

# DEVELOPMENT AND EVALUATION OF ORGANICALLY MODIFIED CLAY AS ADSORBENT FOR WASTE WATER CONTAINING TRACES OF OIL.

- **INTRODUCTION**
- **THEORY**
- **MATERIALS AND METHODOLOGIES**
- **RESULT AND DISCUSSION**
- **CONCLUSION**

**Courtesy:**  
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## CERTIFICATION

The undersigned certifies that the research work was carried out by “MR.EMIEMIE ODAFE CLINTON” and that it is adequate in scope and content for the partial fulfillment of the requirement for the award of B.Eng Degree in Chemical Engineering Department of the Federal University of Petroleum Resources, Effurun, Delta State, Nigeria.

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## **DEDICATION**

This research project work is dedicated to God Almighty, the fountain of all wisdom whose inspiration has made this a reality.

## **ACKNOWLEDGEMENT**

I wish to express my sincere gratitude to my supervisor, Engr. E.O. Ohimor for his dedication and intelligent supervision. His advice and encouragement made this project work a big success. I am greatly indebted to other staffs of the Department of Chemical Engineering: Engr. Dr. A.O. Okewale (HOD), Engr. O. Olayebi, Engr. Teddy Odisu, Dr. Akpofure Rim-Rukeh, Prof. F.A. Aisien, Prof. Kehinde Abiola, Prof. S.E. Ogbeide, and others too numerous to mention.

I also want to appreciate the effort put in me by my friends and all 2015/2016 graduating students of Chemical Engineering Department.

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## **ABSTRACT**

An efficient way to remove traces of oil in oilfield effluent water is through the use of organoclay as a filtration medium. The organoclay samples were prepared from a combination of clay with varied amounts of quaternary ammonium chloride. The effluent water sample was obtained from an oilfield in Delta state. The effects of some parameters, such as ratio of clay to quaternary amine used in producing the various samples of organoclay and time of adsorption, on the efficiency of removal of oil from effluent water by the organoclay were studied. The total hydrocarbon content (THC), pH and turbidity of the effluent water before and after adsorption using each of the five (5) different samples of organoclays were monitored and there were considerable differences when compared with the use of an ordinary clay. The total hydrocarbon content of the effluent water used in this study was 133.35ppm and one of the organoclay samples, of ratio 100g/50ml (m/v) was able to reduce it to 8.96ppm after the adsorption process in a duration of 0.235hrs. Hence, the organoclay has oil removing capabilities due to its ion exchange or polar property.

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# CHAPTER ONE

## INTRODUCTION

### 1.1 BACKGROUND OF STUDY

Discharge of produced water from oil and gas productions is generally regulated. Historically one of the key parameters used for compliance monitoring is the oil concentration in produced water, is because of its potential to pollute the environment.

Measurement of oil in produced water is required from an operational point of view, because process optimization is increasingly being implemented by operators so that less oil is discharged, less chemicals are used, process capacity is increased, and oil and gas production is maximized.

Oil in water is essentially petroleum compounds in water (Total Petroleum Hydrocarbon Criteria Working Group Series 1998). Petroleum compounds can be divided into two main groups: hydrocarbons and heteroatom compounds.

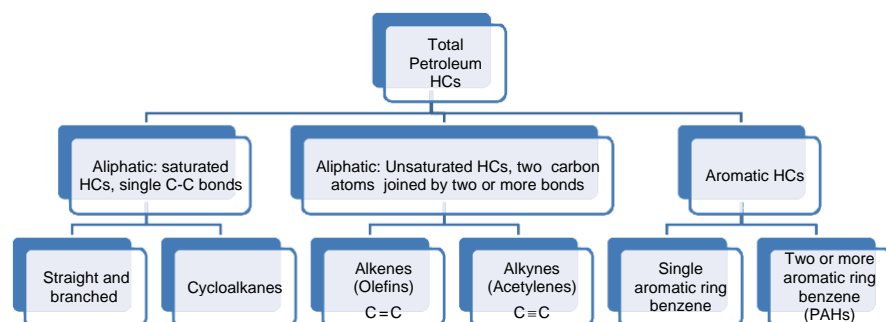
Hydrocarbons are usually measured as Total Petroleum Hydrocarbons (TPHs). These are molecules that only contain carbon and hydrogen. The heteroatom compounds are those that contain not only carbon and hydrogen but also heteroatoms such as sulphur, nitrogen and oxygen.

