et al., 1997; Guibal et al., 1998; Annadurai et al., 2002; Sheng et al., 2004; Aksu, 2005; Ho. 2006; Vijayaraghavan and Yun, 2008; Wang and Chen, 2009; Chojnacka, 2010; Hossain et al., 2012; Liu et al., 2014; Bulut and Karaer, 2015; Saygili et al., 2015; Marchetti et al., 2015. Clays are widely applied in many fields such as treatment of wastewater produced by petrochemical activities (Maretto M. et al., 2014), polymer nano-composites (S. Sinha Ray and M. Okamoto, 2003; H. Fischer, 2003; Q.H. Zeng et al., 2005), adsorbents for heavy metal ions (Bradl, 2004; Volzone, 2004), catalysts (Gil et al., 2000; De Stefanis, 2006), photochemical reaction fields (Shichi and Takaqi, 2000), ceramics (Burst, 1991), paper filling and coating (Bundy and Ishley, 1991), sensors and biosensors (Mousty, 2004) due to their high specific surface area, chemical and mechanical stabilities, and a variety of surface and structural properties (Murray, 1991; Murray 2000).

Clays are natural environment-friendly materials with high specific surface area and now widely used for the adsorption and removal of the organic pollutants (Liu and Liuxue, 2007). Thus, adsorption of surfactant and soluble or insoluble hydrocarbon in produced water onto the clay is one of the best alternatives to consider in produced water management. CrudeSorb is a proprietary adsorption media based on resin, polymer and clay chemistry, which has proven to be extremely efficient at removing oil, grease and soluble organics from water systems. CrudeSorb has been developed for the treatment and polishing of various waste systems and is packaged in radial flow non-ferrous canisters, which allow for a quick media change outs. Besides, most of the wastewater treatment studied at high retention time (Musleh et al., 2014), which is not suitable to be suited in polishing system at the offshore. Smaller volume of equipment operation with high removal of surfactants efficiencies is indeed a key master at offshore operations.

1.1.1 Produced Water Management Objectives

The growing disposal of wastewater into the environment recently makes the water contamination one of the most important tasks to take care of. As water of good quality is a precious commodity and available in limited amounts, it has become highly imperative to treat wastewater for removal of pollutants (Is, F. Thorikulet al., 2013; Yuening et al., 2014)**.** Some of the options available to oil and gas operators for produced water management proposed by Arthur et al. (2005) including produced water re-injection, overboard discharge, reuse in oil and gas operation or consume in beneficial used; such as irrigation (Boysen et al., 2002), range-land restoration, cattle and animal consumption, and drinking water (Tao et al., 1993). Treatment of produced water is an effective option for produced water handling. Treatment of the produced water has the potential to be a harmless and valuable product rather than a waste.

Priority of produced water management is given for overboard discharge because re-injection of produced water is really complex to fathom as it gives adverse effect to the reservoir if the injected water is not compatible to their conditions. From and industrial standpoint, the different contaminants in the produced water may adversely affect equipment leading to scaling and corrosion (Allen, 2008; Quagraine et al., 2005; Cline 1998). On the other hand, disposal well has disadvantages in term of cost for well drilling and well availability. Eventually industry has come to settle on overboard discharge and Neff et al., (1992) reported that produced water from oil and gas industries is permitted to be discharge to the environment.

The key parameters that industry needs to ponder before going for overboard discharge of produced water when it comes to surfactant flooding is its toxicity. Surfactants trigger toxicity to disfavour level where it can affect the ecosystem. Aromatic compounds which are the most important chemical contributing to natural environments toxicity cannot be removed efficiently by oil/water separation techniques (Ahmadun et al., 2009). Water's toxicity and organic loading (Hansen and Davies, 1994) can generally characterize the impact of discharging produced water into the sea. Thus improvement and additional polishing system should be installed in surface facilities line up to remove surfactants and enable the produced water to go for overboard discharge.

As pre-requisite for this project, toxicity study was carried out by researchers in PETRONAS Research Sdn. Bhd to observe the toxicity level of produced water containing surfactants. Based on the test carried out, the foaming surfactant was found to be moderately toxic. Thus, a proper option of managing the produced water needs to be considered upon this moment. The relative toxicity classification by US EPA shows in Table 1.1, the range of aquatic LC50 associated with each relative toxicity level. LC_{50} is defined as the median lethal concentration, which is the concentration of the test substance in water which kills fifty per cent of a test batch of fish within a particular period of exposure.

Table 1.1 – US EPA Relative Toxicity Classification

US EPA Relative Toxicity Classification	
Relative Toxicity	Aquatic LC_{50} (mg/L)
Super Toxic	0.001 – 0.1
Highly Toxic	0.1 – 1.0
Moderately Toxic	1 – 10

1.1.2 Surfactants Removal Technologies

Treatment objectives can be achieved by listing all possible treatment technologies available. The technologies can be differ in their inherent facilities requirements, capital costs, operating expense, and waste streams which is crucial to be considered in oil and gas industry. Some technologies may consume large space for installation, which is not feasible in limited space constraint at the offshore. Equipment costs of produced water treatment are first to be considered before proceed for installation where a large amount of dedicated equipment must be purchased for managing produced water.

Surfactants removal operations involve processes such as chemical and electrochemical oxidation (Lissens, et al., 2003; Mozia et al., 2005), advanced oxidation processes (Paphane and Ramire, 2013), filtration (Liu et al., 2006), coagulation (Rodriguez et al., 2007), reverse osmosis (Wilf and Alt, 2000), membrane technology (Sirieix-Plenet, et al., 2003; Kowalska, et al., 2004; Fernandez, et al., 2005), chemical precipitation (Shiau, et al., 1994; Talens-Alesson, et al., 2002), photocatalytic degradation (Rao and Dube, 1996; Ohtaki et al., 2000; Zhang et al., 2003), adsorption (Ogita et al., 2000; Lin et al., 2002; Adak et al., 2005) and various biological methods (Matthew and Malcolm, 2000; Dhouib, et al., 2003; Chen et al., 2005). However, each method has its merits and limitations and they are often limited by technical and economic issues. Further analysed shall be evaluated beforehand especially on the system volume and retention time as they are crucial parameters that need to take account when installing system in offshore.

As advanced oxidation processes are getting attention from many researchers, here are some downsides of this process including high cost for on-site supply of oxidizer, high cost of reagents, reagent may increase COD concentration, separation of precipitate, and by-product CO_2. There is also a need for the installation of uniform irradiation of UV light on the catalyst for the method to work. This means that the reactor design for AOP process required high investment to achieve effective surfactants removal. Furthermore, wastewater with other anionic species will also affect the surfactants degradation process as UV light will be absorbed by these competing species.

Surfactants containing wastewaters treatment by biological processes such as activated sludge is problematic due to the low kinetics of degradation and to foam production (Dhouib, et al., 2003). On the other hand the problem with reverse osmosis is that even though it can remove as many contaminants as possible it is costly both to install and to run. Furthermore high pressure requirements, even trace amounts of oil and grease can cause membrane fouling in reverse osmosis process. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treatment and the success of this technique depends on the development of an efficient adsorbent (Wang and Peng, 2010).

1.2 PROBLEM STATEMENT

Surfactants are among the most widely disseminated xenobiotics that may enter waste streams and the aquatic environment (Signoillot and Nguyen 1992; Margesin And Schinner, 1998; Einchorn, et al., 2001, 2001; Aboulhassan, et al., 2006). Surfactants are harmful to human beings, fishes and vegetation and are responsible to cause foams in rivers and effluent treatment plants and reduce the quality of water. They cause shorts term as well as long-term changes in ecosystem. Due to the harmful effect that surfactants can give, many environmental and health regulatory authorities have fixed stringent limits for anionic detergent as standard 0.5 mg/L for drinking water and relaxable up to 1.0 mg/L for other purposes (Rao, 1995). Thus removal of surfactants from produced water must be done effectively from surfactant flooding produced water.

Surfactant SS1003 of 750 mg/L is going to be injected in partially depleting oil production wells of Enhanced Oil Recovery (EOR) fields. Based on the study from Team 1 of Enhanced Oil Recovery in PETRONAS Research Sdn. Bhd. stated that about thirty per cent of initial surfactant concentration will be present in produced water (~225 mg/L), which is higher than allowable limit for discharge. Thus a system to eliminate surfactants from produced water is needed before discharging them.

The adsorption process is arguably one of the most popular methods for the removal of surfactants because of its simplicity, convenience, and high removal efficiency. Thus, in the present study the author is comparing the surfactants removal from produced water using commercialized adsorbents (CrudeSorb) and natural local clay (kaolin). Kaolin was used as model adsorbents because it is the most common type of clays found in oil reservoirs and surfactant adsorption occurring on sandstone is known to be attributed to kaolinite component.

The study encompasses of analysis of surfactants removal under various adsorbents dose, contact time and produced water pH value. Adsorption data have been further analysed by fitting with Langmuir and Freundlich models. Kinetic of adsorption has also been carried out with SS1003 surfactants to determine whether the surfactants removal follow pseudo first-order or second-order of kinetic models.

1.3 OBJECTIVES

The objectives of this research project are;

i) To characterize CrudeSorb, a commercialised adsorbents, called and kaolin, a natural adsorbents using X-Ray Diffraction (XRD), Particle Size Analysis (PSA) and SEM.

ii) To study the effect of adsorbent dose, contact time and pH on the surfactant removal efficiency from produced water.

iii) To study the adsorption isotherm and kinetic model exhibited by the adsorbents.

1.4 SCOPE OF STUDY

This research work scope will focus on the removal of surfactants from produced water using a type of adsorbents from CETCO Oilfield Services Company namely CrudeSorb and local clay of kaolin. Characterization of the clays will be done first using XRD to determine the mineralogical and composition of clay. Then the adsorbents were sent to undergo PSA to determine its particle size distribution, and following by SEM analysis to determine its crystalline structure. The clays will be tested at various initial surfactant concentrations, adsorbent dose and pH value of produced water. The adsorption test will be conducted using titration test, and adsorption isotherm will be evaluated. Thus the present study aimed to compare and evaluate on which adsorbent between kaolin and CrudeSorb would give higher surfactants removal from produced water with respect to the above parameters.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

Surfactants are widely used for domestic and industrial cleaning, emulsifying, wetting agents, and in oil and gas industry. Anionic surfactants are the major class of surfactants used in detergents formulations and represent for the surfactants that is injected in EOR field. The concentration of this surfactant in wastewater treatment plants (WWTP) can range from 1.2 to 9.2 mg L1 (Camacho-Muñoz et al., 2014). It has been estimated that nearly 80% of the world's population is exposed to high levels to threat to its water security (Voeroesmarty et al., 2010).

"Produced Water Polishing" is a new concept, applying a secondary treatment process to produced waters prior to final discharge overboard. Offshore operators must monitor the effluent quality before an incident of non-compliance occurs. Therefore, water polishing can be a process employed to prevent pollution or a continuous process of toxicity effluent. When free oil and grease droplets are not the contaminants, but water soluble organics are the problem, continuous polishing may be required. Thus surfactants presence in produced water can be removed from produced water polishing. Continuous CrudeSorb polishing removes the soluble organics that conventional treatment systems will not remove. CETCO's CrudeSorb is a proprietary medias based on resin, polymer and clay technology, which have proven to be extremely efficient at removing oil, grease and soluble organics from water (Blyth and Johnston, 2008).

Organic pollutants are generally classified as suspended materials. This use now is discouraged due to its high toxicity, including carcinogenicity (Slooff, 1988). The optimization of wastewater purification process requires a development of new operations based on low cost raw materials, with high pollutant removal efficiency. The CrudeSorb polishing system is a reliable efficient method to assure regulatory compliance. Use of the Crudesorb media allows the platform operator to meet compliance and maintain production in an economical manner.

2.2 CHARACTERISTICS OF PRODUCED WATER

Produced water is a mixture of organic and inorganic materials. It characteristics depend on the nature of the producing and storage formation from which they are withdrawn, the operational conditions, and chemical used in process facility, (Fakhru'l et al., 2009). The composition of produced water was significantly diverse in term of magnitude of different sources, yet the composition of produced water is qualitatively similar to oil and gas production. The major compounds of produced water include:

a) Dissolved and dispersed oil compounds
b) Dissolved formation minerals
c) Production chemical compounds
d) Production solids (including formation solids, corrosion and scale products, bacteria, waxes and asphaltenes)
e) Dissolved gases

2.2.1 Dissolved and dispersed oil compounds

Oil is a mixture of hydrocarbons including benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenantherene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs) and phenols. Water cannot dissolve all hydrocarbons, so most of the oil is dispersed in water. The amounts of dissolved and suspended oil present in produced water are related to the following factors, (Hansen and Davies, 1994):

i) Oil composition
ii) pH, salinity, total dissolved solids (TDS), temperature
iii) Oil/ water ratio
iv) Type and quantity of oilfield chemicals
v) Type and quantity of various stability compounds (waxes, asphaltenes, fine solids)

The water-soluble organic compounds in produced water are polar constituents and found distributed between the low and medium carbon ranges, (Fakhru'l Razi et al., 2009). Formic acid and propanoic acid are typically organic acid presence in produced water. pH, temperature and pressure increases soluble organics in produced water. The amounts of oil soluble in produced water depend on type of oil, volume of water production, artificial life technique, and age of production, (Bostick et al., 2002). Aromatic compounds which are the most importing chemicals contributing to natural environment toxicity cannot be removed efficiently by oil/water separation techniques. BTEX and phenols are the most soluble compounds in produced water, (Ekins et al., 2007). Aliphatic hydrocarbons, phenols, carboxylic acid, and low-molecular weight aromatic compounds are including as soluble oil compounds in produced water, (Stephenson et al., 1992). At the same time Stephenson et al., (1992) stated that the amount of dispersed oil in produced water depends on the density of oil, the shear history of the droplet, the amount of oil precipitation ad interfacial tension between the water and oil.