Hydrocarbons are in general grouped into three categories: saturated, unsaturated and aromatics.

**Saturated hydrocarbons** are characterised by single C–C bonds with all other remaining bonds saturated by H atoms. This group can be subdivided into aliphatic and alicyclic.

- **Aliphatic hydrocarbons** are straight or branched with a general molecular formula:  $C_nH_{2n+2}$ . The common names for these types of compounds are alkanes and isoalkanes, which are often referred to by the petroleum industry as paraffins and isoparaffins respectively.
- **Alicyclic hydrocarbons** are saturated hydrocarbons containing one or more rings with a general molecular formula:  $C_nH_{2n}$ . They are also called cycloalkanes or naphthenes or cycloparaffins by the petroleum industry.

**Unsaturated hydrocarbons** are characterised by two or more bonds ( $C = C$  for alkenes or  $C \equiv C$  for alkynes) between two carbon atoms. They are not usually found in crude oils, but are produced in cracking processes (converting large molecular



**Fig. 1.0** Hydrocarbon chemistry – total petroleum hydrocarbons (TPHs)

hydrocarbons to smaller ones). Unsaturated hydrocarbons can be sub-grouped into alkenes/olefins and alkynes/acetylenes.

- **Alkenes/olefins** are those that contain two carbon bonds with a general molecular formula  $C_nH_{2n}$ .
- **Alkynes/acetylenes** are those that contain three carbon bonds with a general molecular formula  $C_nH_{2n-2}$ .
- **Aromatic hydrocarbons** are characterized by a benzene ring structure. The benzene ring contains six carbons; each carbon in the ring binds with one hydrogen. Depending on the number of rings that an aromatic hydrocarbon molecule contains, they are often further divided into single ring aromatics and polycyclic aromatics (containing two rings or more).

A summary of the different types of hydrocarbons is given in Fig. 1.0 Having an understanding of the basic hydrocarbon chemistry is useful. It will help with an appreciation of what is meant by oil in water, in particular, when covering topics such as aliphatic, aromatic hydrocarbons, dissolved and dispersed oils, solvent extract clean-up to remove the polar components, etc.

## 1.2 STATEMENT OF PROBLEM

Traces of petroleum hydrocarbon in oilfield effluent water has potential to be transported into the internals of aquatic flora and fauna, when disposed in water bodies. This ultimately can result in the contamination of the food chain with adverse effect on flora and fauna.

## 1.3 AIM

To develop and evaluate organically modified clay as adsorbent for wastewater containing traces of oil.

## 1.4 OBJECTIVES

- Develop organically modified clay on varied conditions of temperature and solid/liquid ratio
- Evaluate their ability to absorb trace oil from oilfield effluent
- Determine the most efficient organically modified clay and its solid/liquid ratio

## 1.5 SCOPE OF RESEARCH

The scope entails buying commercially available bentonite or obtaining well sieved clay within delta state and buying an analytical grade of ammonium chloride. The experimental preparation of the organically modified clay and the test of its adsorbent will be carried out in a standard laboratory.

## 1.6 SIGNIFICANCE OF STUDY

Our environment has been continuously subjected to the upstream activities of numerous petroleum based industries. In most cases, the aquatic environments are the ultimate receivers of spill and other discharges which results to several toxicological effects.

# CHAPTER TWO

## LITERATURE REVIEW

### 2.1 OIL AND GAS PRODUCTION FACILITIES

The oil and gas industry facilities and systems are broadly defined, according to their use in the oil and gas industry production stream:

**Exploration** Includes prospecting, seismic and drilling activities that take place before the development of a field is finally decided.