2.2.2 Dissolved formation minerals

Inorganic dissolved compounds in produced water include anions and cations, heavy metals, and radioactive materials. Both cations and anions affect produced water chemistry in terms of buffering capacity, salinity and scale potential, (Hansen and Davies, 1994). On the other hand, heavy metals in the produced water depend on the age of the wells and formation geology, (Utvik, 2003). Produced water contains trace quantities of various heavy metals such as cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc, (Hansen and Davies, 1994).

2.2.3 Production chemical components

During the oil and gas production several chemicals were injected into the reservoir to treat or prevent operational problems, besides enhancing the oil recovery. Chemicals like surfactant, polymer and alkali are of those chemicals involved in enhanced oil recovery. Treatment chemicals (production treating, gas processing, and stimulation) and production treating chemicals (scale and corrosion inhibitors, biocides, emulsion breakers, antifoam and water treatment chemicals) are used in these processes, (Stephenson, 1992). A wide range of polar and charged molecules like linear alkylbenzene sulfonate (LAS), alkyldimethylbenzenylammonium compounds, 2-alkyl-1-ethylamine-2-imidaolines, and a-di-[alkyldimethylammonium-ethyl]ether have been identified and characterized in commercial formulation in the North Sea oilfields, (Mccormack et al., 2001). The concentration of production chemicals in produced water is as low as 0.1 ppm, (Veil et al., 2004).

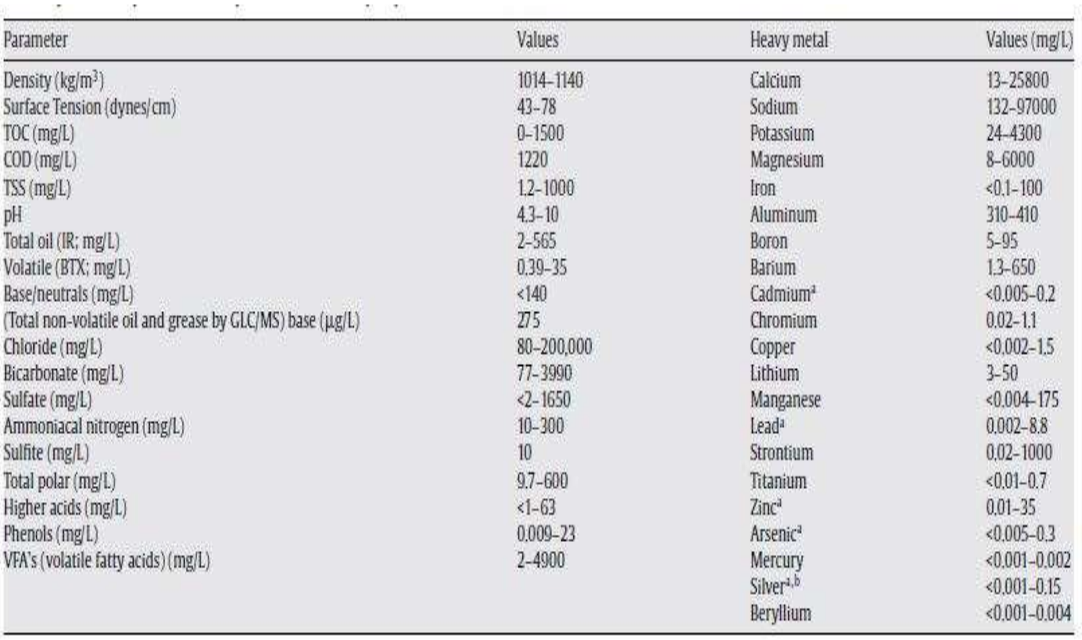
2.2.4 Production solids

Production solids including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes, are presence in produced water. In anoxic produced water, sulphides (polysulfides and hydrogen sulphide) are generated by bacterial reduction of sulphate, (Neff, 2002). Different toxic chemicals in produced water can cause very few microorganisms to live in produced water. Biological analysis indicates that there are 50-100 cells of microorganisms per mL, in which the majority of microorganisms are aerobic Gram-positive bacteria, (Weidong et al., 2001). Bacteria can clog or cause corrosion of equipment and pipelines, (Veil et al., 2004). Some inorganic crystalline substances such as SiO_2,Fe_2O_3, Fe_3O_4, ad $BaSO_4$ are found in the suspended solids in produced water, (Shubo et al., 2009).

2.2.5 Dissolved gases

Carbon dioxide, oxygen and hydrogen sulphide are common gases included in produced water, (Hansen and Davies, 1994). Table 2.1 summarizes a range of produced water characteristics in different oilfields in the world. The data show ranges of pollutants and constituents that are present in produced water.

Table 2.1 Summary of oilfield-produced water parameters in the world



Parameter	Values	Heavy metal	Values (mg/L)
Density (kg/m^3)	1014–1140	Calcium	13–25800
Surface Tension (dynes/cm)	43–78	Sodium	132–97000
TOC (mg/L)	0–1500	Potassium	24–4300
COD (mg/L)	1220	Magnesium	8–6000
TSS (mg/L)	1.2–1000	Iron	<0.1–100
pH	4.3–10	Aluminum	310–410
Total oil (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^{a}	<0.005–0.2
(Total non-volatile oil and grease by GLC/MS) base (μg/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
Ammoniacal nitrogen (mg/L)	10–300	Lead^{a}	0.002–8.8
Sulfite (mg/L)	10	Strontium	0.02–1000
Total polar (mg/L)	9.7–600	Titanium	<0.01–0.7
Higher acids (mg/L)	<1–63	Zinc^{a}	0.01–35
Phenols (mg/L)	0.009–23	Arsenic^{a}	<0.005–0.3
VFA's (volatile fatty acids) (mg/L)	2–4900	Mercury	<0.001–0.002
		Silver^{a,b}	<0.001–0.15
		Beryllium	<0.001–0.004

2.3 TECHNOLOGIES FOR REMOVAL OF SURFACTANTS

Pollution caused by organic compounds like surfactants is a common problem faced by many industries and likely to cause health hazards, harm to ecology, damage to structure or amenities, and interference with legitimate use of water. Following is the available technologies to remove dissolved carbons from produced water.

2.3.1 Stripping

This treatment would work well especially for volatile compound such as BTEX and light phenols. Its efficiency for heavier compounds such as PAHs can be enhanced by increasing temperature (API, 1995). Although stripping is not employed for the treatment of the main produced water flows on oil and gas platforms, it has reputation of being proven technology in the oil and gas industry (OSPAR,2002). On the other hand, the main disadvantage of stripping is that it creates new waste streams that need further treatment; such off-gas treatment required air stripping and separation of hydrocarbon from condensed vapours is required for steam stripping. Costs of implementing stripping for treatment of dissolved compounds can be very high, especially for steam stripping, which is more energy intensive.

2.3.2 Oxidation

Another option available for the treatment of dissolved organic compounds is chemical oxidation or Advanced Oxidation Processes (AOPs). This process uses costly reagents to produce hydroxyl radicals to degrade organic compounds in solution. The main advantage of this technique is the relatively simple operation, while the high-energy consumptions for hydroxyl radical generation and the toxic waste generated by the process are the main drawbacks (API, 1995). Chemical oxidation is believed to require long contact times for an efficient degradation of the target soluble compounds (Klasson et al., 2002). Another interesting alternative is by using UV light to fasten the oxidation process. Nevertheless, fouling of the UV lamps or catalyst may be a major disadvantage and not economically feasible besides they have tendency to create secondary pollution because of excessive use of chemicals.

2.3.3 Extraction

An extraction liquid is immobilized in polymer beads are used by macroporous polymer extraction (MPPE) to extract dissolved compounds from the produced water stream. The size of the process is thought to have a major influence on the removal efficiency of extraction option, as it is expected that achievable performance would be significantly limited on offshore platforms (Grini et al., 2003). Yet, a major drawback of MPPE designed is the loss of activity over time. Therefore, the MPPE media need to be replaced at intervals depending on produced water quality and pre-treatment. A replacement interval of one year has been previously reported (OSPAR, 2002).

2.3.4 Membranes

Dissolved organic compounds and heavy metals can be removed from produced water by reverse osmosis (RO) membranes. This technology is more energy intensive, since it requires higher pressure for operation and high cost in both installation and running of the process. On the other hand, nanofiltration (NF) process utilizes large pore membranes, which is less effective than a RO process for removal compounds with low molecular weight (API, 1995). A major drawback reported for both processes is membrane fouling (API, 1995; OGP, 2002; Hayes and Arthur, 2004). Other disadvantages of membrane treatment are the short lifetime of membrane material and the relatively low flux rates.

2.3.5 Adsorption

Adsorption is a unit operation in which dissolved constituents are removed from the solvent by interphase transfer to the surface of an adsorbate particle. Surfactant adsorption at solid/ liquid interface has been studied for several decades. Adsorption can be carried out with adsorbents that can be regenerated or have to be disposed after their adsorption capacity is exhausted. It is more cost-efficient to use adsorption media with regenerative properties, especially if a low cost on-site regeneration method is available.

2.3.6 Biological treatment

Removal of dissolved aromatic compounds can also be achieved in aerobic and anaerobic bioreactors. The most common technologies are fluidized bed reactors (FBR), moving bed biological reactors (MBBR), submerged fixed film reactors (FBR), moving bed biological reactors (MBBR), submerged fixed film reactors (SFFR) and fixed film activated sludge (FAS) (Voice et al., 1992; Guerin, 2002; Pruden et al., 2003). All these type of systems are based on fixed film approach, which can retain larger concentration of biomass, therefore increasing microbial degradation when operated as continuous processes.

Previous laboratory and pilot-scale studies (Petrasek et al., 1983; Melcer and Bedford, 1988) reported that the degradation of toxic organics in activated sludge reactors was lo and could not be optimized. In upflow anaerobic sludge blanket (UASB) reactors, the organic pollutants are biodegraded by suspended granular biomass. The main drawback of this technology are the requirement for temperatures higher than 28°C (Mohn and Kennedy, 1992) and high organic carbon concentrations (Woods et al., 1989).

The anaerobic fluidized bed reactor (AFBR) packed with sand has presented high rates of degradation (>90%) of anionic and non-ionic surfactants (Oliveira et al., 2010; Motteran et al., 2014). The LAS degradation was evaluated in AFBR at hydraulic retention time of 15 hour that reflects bigger size of reactors. Bear in mind that the system that we are evaluating right now is at the polishing part and in the offshore, minimal surface area is available to compensate all production facilities. Thus, degradation mechanism may not be favour in the removal of surfactants from produced water.

2.4 ADSORPTION

2.4.1 Adsorption Theory

Adsorption is the physical adherence or bonding of ions and molecules onto the surface or another molecule. Adsorption is one of the separation methods where components of fluids adsorbed onto surface of solids which we call the adsorbent (Geankoplis, 2003). When the adsorbent become saturated with the solute (desired components to be removed), the adsorbent will be regenerated by acid-wash or water-wash. Different from absorption process which occurs throughout the whole volume, adsorption only occurs throughout the whole volume, adsorption only occurs at the surface of the particles.

According to Figure 2.1, the mechanism of adsorption process can be explained in three steps which are diffusion, migration and adsorption process.

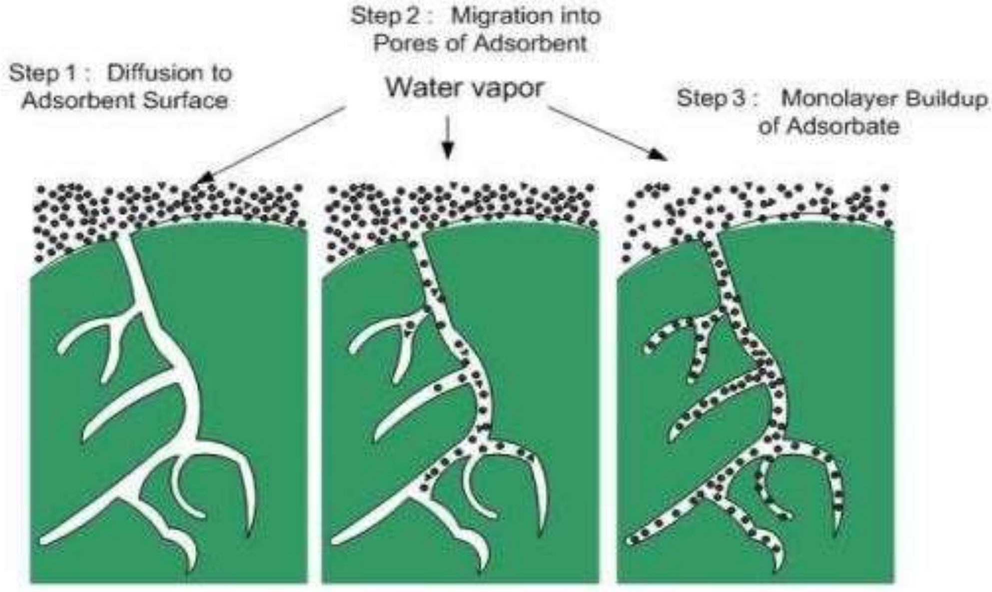


Figure 2.1 Mechanisms of adsorption process

In a general, the adsorption process is a process where an adsorbate onto the solid surface as a result from a chained kinetic stages beginning by external diffusion where it moves from the fluid core to the solid surface. This step is ruled by the eternal global material transfer coefficient. The film resistance to mass transfer is the opposite strength. Once the solute has reached the solid surface the molecules go through the pores torturous and narrow channels. This diffusivity depends on the external movement, adsorbate diffusivity and the surface adsorption diffusivity. Finally, the adsorbate molecule gets linked to the active centre in the adsorbent.

The adsorbents which are the particles in the solvent will diffuse to the surface adsorbent. Then the adsorbates will migrate into the porous structure of adsorbent. Finally, the adsorbates will be adsorbed to the surface of the adsorbent. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treatment and the success of the technique largely depends on the development of an efficient adsorbent (Wang and Peng, 2009). Activated carbon, clay minerals, biomaterials, zeolites, and some industrial solid wastes have been widely used as adsorbent for adsorption of ions and organics in wastewater treatment. The process of adsorption implies the presence of adsorbent, a solid that binds molecules by physical attractive forces, ion exchange or chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable and economical.

Adsorption capacity for specific single organic solutes of a homologous series is thought to be a direct of:

- The adsorbate properties, such as functionality, branching or geometry, polarity, hydrophobicity, dipole moment, molecular weight and size, and aqueous solubility.
- The solution conditions, such as pH, temperature, pressure, adsorbate concentration, ionic strength, and presence of background and competitive solutes.
- The nature of the adsorbent, such as surface area, pore size and distribution, surface distribution, and surface characteristics. (Hossennia et al., 2006; Belford, 1980)

2.4.2 Type of Adsorption

There are basically two type of adsorption process, physical adsorption (physisorption) and chemical adsorption (chemisorption). Physisorption is a type of adsorption in which the adsorbates is adsorbed on the surface of adsorbents only through Van der Waals force, while chemisorption happens when adsorbates adhere to the adsorbent though the formation of chemical bonds. The type of adsorption occurs basically depend on two criteria namely types of adsorbate involved and their respective reaction with adsorbent. Table 2.2 summarizes the differences between physical adsorption and chemical adsorption.

Table 2.2 Differences between physisorption and chemisorption

Physical Adsorption	**Chemical Adsorption**
Van der Waals force of attractions between adsorbent and adsorbate	Chemical bonds formed between adsorbate and adsorbent.
Low enthalpy of adsorption (20-40 kJ/mole)	High enthalpy of adsorption (200-400 kJ/mole)
Process occurs under low temperature.	Process takes place at high temperature.
Process is not specific.	Process is highly specific.
Multi-molecular layers adsorption may be formed.	Monomolecular layer adsorption is formed.
Process is reversible.	Process is irreversible.

(Sourve: Jaan, 2012; Geankoplis, 2003)

The adsorption of surfactants from the solution is affected by its physicochemical properties such as pH (Baviere et al., 1993; Dik et al., 1971; Fuerstenau and Wakamatsu (1975), temperature (Ball and Fuerstenau, 1971; Paria and Kartic, 2004), ionic strength (Baviere et al., 1993; Paria and Kartic, 2004), adsorbent dose (Sophie and Philip, 2004), and electrolyte concentration (Baviere et al., 1993, Ball and Fuerstenau, 1971; Chang et al., 2005).

2.4.3 Characteristic of sorption process

Adsorbents are materials which are porous in structure and have pore volumes of up to fifty per cents of total particle volume (Geankoplis, 2003). Adsorbents are characterized first by surface properties such as surface area and polarity. Large adsorption capacities are usually provided by large specific surface areas, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces.

The accessibility of adsorbate molecules to the adsorption surfaces determined by the sizes of the micropores, so the pore size distribution of micropores is another important property for characterizing absorptivity of adsorbents. Some adsorbents also have larger pores as a result from granulation of fine powders or fine crystals into pellets or originate in the texture of raw materials. These pores called macropores are several micrometers in size. They function as diffusion paths for adsorbate molecules from outside the granule to the micropores. Normally an adsorbent is in the form of small particles, pellets, beads or granule sized from 0.1mm to 12mm. They are often being used as packing beds in adsorption column. Table 2.3 lists the commercially used adsorbent and their respective properties.

Surface polarity corresponds to affinity with polar substances such as water. Polar adsorbents are thus called hydrophilic and alumina silicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbent of this type. On the other hands, nonpolar adsorbents are called hydrophobic. Examples of nonpolar adsorbents are carbonaceous adsorbents, polymer adsorbent and silicate. These adsorbents have more affinity for oil than water (Suzuki, 1990).

It has been shown that the nature of the adsorption isotherm depends to a large extent on the type of surfactant used, the morphological and mineralogical characteristics of the rock, and the type of electrolytes present in solution (Singh and Pandey, 1982). The adsorption of surfactants can be affected by the surface charge on the rock surface and fluid interfaces (Stumm and Morgan, 1970; Harkot and Janczuk, 2009; Wei et al., 2012). Positively charged cationic surfactant is attracted to negatively charged surfaces, while negatively charged anionic surfactant is attracted to positively charged surfaces.

Table 2.3 commercially used adsorbent and properties and applications (Geankoplis, 2003)

Adsorbent	**Application and Properties**
Silica Gel	• Drying of gases, refrigerants, organic solvents, transformer oils. • Desiccant in packings and double glazing. • Dew point control of natural gas. • Surface area of 600-800 m^2/g • Average pore diameter of 20-50Å
Activated Alumina	• Drying of gases, organic solvent, transformer oils • Removal of HCl from hydrogen • Removal of fluorine in alkylation process • Surface area of 200-500 m^2/g • Average pore sizes of 20-140Å
Activated Carbons	• Microcrystalline structure • Nitrogen from air • Water purification • Surface area of 300-1200 m^2/g • Average pore diameter of 10-60Å
Zeolites	• Drying of gases • Sweetening sour gases and liquids • Separation of ammonia and hydrogen
Polymers & Resins	• Removal of colors from syrup • Removal of organics from hydrogen peroxide • Separation of atty acids from water and toluene.
Clay	• Treatment of edible oils • Removal of organic pigments. • Refining of mineral oil • Removal of polychlorinated biphenyl (PCBs).

2.4.4 Equilibrium Relation for Adsorption

There are several isotherm models for predicting the adsorbent concentration and adsorbate concentrations in adsorption process. Both of the parameters can be related using three isotherms as plotted in Figure 2.2.

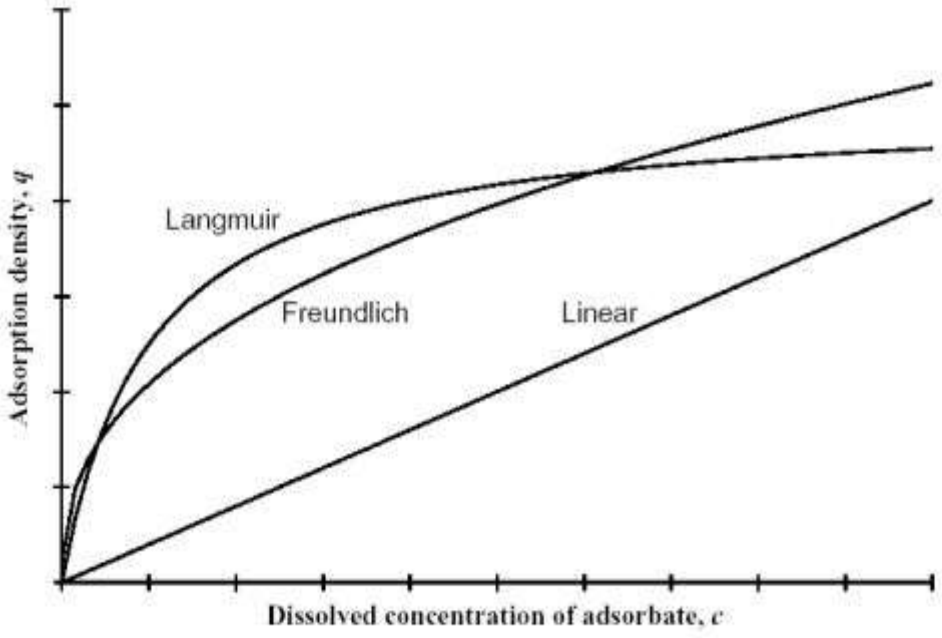


Figure 2.2 Type of adsorption isotherm

2.4.4.1 Linear Isotherm

From Figure 2.2 shows the relationship on linear isotherm. It is also expressed as in Equation 2.1.

$$q = Kc \qquad (2.1)$$

Where K is the constant expressed in m^3/kg adsorbent. Although the linear isotherm is not common in the entire adsorption process, but it can be applied for dilute region in adsorption process to determine data for many systems.

2.4.4.2 Freundlich Isotherm

Freundlich isotherm is mostly applicable to physical adsorption and useful for liquid system. Equation 2.2 shows the correlation of q and c in an equation form:

$$q = Kc^n \qquad (2.2)$$

The value of K and n can be determined graphically, providing a series of q and c value determined through experiment.

$$\log q = \log K + n \log c \qquad (2.3)$$

By plotting the graph of log q against log c, the slope of the graph will determine the value of n while y-intercept of the graph will be the logarithm value of K according to the Equation 2.3.

2.4.4.3 Langmuir Isotherm

The Langmuir isotherm is the strongly favourable type of isotherm for an adsorption process. Equation 2.3 shows the relationship between q and c in Langmuir isotherm.

$$q = \frac{q_0 + c}{K + c} \qquad (2.4)$$

Where q is expressed as kg of adsorbate/ kg solid while K is kg/m. The equation is applied with assumption of monolayer adsorption, actives sites on adsorbent are fixed, adsorption reached equilibrium and adsorption process is reversible. The value of q, and K can be determined by plotting graph of 1/q against 1/c according to Equation 2.5.

$$\frac{1}{q} = \frac{K + c}{q_o c} = \frac{K}{q_o}\left(\frac{1}{c}\right) + \frac{1}{q_o} \qquad (2.5)$$

Where the slope is K/q_o and intercept is $1/q_0$.

2.4.5 Adsorption Isotherm

The adsorption of a substance from a liquid phase to the surface of a solid phase in a system leads to a thermodynamically defined distribution of that substance between the two phases when the system reaches equilibrium that is when the rate of adsorption of solute onto the surface of the adsorbent is the same as the rate of its desorption from the surface of the adsorbent. Therefore, there is no further adsorption occurs.

Studies of adsorption kinetics and equilibrium of different surfactants are very practical tests in laboratory for study of surfactant adsorption onto rock surface. These phenomena depend on the nature of the surfactants and also the solid-liquid interface (Paria et al., 2005; Zhang and Somasundaran, 2006; Ayrancia and Duman, 2007). Recently Ahmadi et al. (2012) have studied the adsorption behavior of the Glycrihiza Glabra, a novel nonionic surfactant, onto carbonate rock and Ahmadi and Shadizadeh have investigated the effect of nanosilica on adsorption behavior of Zyziphus Spina Christi onto rock surface. Ahmadi et al., (2012) concluded that adsorption isotherm follows the Langmuir model. On the other hand when nanosilica is used the Linear, Langmuir, and Temkin equilibrium adsorption models were not suitable for predicting the surfactant adsorption, but the Freundlich equilibrium adsorption was in good agreement between the experimental data.

The adsorption isotherm is the plot of surfactant concentration against the adsorption density (mg/g). In Figure 2.3 shows the adsorption isotherm on Berea sandstone at room temperature. The composition of core samples was determined and it shows that Silica and Alumina have the highest fractions among others and, therefore, the surface chemistry of Berea core depends in these two species. A typical isotherm usually shows our regions (Paria and Khilar, 2004).

Region 1 which occurs at lower surfactant concentration and monomers is adsorbed onto substrate due to electrostatic interaction between head group charge and net charge present onto the surface of the adsorbent. In this region, adsorption obeys Henry's law and increase linearly with surfactant concentration until it reaches Region 2. In region 2 there is a sharp increase in adsorption density due to the formation of surfaces aggregates, called colloids (surface colloids) which include hemi-micelles, admicelles, etc. These surface aggregates are formed due to lateral interactions between hydrocarbon chains and surface monomers. Thus, the additional driving forces originating from the lateral interaction of monomers, the adsorption density increases sharply.

In Region3, the adsorption density increases with lower gradient, because in this region the solid surface is electrically neutralized by the adsorbed surfactant monomers and adsorption takes place due to lateral interactions only. In region 4, the surfactant reaches CMC; therefore, any further increase in surfactant concentration contributes to the micellization in solution and hence adsorption is constant. In this region, surfactant molecules adsorb onto the surface with reverse orientation which results in decreasing hydrophobicity of the particles (Paria and Khilar, 2004; Somasudaran and Zhang, 2006).

In the beginning of the adsorption isotherm, region 1 is identified by the oppositely charge interaction resulting in a higher adsorption rate. It is less dependent on surfactant concentration. A steady and higher adsorption occurs in the region 2. The region 3 is difficult to identify because of its occurrence over a narrow range. The region 4 specifies the upper limit of adsorption which shows that there is no further increase in adsorption density beyond 0.96 mg/g. This plateau is region 4.