**Upstream** Typically refers to all facilities for production and stabilization of oil and gas. The reservoir and drilling community often uses upstream for the wellhead, well, completion and reservoir only, and downstream of the wellhead as production or processing. Exploration and upstream/production together is referred to as E&P.

**Midstream** Broadly defined as gas treatment, LNG production and regasification plants, and oil and gas pipeline systems.

**Refining** Where oil and condensates are processed into marketable products with defined specifications such as gasoline, diesel or feedstock for the petrochemical industry. Refinery offsites such as tank storage and distribution terminals are included in this segment, or may be part of a separate distributions operation.

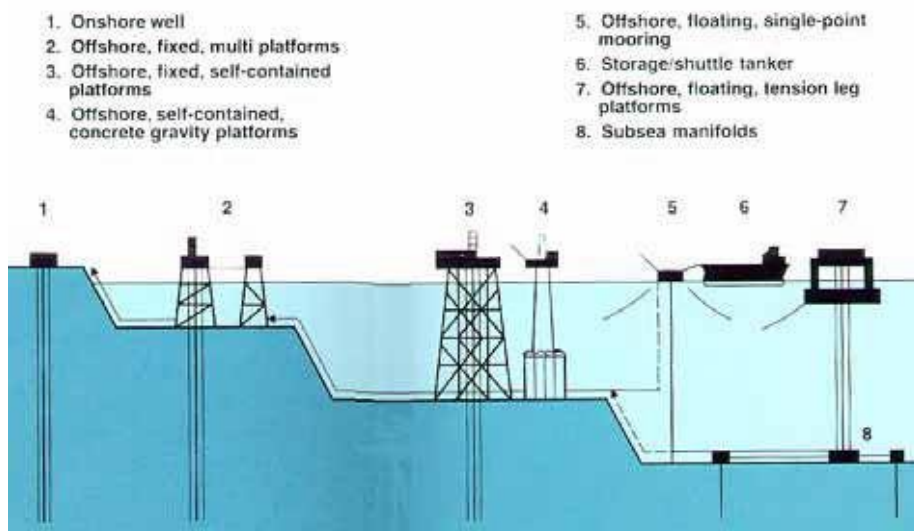
**Petrochemical** These products are chemical products where the main feedstock is hydrocarbons. Examples are plastics, fertilizer and a wide range of industrial chemicals.

#### 2.1.1 PRODUCTION

Production is divided mainly into two different sections namely;

- Onshore
- Offshore

This illustration gives an overview of typical oil and gas production facilities:



*Figure 2. Oil and gas production facilities*

### 2.1.2 ONSHORE

Onshore production is economically viable from a few dozen barrels of oil a day and upwards. Oil and gas is produced from several million wells world-wide. In particular, a gas gathering network can become very large, with production from thousands of wells, several hundred kilometers/miles apart, feeding through a gathering network into a processing plant. The picture shows a well equipped with a sucker rod pump (donkey pump) often associated with onshore oil production. However, as we shall see later, there are many other ways of extracting oil from a non-free flowing well. For the smallest reservoirs, oil is simply collected in a holding tank and picked up at regular intervals by tanker truck or railcar to be processed at a refinery (F, 2012). But onshore wells in oil rich areas are also high capacity wells with thousands of barrels per day, connected to a 1,000,000 barrel or more a day gas oil separation plant (GOSP). Product is sent from the plant by pipeline or tankers. The production may come from many different license owners, therefore metering and logging of individual well-streams into the gathering network are important tasks. Recently, very heavy crude, tar sands and oil shale have become economically extractable with higher prices and new technology. Heavy crude may need heating and diluents to be extracted. Tar sands have lost their volatile compounds and are strip mined or can be extracted with steam. It must be further processed to separate unconventional reserves may contain more than double the hydrocarbons found in conventional reservoirs