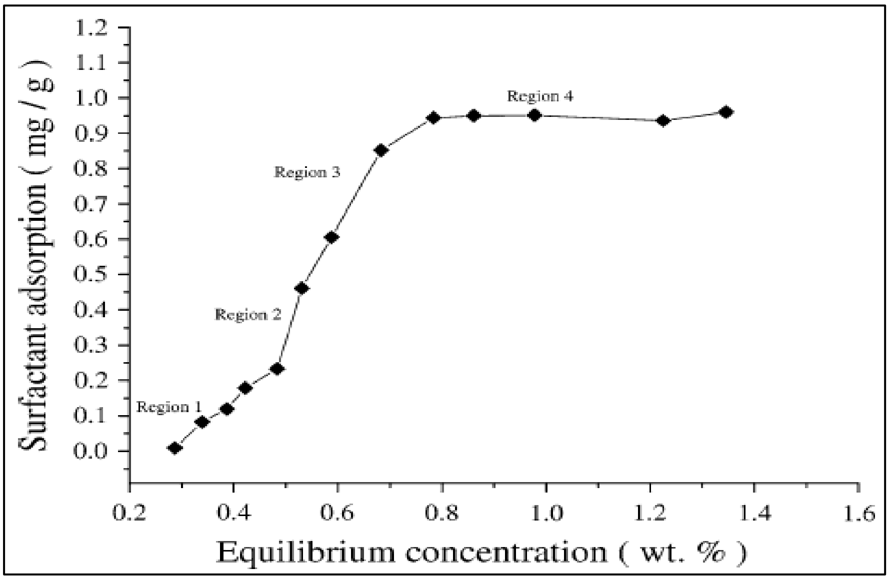


Figure 2.3 Adsorption Isotherm on Berea sandstone

2.5 SURFACTANTS ADSORPTION

Adsorption techniques are rapidly gaining prominence as a treatment process that provides high quality effluents that are low in concentration of dissolved organics (G.M. Walker and L.R. Weatherly, 1998). Adsorption processes with clay could constitute a simple, selective, and economical alternative to conventional physical-chemical treatments. The optimization of wastewater purification process requires a process of low cost raw materials, with high pollutant removal efficiency. Each year there are numerous academic publications on all aspects of adsorption. Adsorptions studies using low-cost adsorbents were reviewed (Gadd, 1993; Volesky and Holan, 1995; Chng et al., 1997; Guibal 1998; Annadurai et al., 2002; Sheng et al., 2004; Aksu, 2005; Ho, 2006; Vijayaraghavan and Yun 2008; Wang and Chen, 2009; Chojnacka, 2010 Hossain et al., 2012).

Adsorption is a widely accepted for the removal of soluble hydrocarbons and organics of the produced water. Adsorption column is filled with porous solid material known as adsorbent. Present hydrocarbon and organics in the produced water will adhere to the surface of adsorbent and eventually remained in the pore structure of the adsorbent. Low or no hydrocarbon and organics are expected in the effluent of produced water. High surface area with high porous adsorbent is desire to boost adsorption performance. Some of the many adsorbents used for produced water treatment, are activated carbon, nutshell media, and modified organoclay. On the other hand, the major concern of adsorption operation is the requirement retention time which limits throughput capacity.

2.5.1 Mineralogical of clays

Adsorption and wettability changes are determined mainly by the chemical structure and mix of surfactants, surface properties of the rock, composition of the oil ad reservoir fluids, nature of the polymers added and solution conditions such as salinity, pH and temperature, as stated by Somasundaran and Zhang (2004). The mineralogical composition of clay plays and important role in determining interactions between the clay minerals and externally added reagent, such as surfactant and their efforts on solid-liquid interfacial properties such as surface charge and wettability. Clay minerals have been widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high specific surface area, and consequential strong asorption capacity (Bailey et al., 1999; Sen Gupta and Bhatacharyya, 2006; Du and Hayashi, 2006). Several authors, including Rodriguez-Cruz et al (2005), Sanchez-Martin et al. (2008) and Zhu et al. (2003) attempted to investigate the effect of mineralogical composition of the clay fraction on surfactant adsorption. However the surfactant adsorption cannot be predicted based upon adsorbent attributes (Muherei, 2009).

It has been shown that the nature of adsorption isotherm depends to a large extent on the type of surfactant that is used, the morphological and mineralogical characteristics of the rock, the type of electrolytes present in the solution, and the presence of co-surfactants and alcohols. The adsorption of surfactants can be influenced by the charge on the rock surface and fluid interfaces (Liu et al., 2004). The adsorption of cationic and non-ionic surfactants was higher by montmorillonite and illite, and the adsorption of anionic surfactant was found to be higher by kaolinite and sepiolite (Sanchez-Martin et al., 2008).

On the other hand according to Liu et al. (2004), the adsorption of surfactants can be influenced by the charge on the rock surface and fluid interfaces. The clay is actually charged by nature. Surfactant adsorption solely depends on the charged of both surfactants and the clay for the normal adsorption to take place. Opposite charged attract each other for adsorption, on the other hand same charged prevent surfactants from adsorb to the adsorbent. The anionic surfactants experience a repulsion forces when it was introduced to a solid containing negative surface charge. Anionic surfactant adsorption decreases onto a negatively charge surface. In this project, we were dealing with clay that sent from one of the oil field company. It may be seem that the adsorption of surfactants by the clay minerals depends on both the nature 0f the surfactants and the structure of the clay minerals.

2.5.2 Bentonite type of Clay

Clay such as bentonite has been largely studied since they show catalytic or adsorptive properties. As far as adsorptive properties are concerned, bentonite has been used to remove a number of chemical species: amines (Breen 1991); organic pigments (Gonzalez-Pradas et al., 1991); cations, phenols and ketones (Stockmeyer and Kruse, 1991); phosphates (Gonzales-Pradas et al., 1993); chlorophyll (Gonzalez-Pradas et al., 1994); non-ionic contaminants (Smith and Jaffe,1994). Bentonite is a kind of expandable clay composed of primarily of montmorillonite with permanent negative charges on its surface resulting from the isomorphous substitution on central atoms in the octahedral/tetrahedral by cations of lower valence. Such structures enables bentonite to be intercalated by organic and inorganic cations and the resulting materials has high specific area sassocited with their small particles size.

CrudeSorb is a proprietary sorbent of CETCO Oilfield Services Company. It is an organolcay produce from bentonite modified with quaternary amine. The clay mineral montmorillonite, a chemically altered to volcanic ash, is the major constituents of bentonite. Montmorillonite has an ion-exchange capacity of 70-90 meq/g. In this way, swelling in water is minimized while swelling in organic fluids is enhanced (Vinka et al., 2007). In the case of CrudeSorb the quaternanry amine is the dimethyl ammonium chloride (12-18 carbons). According to the manufacturers, the modified bentonite is thermally stable up to 220°C.

Some organically modified clay is able to remove anions from the liquid phase. Two mechanisms have been indicated as explanation for this behaviour:

- The organolcays have a certain anion exchange capacity caused by the exchange of the chlorine end of the amine with an anion present in the liquid phase. The long-chain quaternary amines have much lower anion exchange capacity than the short-chains (C12). Since commercial quaternary amine surfactants contain a mixture of C12-C22 amines, it is believed that this anion exchange ability is due to the short-chain impurities (Alther, 1995).
- Usually not all the quaternanry amine chains are attracted to the clay platelets by ion exchange. Some of them tie to the attached chains by a form of tail-tail interaction. The result of this tail-tail interaction is that a positive charge extends into the water, causing negatively charged anions to be removed by ionic attractions (Alther, 2002).

2.6 FACTORS AFFECTING ADSORPTION

There are a number of factors which affect the adsorption process other than the qualities of adsorbent itself which includes dosage of adsorbents, pH, temperature, salinity, contact time, initial concentration of adsorbates, ionic strength, divalent ions and in addition the type, concentration and composition of the surfactants involved (Grigg and ai, 2004; Al-Zboon, Al-Harahsheh, & Hani, 2011; Dang et al., 2011; Lv et al., 2011).

2.6.1 Effect of pH

The pH of solution is one of the most important parameter that should be considered prior to adsorption. Hu et al., (1989) and Ornek et al., (2007) reported that pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbent. Moreover a change in pH also results in change in charge profile of adsorbate species, which consequently influences the interactions of adsorbate and adsorbent.

The charge on clays depends on various factors such as the nature of the colloids, pH, ionic strength and other solution properties where, pH is the most prominent factor (Paria and Khilar, 2004). The pH value at which the net charge on a surfactant zero is termed as point of zero charge (PZC) (Appel et al., 2003). The adsorption of anionic surfactants is higher on positively charged surfaces (pH below PZC)) than on negatively charged surfaces while the cationic surfactants adsorb more on negatively charge surfaces.

The use of alkali has proven to reduce the adsorption of anionic surfactants (Hirasaki et al., 2008). Alkali increases the pH and decreases the number of positive sites available for the adsorption on the surface. Conventional alkali such as sodium carbonate has been used to reach a low interfacial tension (IFT) by generating in situ surfactants by reacting with acidic compound present in the crude oil. It can also act as a sacrificial agent resulting in the decreased adsorption because it consumed the multivalent cations which would otherwise precipitate with surfactants and cause plugging in rock pores hereby reducing permeability (Grigg et al., 2004; Hirasaki et al., 2008).

2.6.2 Effect of Adsorbent Dose

The rate of adsorption would increase significantly with the increase of dosage of adsorbents as more adsorbents provide more binding site for adsorbates. Nevertheless, the consumption of adsorbates must feasible to achieve balance between removal efficiency and cost optimization. The usage of clay in surfactants removal from produced water should be evaluated thoroughly to find appropriate amount of clay needed to remove desired surfactants concentration. Researcher observed a direct relationship between the adsorption of the anionic surfactant and the amount of clay minerals in the adsorbents as the amount of surfactant that was adsorbed by the adsorbents increased when the percentage of clay minerals in adsorbents increased.

2.6.3 Effect of Temperature

The adsorption of surfactant is found to be slightly decreased at higher temperature due to the onset of higher translational kinetic energy. The force of interaction between the surfactant and clay becomes weaker at high temperature. The relatively high kinetic energy and subsequent high entropy are factors behind the low adsorption of surfactants at high temperature (Paria and Khilar, 2004). The frequent perturbations of the surfactant monolayers caused by the high kinetic energy resist the formations of any organized layer of surfactants molecules and subsequently lead to the low adsorption at high temperature.

2.6.4 Effect of Salinity

Influence of salinity on adsorption process can be explained through the presence of sodium chloride (NaCl). Sodium chloride decreases the functional group electrostatic repulsion in the adsorbed layer. Electrical double layer can be compressed strongly by increasing the salt concentration; as a result, adsorption of anionic surfactant will increase with an increase of salt concentration (Dang et al., 2011). Bai and Grigg (2005) also reported the same trend of surfactant adsorption by increasing salt concentration.

CHAPTER 3

METHODOLOGY

3.1 OVERVIEW

This research works was divided into three main stages mainly characterization of clay, preparation of produced water with surfactants, and adsorption experiment using titration test. Figure 3.1 shows the summary of research methodology for this research project.

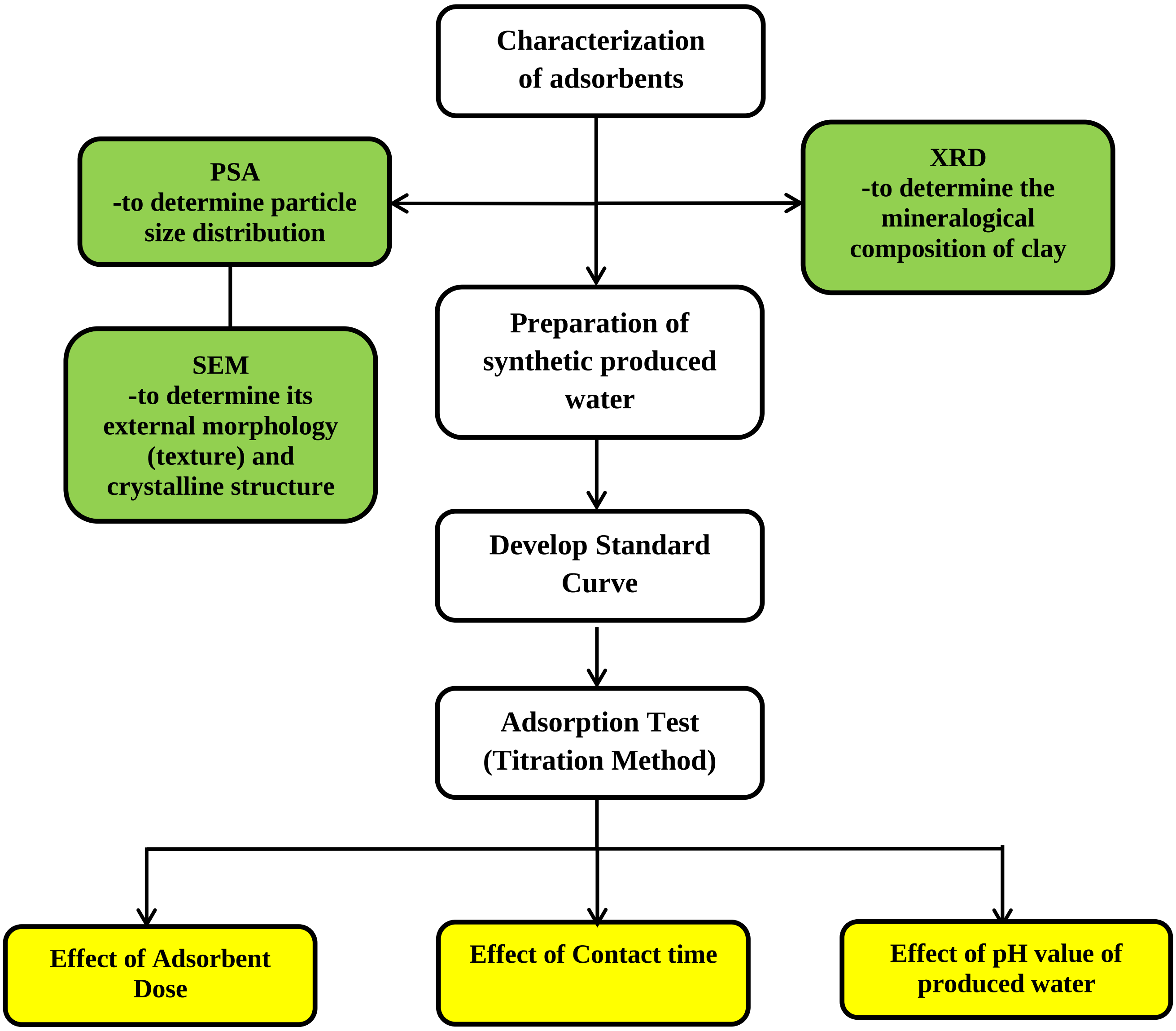


Figure 3.1 Summary of research methodology

3.2 MATERIALS

Anionic surfactant of 16-18 carbons chain with branching (five carbons chain) in the middle and a sulfonate head group was synthesized in our laboratory. Standard 0.004 M solution of Hyamine was purchased from Fisher Scientific. Clay was obtained by CETCO Oilfield Services Company to be revised.

3.3 ANALYTICAL METHODS

Surfactant concentration was measured by titration method. A specific amount of surfactant sample was titrated against 0.004 M Hyamine solution using titration. The volume of Hyamine solution used for each titration was recorded to measure surfactant concentration. All solutions were prepared using deionized water.

3.4 CHARACTERIZATION OF ADSORBENTS

Commercialised adsorbents were obtained from CETCO Company. Thus first characterization of clay is required especially XRD is to determine the mineralogical compositions of the raw material components as well as qualitative and quantitative phase analysis of multiphase mixtures.

3.5 PREPARATION OF SYNTHETIC PRODUCED WATER

In this research, synthetic produced water is going to be used for the adsorption of surfactants study. This would be appropriate to replicate the actual properties of produced water prior to the research. Table 3.1 shows the chemical composition of synthetic produced water. The produced water is then mixes with certain amounts of surfactants to imitate the expected produced water effluent from EOR field. Initial surfactants concentration is fixed 500 ppm for the adsorption test.

Table 3.1 Chemical compositions of synthetic produced water

Mineral	**Content**						**Chemicals**
	Ions		**Chemicals without Water**				**Added to**
	[mg/L]	**[mol/L]**	**[mol/L]**	**[grams/L]**	**Name**	**[grams/L]**	**Make Solution**
Ca	46.7	0.0012	0.0012	0.1293	CaCl2	**0.1713**	CaCl2 (H2O)2
Mg	63.45	0.0026	0.0026	0.2480	MgCl2	**0.5299**	MgCl2 (H2O)6
Na	4719.36	0.2053	0.1445	8.4540	NaCl	**8.4526**	NaCl
Fe	0.84	0.0000	0.0000	0.0024	FeCl3	**0.0024**	FeCl3
Ba	1	0.0000	0.0000	0.0015	BaCl2	**0.0018**	BaCl2(H2O)2
Sr	0.36	0.0000	0.0000	0.0007	SrCl2	**0.0011**	SrCl2(H2O)6
K	212.47	0.0054	0.0054	0.4048	KCl	**0.4048**	KCl

3.6 ADSORPTION EXPERIMENT

The adsorption process of surfactants is carried out in batch experiments. Several variables including pH, clay ratio, and contact time is studies in this work. Various ways of determining the surfactant concentration in the solution after separation include: ion-selective electrodes, UV/Vis spectroscopy, refractive index, chromatography, surface tension or titration. For this project the latter method has been applied. This method, require separation of particles from the solution when the liquid is transferred into titration, provided that the particles are completely wetted by the liquid. The amount of surfactant that was adsorbed was quantified by subtracting the concentration of surfactants after adsorption from the initial concentration. The experiments were conducted repetitively to reduce the error and because the results are solely based on the preparation of the sample as well as the weight of the surfactant that have been put through the titration test. The experimental result is fitted to the Langmuir model and to Freundlich model.

3.6.1 Standards Operating Procedure (SOP) for Titration Test

i) Developing Standard Curve

1. 5ml of 500 ppm of surfactant SS1003 was pipetted in a conical flask.
2. 15 ml of acid indicator was added further in the conical flask.
3. 10 ml of chloroform of choloroform was measured and added in the same test tube.
4. The solution was then shake (pink color appeared).
5. Solution was then titrated with 0.004 mol/L of Hyamine.
6. Solution was then shake vigorously upon additional volume of Hyamine and color changes is observed.
7. The volume of Hyamine use was recorded for color to change from pink to colourless.

   Note: Repeat the experiment at 100 ppm and 300 ppm of surfactant.
8. Plot graph volume of Hyamine versus surfactant concentration (wt%).

The adsorption experiments were conducted using CrudeSorb and Kaolin as adsorbent to remove SS1003 surfactants from produced water. pH and contact time will be the main parameters to be investigated in this research study. The adsorption experiment design is summarized in Table 3.2 as shown below.

Table 3.2 Experimental design of adsorption test

Investigated Parameter	**Initial Surfactant Concentration (wt%)**	**Temperature (^{0}C)**	**pH**	**Contact time (min)**	**Adsorbent Dose (g)**
pH	0.05	25	2,4,7,10,12	5	1.5
Contact Time (minutes)	0.05	25	7.2	5,10,15,30, 45,60	1.5
Adsorbent Dose (g)	0.05	25	7.2	5	0.5, 1.0, 1.5, 4.5, 7.0

3.6.2 Effect of pH

As the pH of solution has a significant effect on adsorption activities of adsorbents, the effect of pH on surfactant removal percentage is the present study as well.

1. 10 of 500 ppm surfactant solution was measured and put in test tube.
2. 0.1 M of Sodium Hydroxide (NaOH) or 0.1 M of hydrochloric acid (HCl) were added until desired pH was obtained, and 500 ppm of surfactants solution was added until 30ml.
3. 1.5g of CrudeSorb was weighed and added in the test tube.
4. Test tube was then put in shaker at 100 ppm for 5 minutes.
5. Then the test tube was put in centrifuge at 3000 ppm for 3 minutes.
6. 5ml of the surfactant solution was pipetted in a conical flask.
7. 15 ml of acid indicator was added further in the conical flask.
8. 10 ml of chloroform of chloroform was measured and added in the same test tube.
9. The solution was then shake (pink color appeared).
10. Solution was then titrated with 0.004 mol/L of Hyamine. Solution was then shake vigorously upon additional volume of Hyamine and color changes is observed.

11. The volume of Hyamine use was recorded for color to change from pink to colourless.

    Note: the experiment is repeated for adsorption on CrudeSorb and kaolin at pH 2, 4, 10, and 12.

3.6.3 Effect of Contact Time

Different adsorbent adsorb at different rate, thus more effective adsorbent is able to adsorb more adsorbates and achieve equilibrium at a shorter contact time.

1. 30ml of 500 ppm surfactant solution was measured and put in test tube.
2. 1.5g of CrudeSorb was weighed and added in the test tube.
3. Test tube was then put in shaker at 100 ppm for 5 minutes.
4. Then the test tube was put in centrifuge at 3000 ppm for 3 minutes.
5. 5ml of the surfactant solution was pipetted in a conical flask.
6. 15 ml of acid indicator was added further in the conical flask.
7. 10 ml of chloroform of chloroform was measured and added in the same test tube.
8. The solution was then shake (pink color appeared).
9. Solution was then titrated with 0.004 mol/L of Hyamine. Solution was then shake vigorously upon additional volume of Hyamine and color changes is observed.
10. The volume of Hyamine use was recorded for color to change from pink to colourless.

    Note: The experiment is repeated for adsorption on CrudeSorb and kaolin at 10, 15, 30, 45, and 60 minutes.

3.6.4 Effect of Adsorbent Dose

The adsorption test is study at different adsorbent dosage.

1. 30ml of 500 ppm surfactant solution was measured and put in test tube.
2. 1.5g of CrudeSorb was weighed and added in the test tube.
3. Test tube was then put in shaker at 100 ppm for 5 minutes.
4. Then the test tube was put in centrifuge at 3000 ppm for 3 minutes.
5. 5ml of the surfactant solution was pipetted in a conical flask.
6. 15 ml of acid indicator was added further in the conical flask.
7. 10 ml of chloroform of chloroform was measured and added in the same test tube.
8. The solution was then shake (pink color appeared).
9. Solution was then titrated with 0.004 mol/L of Hyamine. Solution was then shake vigorously upon additional volume of Hyamine and color changes is observed.
10. The volume of Hyamine use was recorded for color to change from pink to colourless.

    Note: The experiment is repeated for adsorption on Kaolin and CrudeSorb at 0.5, 1.0, 4.5, and 7.0g.

3.6.5 Kinetic and Isotherm Study

Experimental data obtained from the contact time experiment will be used to determine which kinetic model and isotherm that the adsorption activities of CrudeSorb and kaolin are fitted to. The calculation process was aided with Microsoft Office Excel Spreadsheet.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 CHARACTERIZATION OF ADSORBENTS

CrudeSorb and kaolin samples were analysed for their mineral composition using XRD technique and tabulated in Table 4.1 and Table 4.2.

Table 4.1 Calculated whole rock composition of CrudeSorb and kaolin samples

Sample	Quartz (%wt)	Plagioclase (%wt)	K-Feldspar (%wt)	Calcite (%wt)	Dolomite (%wt)	Siderite (%wt)	Pyrite (%wt)	Total Clay (%wt)
Crude Sorb	9.3	23.3	16.1	4.0	0.4	2.5	3.5	40.9
kaolin	1.3	3.0	2.6	0.0	0.0	4.8	1.3	87.0

Table 4.2 Clay Mineralogy of CrudeSorb and kaolin samples

Sample	Kaolinite (%wt)	Chlorite (%wt)	Illite (%wt)	Mixed Layer (%wt)	Smectite (%wt)
CrudeSorb	12.3	8.6	41.3	33.2	4.6
kaolin	61.4	38.6	0.0	0.0	0.0

Result from XRD shows that CrudeSorb is made up of 59.1% rock and 40.9% clay. From this data we can conclude adsorption of surfactants may not only occur on the clay alone but on the rock as well, as more than half of the CrudeSorb composition is made up of rock and 13% on kaolin. The main peak was presented at 23wt% Plagioclase, following by K-Feldspar at 16.1 wt% and 9.3wt% Quartz and trivial rock composition yet significant like Calcite, Dolomite, Siderite, and Pyrite were identified on CrudeSorb. On the other hand, kaolin is made up of only 13% of rock composition including Quartz, Plagioclase, K-Feldspar, Siderite and Pyrite. Based on XRD's results from Table 4.2, it shows total clay in kaolin is mainly made up of Kaolinite at 61.4 wt% and remaining is Chlorite. On the contrary, CrudeSorb is made up of various clays including Illite, mixed layer, kaolinite, Chlorite and Semectite.

Besides, CrudeSorb and kaolin were sent to undergo Particle Size Analysis (PSA) to determine its particle size distribution. From the results it shows that CrudeSorb has 623.015 µm diameter, while kaolin has 4.290 µm. From PSA, the result portray kaolin has smaller diameter compare to CrudeSorb. Micrographies by SEM showed by Figure 4.1 the sample is essentially constituted by agglomeration of structure on kaolin. Whereas in Figure 4.2 shows the CrudeSorb's SEM image of crystalline structure.

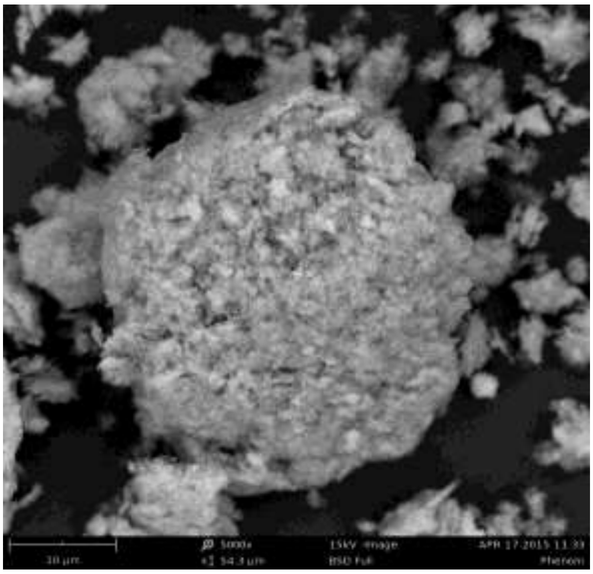


Figure 4.1 Image of kaolin clay by SEM at 5000 magnification

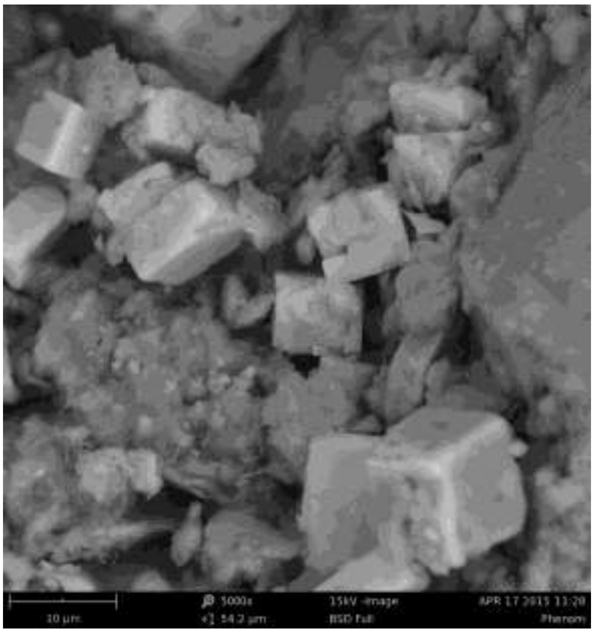


Figure 4.2 Image of CrudeSorb by SEM at 5000 magnification

4.2 STANDARD CURVE

Standard Curve was developed initially as reference for titration test later on. The consumption of 0.004 M of Hyamine solution was monitored when titrate with 100 ppm, 300 ppm, and 500 ppm of surfactant SS 1003 (anionic). Table 4.3 shows the result of titration test. From the results it shows that volume of Hyamine solution increases when concentration of surfactants increases.