### 2.1.3 OFFSHORE

A whole range of different structures are used offshore, depending on size and water depth. In the last few years we have seen pure sea bottom installations with multiphase piping to shore and no offshore topside structure at all. Replacing outlying wellhead towers, deviation drilling is used to reach different parts of the reservoir from a few wellhead cluster locations. Some of the common offshore structures are:

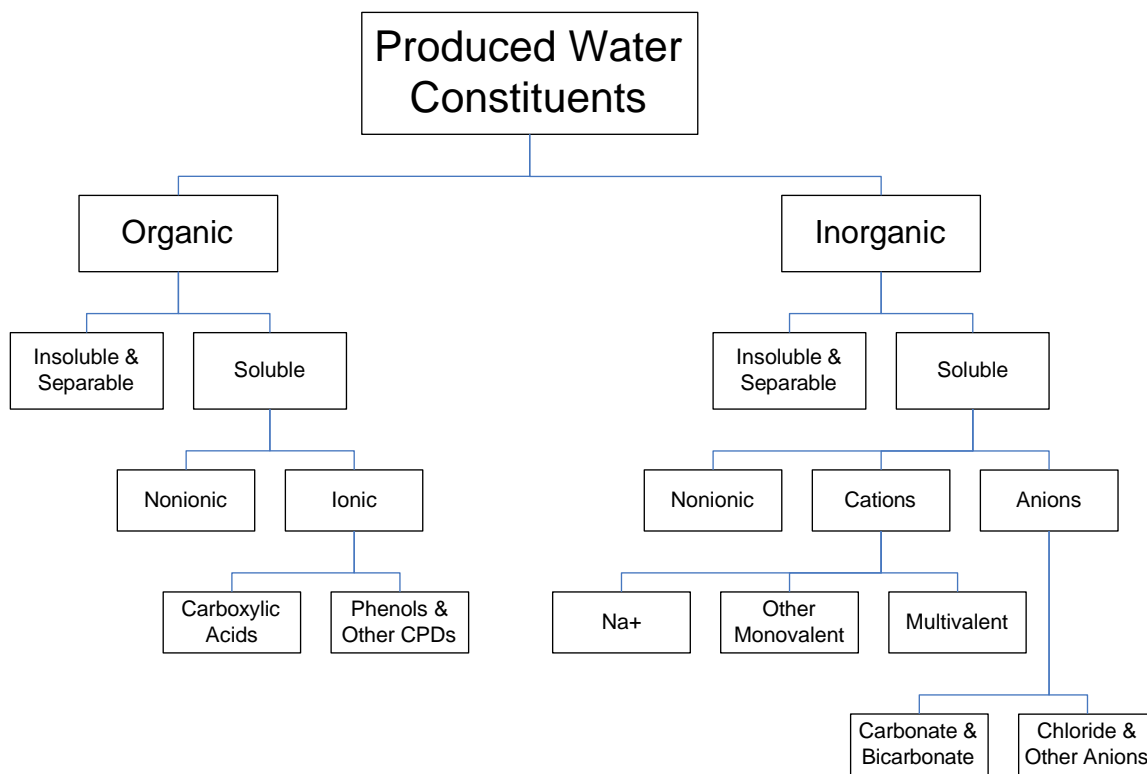
- A shallow water complex,
- A gravity base
- Compliant towers

#### **2.1.4 PRODUCE WATER**

Water produced during oil and gas extraction operations constitutes the industry's most important waste stream on the basis of volume. The oil and gas industry produces approximately 14 billion bbls of water annually. The water varies greatly in quality and quantity and in some cases the water can be a useful by-product or even a salable commodity. Produced water is most often considered a waste, but the industry is beginning to consider this material as a potential profit stream (Al-Megren, 2012). Whether waste or commodity, produced water has management costs that need to be kept in-line with each specific production project and region or it could adversely affect the life of the well, thereby leaving substantial recoverable reserves in the ground. Produced water handling practices must also be environmentally protective or the operator could face regulatory action. Produced water handling methodology depends on the composition of produced water, location, quantity and the availability of resources.

Some of the options available to the oil and gas operator for managing produced water might include the following:

1. *Avoid production of water onto the surface* – Using polymer gels that block water contributing fissures or fractures or Downhole Water Separators which separate water from oil or gas streams downhole and reinject it into suitable formations. This option eliminates waste water and is one of the more elegant solutions, but is not always possible.
2. *Inject produced water* – Inject the produced water into the same formation or another suitable formation; involves transportation of produced water from the producing to the injection site. Treatment of the injectate to reduce fouling and scaling agents and bacteria might be necessary. While waste water is generated in this option, the waste is emplaced back underground.
3. *Discharge produced water* – Treat the produced water to meet onshore or offshore discharge regulations. In some cases the treatment of produced water might not be necessary.
4. *Reuse in oil and gas operations* – Treat the produced water to meet the quality required to use it for drilling, stimulation, and workover operations.



**Figure 2 - Produced Water Constituents (Hayes, 2004)**

Natural water or formation water is always found together with petroleum in reservoirs. It is slightly acidic and sits below the hydrocarbons in porous reservoir media. Extraction of oil and gas leads to a reduction in reservoir pressure, and additional water is usually injected into the reservoir water layer to maintain hydraulic pressure and enhance oil recovery. In addition to injected water, there can be water breakthrough from outside the reservoir area, and as oil and gas production continues, the time comes when formation water reaches production well, and production of water begins alongside the hydrocarbons. This water is known as produced water or oilfield brine, accounting for the largest volume of byproduct generated during oil and gas recovery operations. It is a mixture of injected water, formation water, hydrocarbons and treating chemicals, generally classified as oilfield produced water, natural gas produced water and coal bed methane (CBM) produced water depending on the source. Oilfields are responsible for more than 60% of daily produced water generated worldwide. The rate of oilfield produced water production is expected to increase as oilfield ages. Other factors have been reported to affect the quantity of produced water generated in an oilfield.

Generally, produced water is composed of dissolved and dispersed oil components, dissolved formation minerals, production chemicals, dissolved gases (including CO<sub>2</sub> and H<sub>2</sub>S) and produced solids. There is a wide variation in the level of its organic and inorganic composition due to geological formation, lifetime of the reservoir and the type of hydrocarbon produced. Treatment of produced water has been attempted and is proven to be an effective option for produced water handling. Studies conducted to identify, verify and compile existing and newly developed techniques demonstrate the economic benefits of produced water treatment. Treating oilfield water can help facilitate additional water management options for



operators such as beneficial uses that in the short and long term can potentially provide certain community and economic advantages. Treated produced water has the potential to be a valuable product rather than a waste.

The general objectives for operators when they plan produced water treatment are:

1. *De-oiling* – Removal of free and dispersed oil and grease present in produced water.
2. *Soluble organics removal* – Removal of dissolved organics.
3. *Disinfection* – Removal of bacteria, microorganisms, algae, etc.
4. *Suspended solids removal* – Removal of suspended particles, sand, turbidity, etc.
5. *Dissolved gas removal* – Removal of light hydrocarbon gases, carbon dioxide, hydrogen sulfide, etc.
6. *Desalination or demineralization* – Removal of dissolved salts, sulfates, nitrates, contaminants, scaling agents, etc.
7. *Softening* – Removal of excess water hardness.
8. *Sodium Adsorption Ratio (SAR) adjustment* – Addition of calcium or magnesium ions into the produced water to adjust sodicity levels prior to irrigation.
9. *Miscellaneous* – Naturally occurring radioactive materials (NORM) removal.

Selection of produced water treatment structure is often a challenging problem that is steered by the overall treatment objective. The general plan is to select the cheapest method – preferably mobile treatment units which assure the achievement of targeted output criteria. In this way technology can be positioned in the field for optimum convenience and the technology can be fine-tuned to meet specific end-uses for the water (Devold, 2006). The following sections discuss the major objectives of produced water treatment, the technology alternatives commercially available at the present time, and a summary of the advantages and disadvantages of the various technologies.