Table 4.3 Concentration of surfactants vs. volume of Hyamine

Concentration of Surfactants (wt%)	**Volume of Hyamine (ml)**		
	First Run	**Second Run**	**Average**
0.05	0.58	0.59	0.585
0.03	0.32	0.32	0.32
0.01	0.1	0.1	0.1

Standard Curve can be developed once all the results have been obtained, by plotting concentration of surfactants versus volume of Hyamine needed as shown in Figure 4.3. This standard curve will be the author reference in the whole titration test later on. Based on this standard curve, the author can calculate the final surfactant concentration by dividing the volume of Hyamine used during the adsorption test by 11.386.

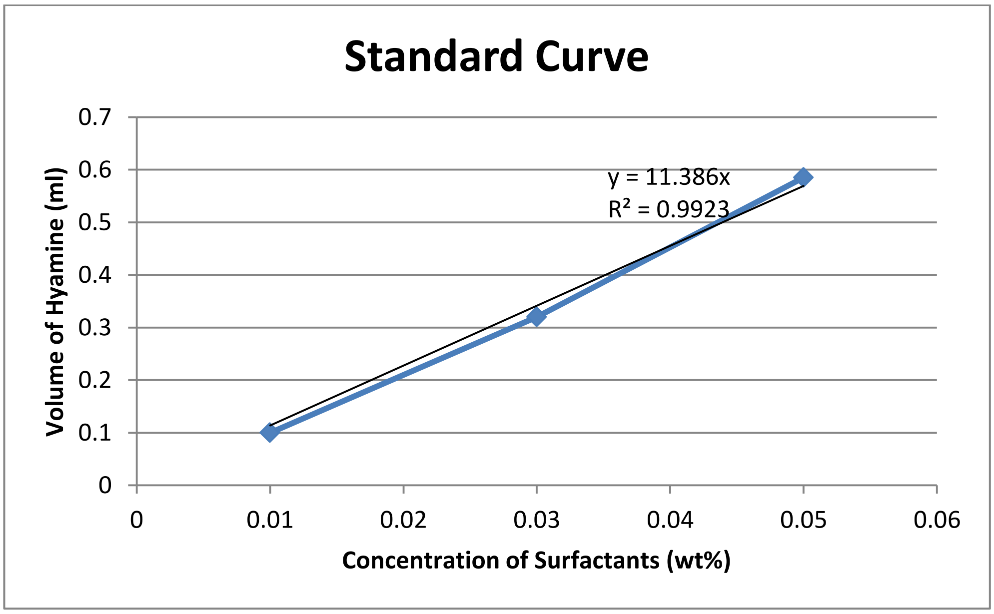


Figure 4.3 Standard Curve

4.3 ADSORPTION TEST RESULT

Initial adsorption test had been carried out to determine the adsorption ability of CrudeSorb and kaolin towards SS 1003 type surfactant. The effect of adsorbent dosage, contact time and pH has been tested to observe the surfactants removal efficiency by both adsorbent.

4.3.1 Effect of adsorbent dose on the extent of surfactants adsorption

Adsorption of the surfactant on CrudeSorb and kaolin depends on its dose as shown in Figure 4.2. 500 ppm of initial surfactant concentration has been used for adsorption study. From Figure 4.4 it has been found that adsorption increases with adsorbent dose and then remains constant after certain dose of surfactant. As the amount of adsorbent increases the adsorption sites also increase and the adsorption process takes place easily with increase in order. Kaolin performed better on surfactant adsorption as compared to CrudeSorb for the first 3.0g of adsorbent dose. Further increased in adsorbent dose caused the extent of surfactants removal to be maximum for CrudeSorb, while kaolin still struggling to reach 93%.

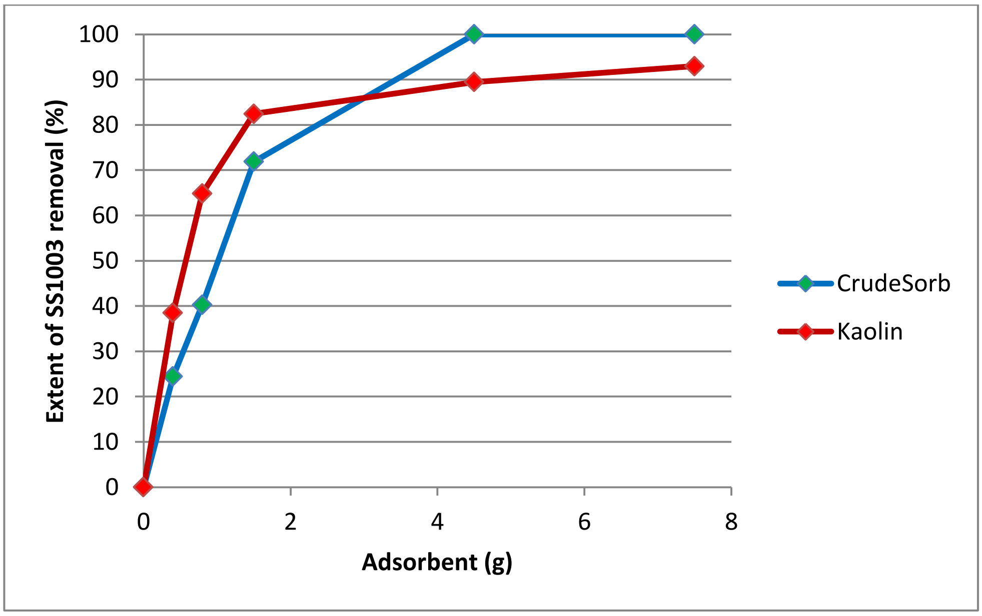


Figure 4.4 Effect of the amount of CrudeSorb and kaolin on the surfactants adsorption

4.3.2 Effect of pH on the extent of surfactants adsorption

The pH of the aqueous solution is one of the important controlling parameters in the adsorption of surfactant on CrudeSorb and Kaolin. Figure 4.5 shows the effect of pH on the extent of adsorption of SS 1003 surfactants (anionic) on both tested adsorbent.

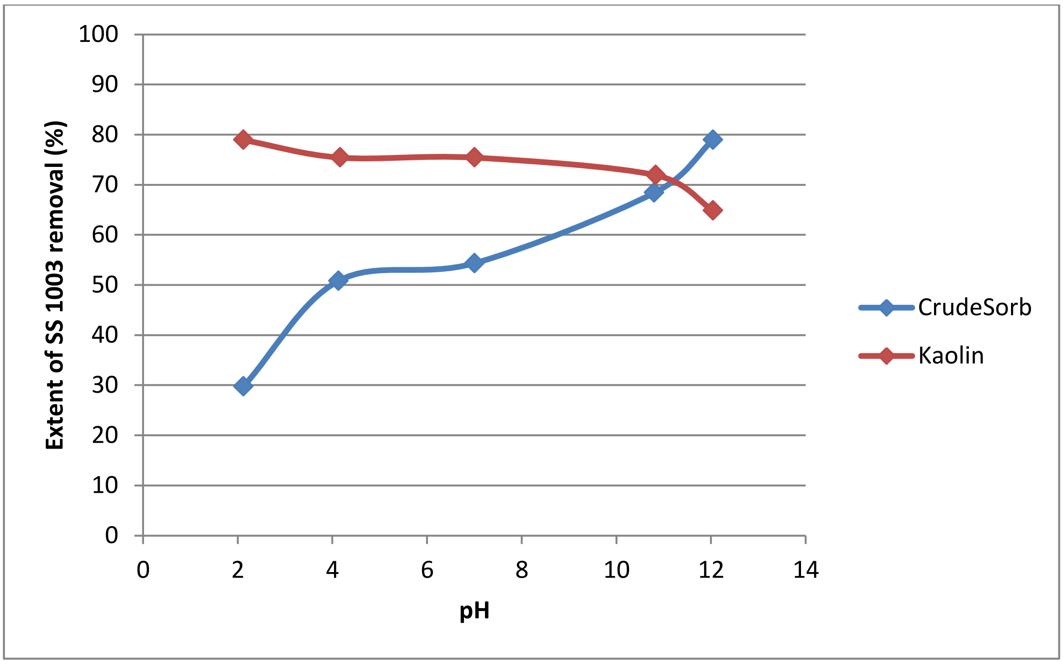


Figure 4.5 Effect of pH on the surfactants adsorption

Kaolin exhibited high adsorption efficiency at low pH for surfactant SS 1003. As pH increases the adsorption decreases for anionic surfactant on kaolin. The adsorption capacity at alkaline solution is lower due to the decrease of positively charged sites on kaolin and the competition between OH^- and surfactant for the adsorption site. A number of research works has been reported regarding the effect of pH of solution on adsorption of surfactants on rock surfaces (Somasundaran et al., 1979; Somasundaran 1985; Baviere et al., 1993; Somasundaran and Zhang, 2006; Dang et al., 2011). The optimum pH for surfactants removal on kaolin was recorded at pH 2. At low pH, SS 1003 adsorption capacity of kaolin is high due to acidic nature of the solution which makes the kaolin surface more positive and that is why the interaction of kaolin surface with SS 1003 (anionic surfactant) is high and hence adsorption capacity is high. On the other hand there seems reversing in pattern of surfactant adsorption onto CrudeSorb. At low pH value, the adsorption capacity of surfactant concentration is lower, but as pH increased the surfactants adsorption increased. The optimum pH for surfactants removal on CrudeSorb is recorded at pH 12. Overall surfactant removal from produced water reaches 80% by both CrudeSorb and kaolin adsorbents from 500 ppm of surfactants at their respective optimum pH conditions.

4.3.3 Effect of contact time on adsorption of surfactants

As a prerequisite step for adsorption isotherm experiments, an adsorption equilibrium time was determined by monitoring the amount of adsorption as a function of time. Figure 4.4 shows the adsorption equilibrium profiles of the two adsorbents as functions of time. The adsorption equilibrium for all surfactants was completely attained upon reaching 60 minutes. When the adsorption rate of surfactant was defined the amount of adsorption per unit time (mg/g min), it shows CrudeSorb exhibited high surfactants adsorption compare to kaolin. From Figure 4.6, the author observed at 15 minutes of contact time, the amount of surfactants adsorbed approached the maximum capacity of surfactants loading for 1.5g of adsorbents. Longer contact time between produced water with adsorbents encouraged the surfactants removal. After a certain period of time there is no further adsorption because of gathering of huge adsorption sites.

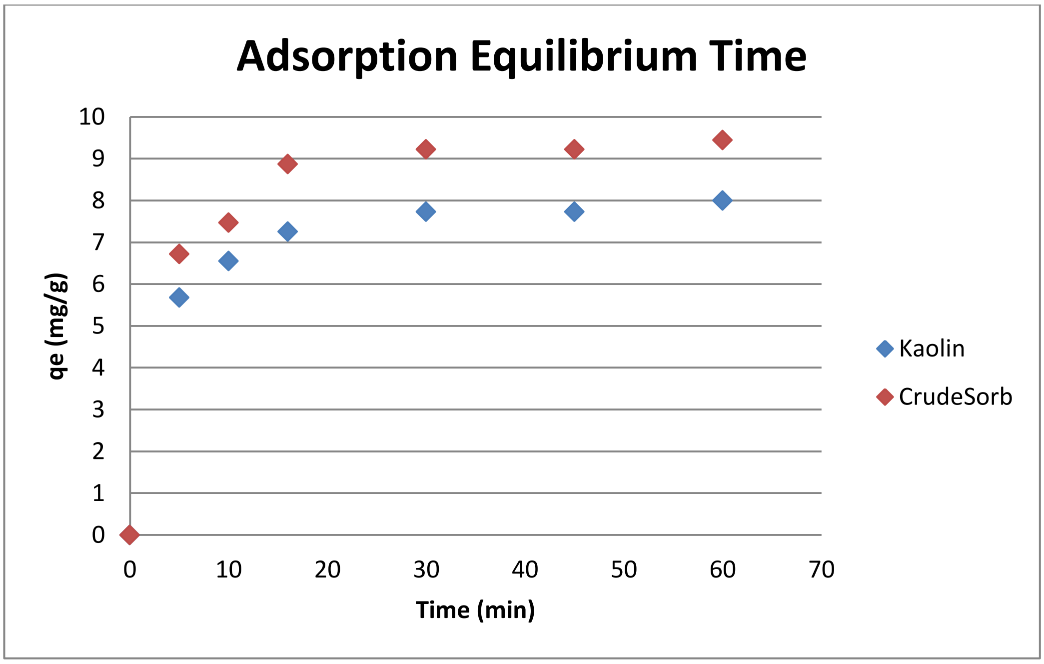


Figure 4.6 Adsorption Equilibrium profile as function of time

4.4 ADSORPTION BEHAVIOURS

The Langmuir adsorption isotherm and the Freundlich adsorption isotherm are two common isotherms used to describe the equilibrium adsorption isotherm. These two general models are known to describe adsorption behaviours from a liquid solution onto solid adsorbent properly.