### **2.1.5 PRODUCED WATER TREATMENT OBJECTIVES**

Produced water usually represents a waste product in the petroleum industry; it is more often than not only a cost that must be controlled to enhance project economics. Water management and cost control can be done by choosing appropriate water disposal options or by finding an appropriate beneficial use for the water. Waste options and beneficial uses are, however, highly dependent upon water quality and may require water treatment prior to disposal or use. Treatment of produced water may be required in order to meet pre-disposal regulatory limits or to meet beneficial use specifications. If the oil and gas operator aims to utilize a low-cost disposal option such as discharge to surface waters, the produced water must meet or exceed limits set by regulators for key parameters. The parameters might be specific constituents of concern such as ammonia or barium that can be toxic to sensitive animal and plant-life. Or the parameters may be more broadly-based such as Total Dissolved Solids (TDS) or Sodium Adsorption Ratio (SAR) that

can affect several aspects of the environment. The regulatory community may make these limits seasonal so that spring run-off water is more carefully protected. In that case treatment options may also be seasonal.

If the oil and gas operator wishes to convey his produced water to a secondary user, the operator must be sure that the water falls within the specifications of the user. Specifications might be chemical (e.g., TDS), physical (temperature), or biological (coliforms per L). Specifications, regulatory limits and produced volume will define treatment objectives for the operator. Produced water treatment objectives may be mandated for several reasons and may be made necessary because of the presence of a number of constituents. The section below discusses some of these common treatment objectives.

### **2.1.6 PRODUCTION ISSUES**

This involves the various process issues that may arise in the oil and gas production facilities in the production of its various products, and they are;

- Foaming
- Wax/asphaltene
- Scale formation
- Emulsions
- Fouling
- Hydrogen sulphide gas emission
- Effluent water discharge compliance
- Gas flaring, Etc.

#### **1) FOAMING**

This occurs in oil and gas production as a result of forced and rapid oil and gas separation due to impurities other than water which are impractical to remove before the steam enters the separator. The problem of foaming may be encountered in different segments of the oil and gas production from the drilling mud to the gas-oil separation, gas dehydration and gas scrubbing (Bahadori, 2014).it may also be encountered in the refinery in processes like crude distillation, vacuum distillation and cracking process(Dow corning).The presence of foams results in cavitation in pumps and excessive process fouling and ultimately affect production.

#### **2) WAX DEPOSITION**

Crude oil contains heavy organics such as asphaltenes, resins and paraffin wax and this heavy organics may be deposited in flow lines resulting in plugging of flow lines, formation damage, loss of hydrocarbon and overall increased production cost. They are deposited where there is change in thermodynamic equilibrium such that the temperature falls below the cloud point (the temperature at which wax will be

formed). The major principle of inhibiting wax deposition is to increase the temperature of the crude above its cloud point temperature (Bahadori, 2014). Several models or experimental work has been carried out to determine the cloud point temperature of crude and average value of 3-5F has been agreed upon. Wax deposition can be prevented by using electric heater to raise the temperature of the crude oil as it enters the well hole. However, high level of production may also keep the well hole temperature above the cloud point and high flow rates tend to minimize wax adherence to metal surface because of the shearing action of the flowing liquid.

### **3) SCALE FORMATION**

Water is a major component of oil and gas production. It could be in the form of formation water or injected water which under some condition such as temperature and pressure can lead to precipitation and deposition of mineral scales such as calcium carbonate ( $\text{CaCO}_3$ ) and sulphates of barium, strontium and calcium (Bahadori, 2014). The formation of scales is a major problem in oil and gas production. Scale may lead to plugging as flow lines, valves and surface equipment hence a inhibition technique or scale removal technique is employed and this would cost the oil and gas industry a whole lot of money resulting in millions of dollars. A scale removal technique involves both chemical and mechanical approaches.