4.4.1 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is based on the basic assumption that adsorption takes place at specific homogeneous sites and no adsorption can take place at the site which a solute already occupies. This equation relates the amount of solid adsorbate adsorbed, q_m, to the equilibrium liquid concentration at a fixed temperature.

The fundamental feature for the model is that rate of adsorption is proportional to concentration gradient of solute and amount of bare surface (Parfit and Rochester, 1983). The Langmuir adsorption model can be described by the following equation:

$$q = \frac{q_m b C_{Ae}}{b C_{Ae} + 1} \qquad (4.1)$$

Where C_{Ae}, q_m and b are the equilibrium surfactant concentration (wt %), the maximum amount of solute adsorbed (mol/g adsorbent), and the Langmuir equilibrium constant, respectively. This equation is rearranged into the following linearized form:

$$\frac{C_{Ae}}{q} = \frac{C_{Ae}}{q_m} + \frac{1}{b q_m} \qquad (4.2)$$

From the plot of C_{Ae}/q versus C_{Ae}, the slope and the intercept correspond to $1/q_m$ and $1/bq_m$, respectively. Therefore, q_m and b are readily calculated from the slope and the intercept (Foo and Hameed, 2010).

The Langmuir model was applied to the adsorption isotherms and all the data showed quite good fits to the Langmuir adsorption equation with $R^2 > 0.99$ (Figure 4.7 and Figure 4.8). The adsorption isotherm data was then fitted to the linearized equation to estimate the maximum amount of surfactant adsorption, q_m, and the Langmuir equilibrium constant, b with excellent linear fit of $R^2 > 0.99$. The obtained parameters are given in Table 4.4. The maximum amount of surfactant adsorption was in the order of CrudeSorb > Kaolin.

Table 4.4 Estimated parameters of q_m and b in the Langmuir adsorption model

Adsorbent	Langmuir Adsorption model Parameter		R^2
	q_m (mg/g)	b	
CrudeSorb	0.00337975	71.652056	1.00
Kaolin	0.00088992	106.370693	0.9962

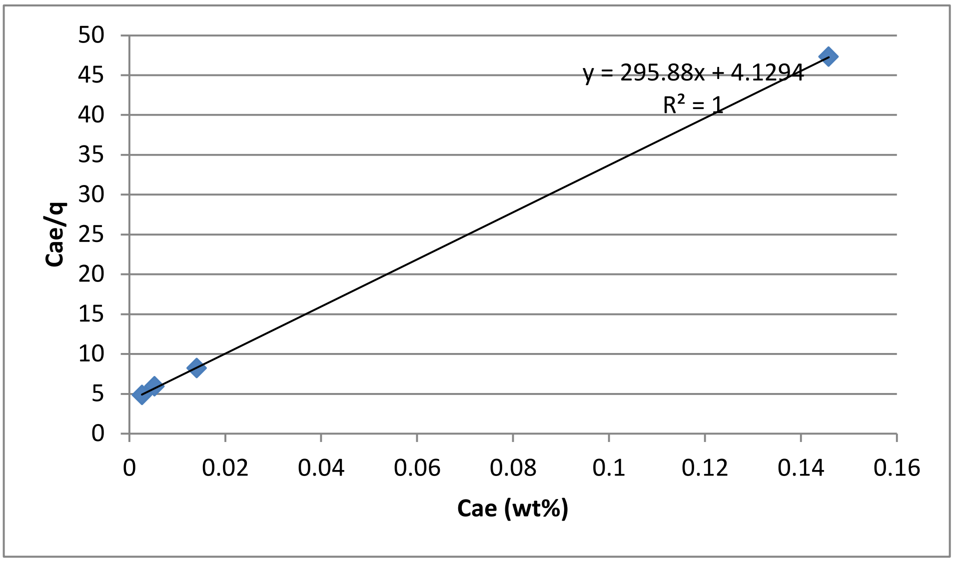


Figure 4.7 Application of Langmuir Model to adsorption isotherm on CrudeSorb

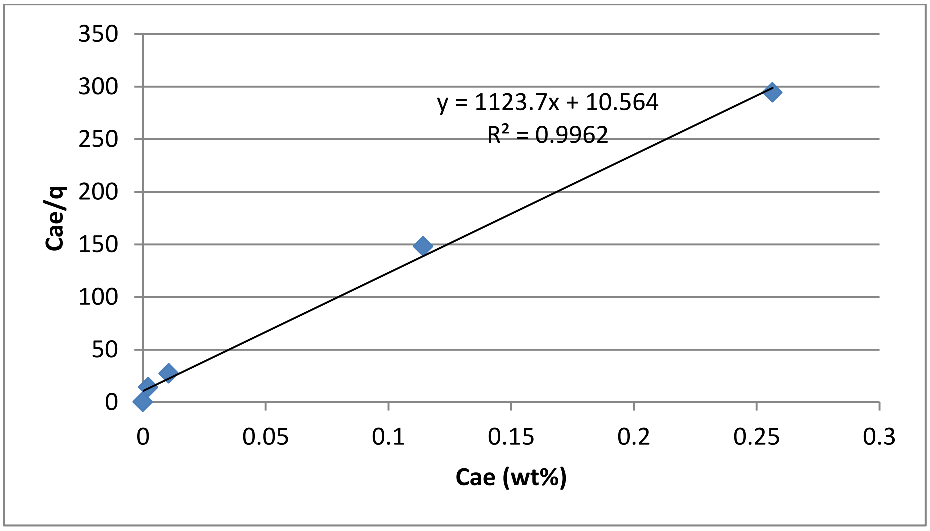


Figure 4.8 Application of Langmuir Model to adsorption isotherm data on kaolin

4.4.2 Freundlich Adsorption Isotherm

The Freundlich isotherm model, which is known to be widely used in heterogeneous systems, was applied to the isotherm data on heterogeneous kaolinite and CrudeSorb. The basic assumption of the Freundlich model is that adsorbent surface is composed of heterogeneous sites with different energy and amount of solute adsorbed per unit mass of adsorbent is a function of solute concentration. This model does not confine the adsorption layer to a monolayer but allows multilayers (Adamson and Gast 1997). The Freundlich model quantitatively states that the adsorption amount is proportional to the equilibrium concentration of the solute as follows:

$$q = aC_{Ae}^{1/n} \qquad (4.3)$$

Where a, C_{Ae} and n denote the Freundlich equilibrium constant, the surfactant concentration (wt%) and the Freundlich constant, respectively. The constant *a* and *n* imply adsorption capacity and intensity, respectively (Adamson and Gat, 1997; Foo and Hameed, 2010). By taking logarithm, this equation is linearized into the equation:

$$\ln q = \ln a + \frac{1}{n}\ln C_{Ae} \qquad (4.4)$$

When ln q is plotted against ln C_{Ae}, the slope and the intercept are 1/n and ln a, respectively and thus *a* and *n* are readily determined. As shown in Figure 4.8 and 4.9 the model fits were partially good, $R^2 > 0.93$. At a fixed temperature, the Freundlich constants a and 1/n are related to adsorption capacity and adsorption intensity. The constant 1/n is related to the heat of adsorption, ΔH_a by the equation:

$$\frac{1}{n} = \frac{RT\ ln\theta}{\Delta H_a} \qquad (4.5)$$

Where θ is the surface coverage. Thus, at a constant surface coverage the smaller 1/n value indicates the larger heat of adsorption, means higher adsorption intensity. When, $0.1 < 1/n < 0.5$, adsorption is favourable; $0.5 < 1/n < 1$, it is easy to adsorb; $1/n > 1$, it is difficult to adsorb (Samiey and Dargahi, 2010). As listed in Table 4.5 Kaolin showed the lowest value of 1/n value.

Table 4.5 Estimated parameters of a and 1/n in the Freundlich adsorption model

Adsorbent	Freundlich Adsorption model Parameter		R^2
	a	1/n	
CrudeSorb	0.007718	0.4156	0.9302
Kaolin	0.00157642	0.3533	0.9618

From Figure 4.9 shows the plotted ln Cae vs ln q of R^2 equal to 0.9302 on CrudeSorb, while Figure 4.10 shows R^2 of 0.9618 on kaolin. These partially linear graphs apparently show the Freundlich isotherm model may be suit to explains the adsorption process.

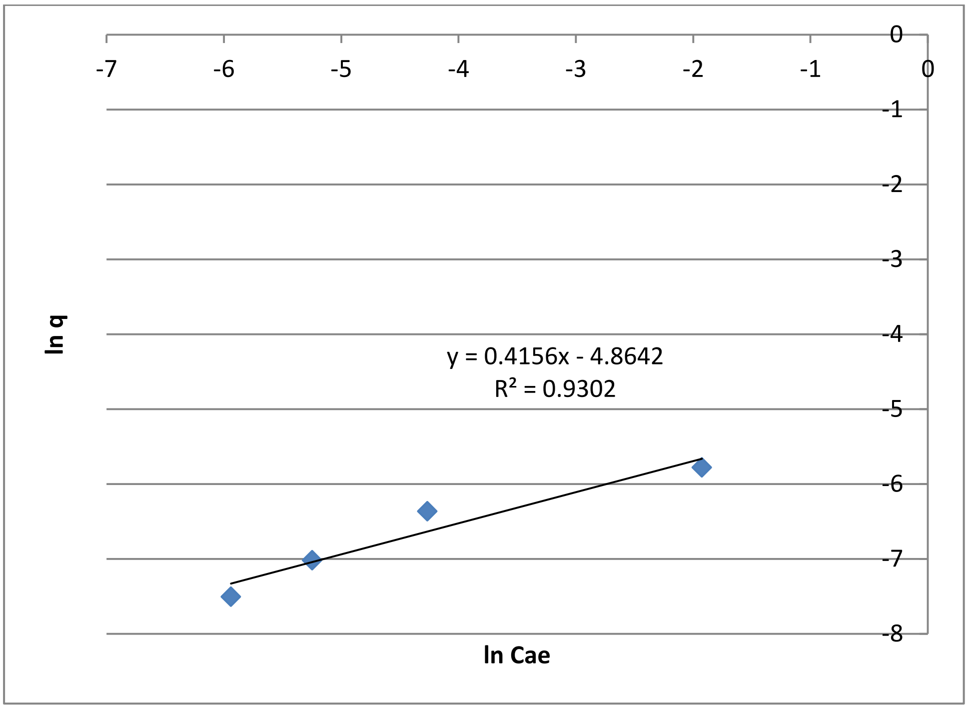


Figure 4.9 Application of Freundlich Model to adsorption isotherm data on CrudeSorb

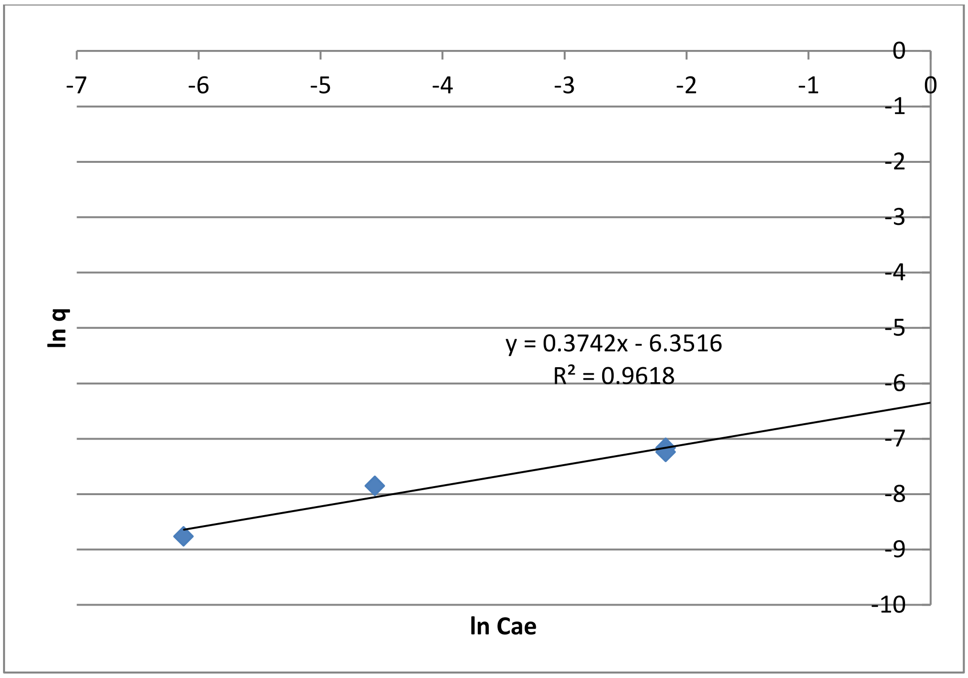


Figure 4.10 Application of Freundlich Model to adsorption isotherm data on Kaolin

Table 4.4 and Table 4.5 show the parameters obtained the two models used. In case of Langmuir model, the regression coefficients (R^2) for the linear equations fittings are found to be greater than 0.99 whereas the value of R^2 for the Freundlich Isotherm model are found to less than 0.97. Therefore, the author can concluded that the surfactant adsorption on both kaolin and CrudeSorb follow the Langmuir isotherm model.

4.5 ADSORPTION KINETICS

Adsorption is a physicochemical process that involves the mass transfer of adsorbate from the liquid phase to the adsorbent surface. A study of kinetic of adsorption is desirable as it provides information about the mechanism of adsorption, which is important to evaluate the efficiency of the process. The experimental data of adsorption o surfactants on CrudeSorb and Kaolin have been analysed by two different models, pseudo first-order and second-order model.

The linearized form of the pseudo-first order equation of Lagergen is generally expressed as follows:

$$\log(q_e - q_t) = log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (4.6)$$

The plot of log (q_e-q_t) versus t should give a linear relationship; k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

The pseudo second-order kinetic model is represented by the following linear equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (4.7)$$

If pseudo-second order kinetics is applicable, the plot of t/q_t against t of equation 4.7 should give a linear relationship; q_e and k_2 can be determined from the slope and intercept of the plot.

Where and the amount adsorbed at equilibrium q_e can be determined using Equation…

$$q_e = \frac{(c_i - c_e)V}{M} \qquad (4.8)$$

Where,

q_t = Amount adsorbed (mg/g) at time t

k_1 = Rate constant for pseudo first-order rate of reaction model

k_2 = Rate constant for pseudo second-order rate of reaction model (g/mg/min)

c_i = Initial adsorbate concentration

c_e = Adsorbate concentration at equilibrium

V = Volume of solution, L

M = Mass of adsorbent used, g

The results presented in Table 4.6 were obtained from the sorption experiment were analysed with the pseudo-first order kinetic model. Figure 4.11 and 4.12 show pseudo first-order kinetic model of surfactant adsorption on Kaolin and CrudeSorb, respectively.

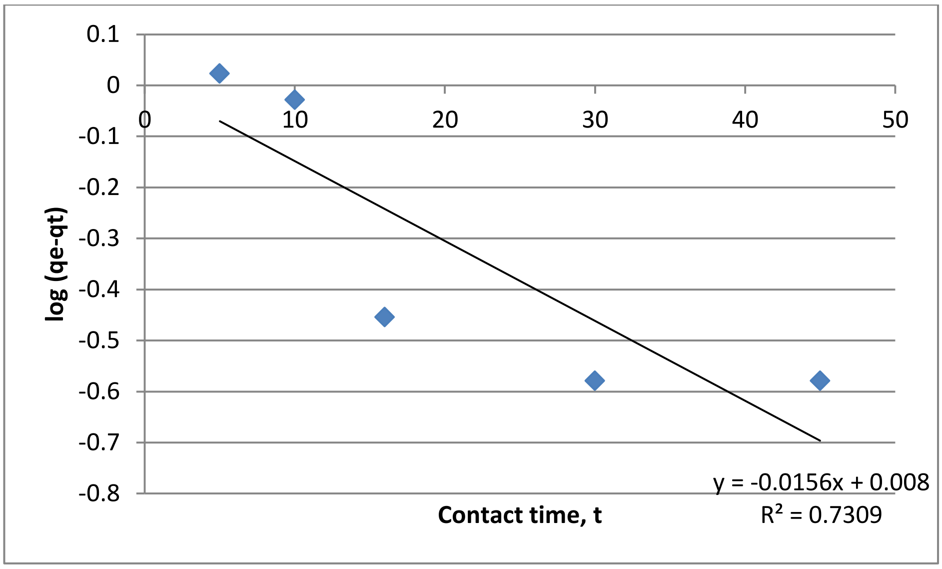


Figure 4.11 Pseudo first-order kinetic model of surfactants adsorption on kaolin

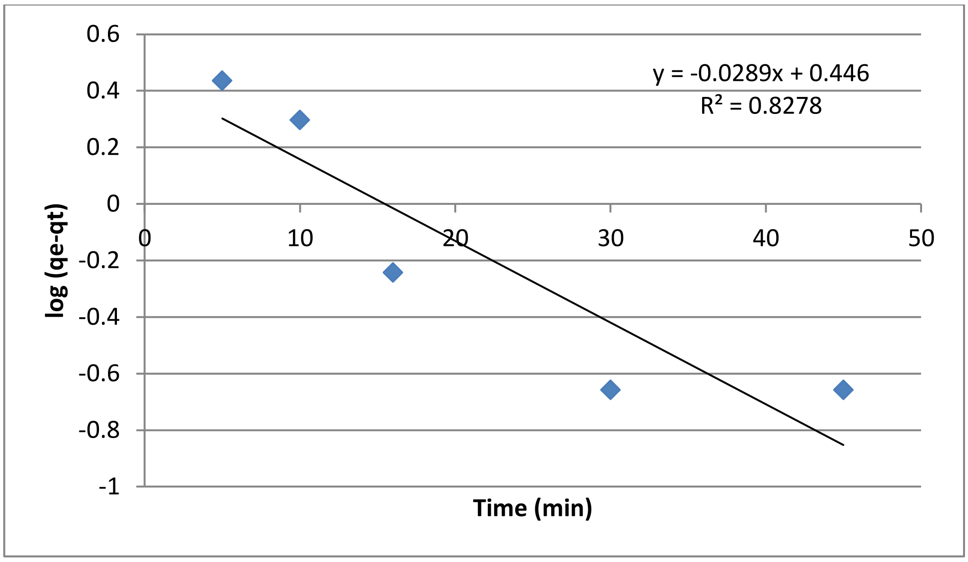


Figure 4.12 Pseudo first-order kinetic model of surfactants adsorption on CrudeSorb

Table 4.6 Pseudo first-order kinetic parameters for the surfactants adsorption on CrudeSorb and kaolin

Type of Adsorbent	**Initial Surfactant Concentration, wt%**	**$k_{1,}$ (mg/g.min)**	**R^2**	**q_e from graph (mg/g)**	**q_e from experiment (mg/g)**
Kaolin	0.05	0.0359268	0.7309	1.00803	7.99271
CrudeSorb	0.05	0.00083521	0.8278	1.56205	9.16564

It can be inferred from Figure 4.13 and Figure 4.14 that the possibility of the chemisorptions playing a significant role in the rate determining step cannot be rule out. This fact is attested by the very high linearity of the plot as shown in Table 4.7. The pseudo second-order parameters, q_e, h and k, obtained from the pseudo second-order plot are presented in Table 4.7.

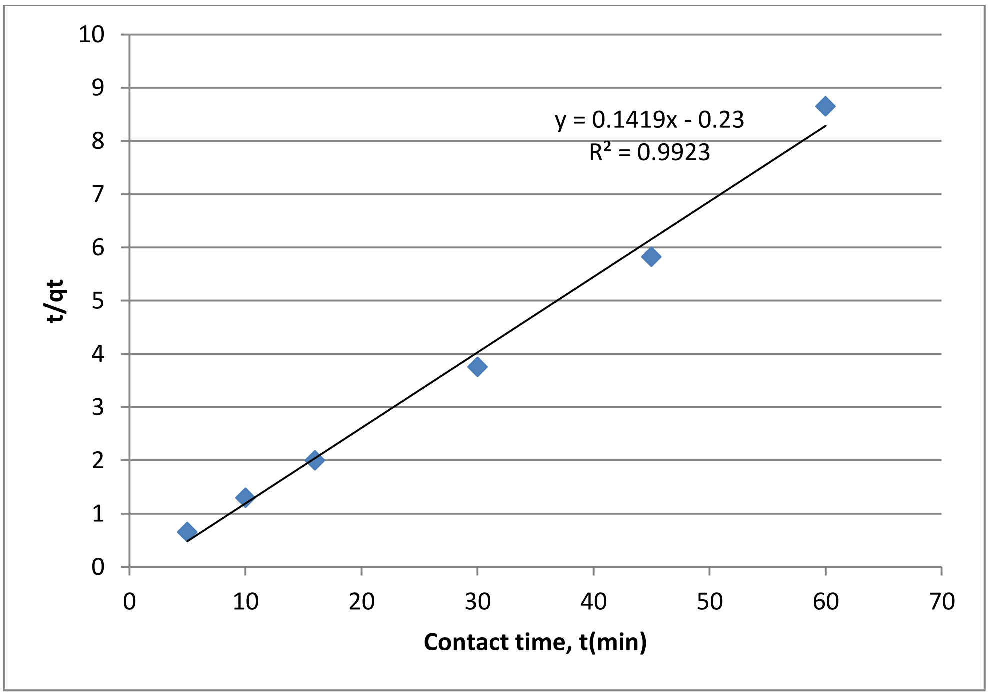


Figure 4.13 Pseudo second-order kinetic model of surfactants adsorption on kaolin

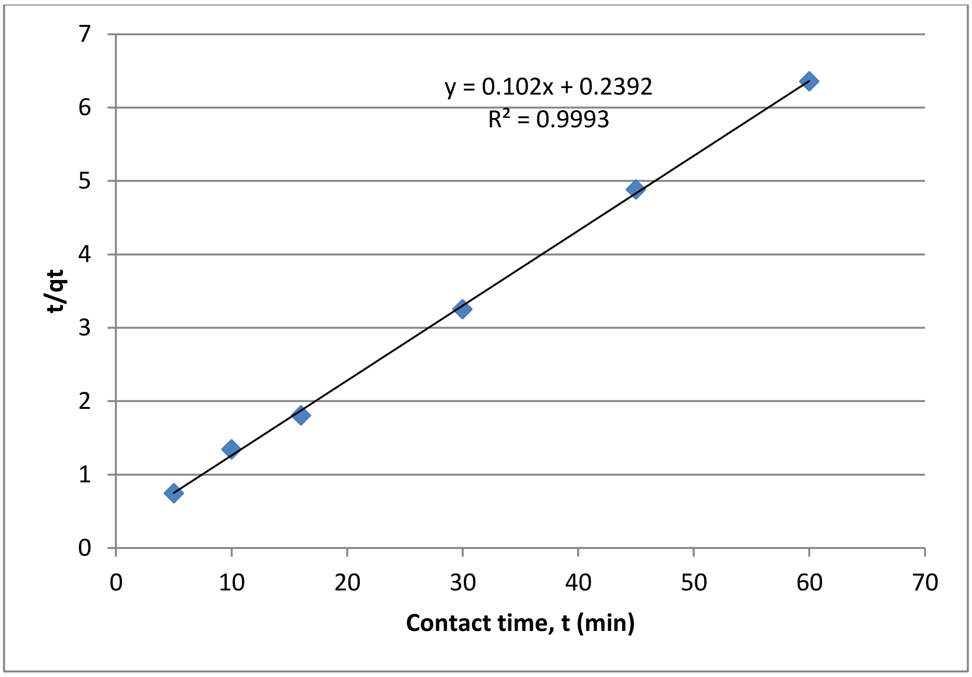


Figure 4.14 Pseudo second-order kinetic model of surfactants adsorption on CrudeSorb

Table 4.7 Pseudo second-order kinetic parameters for the surfactants adsorption on CrudeSorb and kaolin

Type of Adsorbent	**Initial Surfactant Concentration, wt%**	**$k_{2,}$ (mg/g.min)**	**R^2**	**q_e from graph (mg/g)**	**q_e from experiment (mg/g)**
Kaolin	0.05	-0.08755	0.9923	7.047216	6.938345
CrudeSorb	0.05	0.000953	0.9993	9.803922	9.441419

As we compare the R^2 values tabulated in Table 4.6 and 4.7, the author can deduce that the adsorption activities of both adsorbent fitted pseudo second-order reaction kinetic model. The q_e values calculated from the graph equation shows high agreement with the experimental values and the value of R^2 is also relatively higher as compare to using pseudo first-order reaction kinetic model. These had indicates that the pseudo-second order kinetic model best describe the adsorption activities of CrudeSorb and kaolin.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 CONCLUSION

CrudeSorb and Kaolin has been successfully analysed by X-Ray Diffraction (XRD) method, and it shows that CrudeSorb are made up of 59.1% rock material, and remaining is clay. However, Kaolin only consists of 13% rock composition and another 87% is clay. Results from PSA shows CrudeSorb has higher particle size diameter of 623.015 µm compare to only 4.290 µm of kaolin.

In the adsorption test, the optimum pH value of adsorption activity on CrudeSorb is at pH 12. On the other hands, kaolin performed better surfactant removal at low pH value of 2. The adsorption of surfactants is higher with higher amount of adsorbents, regardless whether it is CrudeSorb or kaolin until there is no further adsorption because of gathering of huge adsorption sites. Extent removal of 500 ppm of surfactants reached 100% upon the usage of CrudeSorb at 4.0 g, whereas kaolin is at 92%.

From the adsorption isotherm study, the author can conclude that both kaolin as well as CrudeSorb fitted the Langmuir Isotherm. The high values of R^2 obtained from the two models suggest and close q_e values between experimental and graph proved the applicability of the second-order kinetic model to describe the adsorption kinetic data of surfactants onto CrudeSorb and kaolin.

This project has proven that the adsorption capability of commercialised adsorbents of Crudesorb is comparatively equal to the surfactants adsorption on local natural adsorbents of kaolin.

5.2 RECOMMMENDATIONS

For future works, it is suggested to do dynamic adsorption for further analyse the CrudeSorb efficiency in removing surfactants. The original produced water should be obtained to study how the adsorption activities by diverted from the synthetic produced water. Desorption test should be study to investigate the practicality and lifespan of the CrudeSorb. Furthermore impressive results shown by kaolin should be a benchmark to use natural cay, kaolin and modified them to fit the purpose of removing surfactants from produced water.

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