### **4) EMULSION**

Crude oil is seldom produced alone from reservoirs. It is always produced as a complex mixture of hydrocarbon and water. This occurrence causes the water phase to be dispersed and stabilized as fine droplets in the oil phase and hence forms emulsion as they flow through the reservoir pores into the well tubing and finally through the surface production facilities (Bahadori, 2014). Handling emulsion formation in oil and gas production accounts for a high percentage of the expenses incurred in daily production. The method employed in the deemulsification of crude oil are heat, electric, chemical and polymer method and also natural treatment. Since crude oil is co-produced with water, emulsions may be encountered in almost all phases of oil production and processing: inside the reservoir, transporting through pipelines and crude storage.

### **5) HYDROGEN SULPHIDE GAS EMISSION**

Hydrogen sulphide occurs naturally alongside formation of crude oil, through it varies from one oil well to another. Crude oil with a high amount of this gas deposition is regarded as sour crude and will need to go through a sweetening plant which removes hydrogen sulphide. Oil and gas production operation emits hydrogen sulphide during the extraction, storage, transporting or processing stages and the presence of the gas tend to have grave impact on the material used and health impact on the workers and the environment. One of the adverse effect of hydrogen sulphide in oil and gas production operations is corrosion of the equipment's.

## 6) GAS FLARE

The flare subsystem include Flare, atmospheric ventilation and blow down. The purpose of the Flare and Vent Systems is to provide safe discharge and disposal of gases and liquids resulting from:

- Spill-off flaring from the product stabilization system. (Oil, Condensate etc.).
- Production testing
- Relief of excess pressure caused by process upset conditions and thermal expansion.
- Depressurization either in response to an emergency situation or as part of a normal procedure.
- Planned depressurization of subsea production flow lines and export pipelines.
- Venting from equipment operating close to atmospheric pressure (e.g Tanks)

The systems are typically divided into a High Pressure (HP) Flare and a Low Pressure (LP) flare system. The LP system is operated marginally above atmospheric pressure to prevent atmospheric gases such as Oxygen to flow back into the vent and flare system and create a combustible mixture. With low gas flow, inert gas is injected at the flare nozzle to prevent air ingress. Traditionally, considerable amounts of hydrocarbons have been more or less continuously flared. In these cases, a continuously burning pilot is used to ensure ignition of hydrocarbons in the flare (Bahadori, 2014). Stronger environmental focus has eliminated continuous flaring and the pilot in many areas. Vapors and flare gas are normally recovered, and only in exceptional situations does flaring occur. To avoid the pilot flame, an ignition system is used to ensure safe ignition even when large volumes are discharged. One patented solution is a “ballistic ignition” system which fires burning pellets into the flare gas flow.

### 2.1.7 EFFLUENTS

The wastewater treatment is carried out in a dedicated state-of-art completely automated & PLC operated effluent treatment plant (ETP) supplied by Ion Exchange. The effluent treatment area is designed to contain and treat all internal process/utility waste water and storm/firewater, with the objective of zero discharge from the new refinery complex. The treated water is recycled back to the high total dissolved solids treatment train or guard tanks, as required (V., 2006). Effluents are segregated into four identical wastewater streams designed for a treatment capacity of 500 m<sup>3</sup>/h each and maximisation of reuse.

**The low total dissolved solids (LTDS) stream**, a mixture of process/oily waters which include non-phenolic waste waters, is treated to an effluent quality adequate for reuse for cooling water make up, fire water make up and irrigation water for development and maintenance of the local green belt.

**The high total dissolved solids (HTDS) stream** is a mixture of process /oily wastewaters that have been in contact with process streams, such as in the crude unit desalters, and have absorbed or dissolved mineral ions such as sodium chloride. This stream also contains (treated neutralised) process solvents such as spent caustics, and phenolic waste water. This water is treated to an effluent quality adequate for re-use as partial make up in a sea water cooling tower.

### **2.1.8 OILFIELD WASTEWATER EFFLUENT**

Separation of oil and water is done at the flow station in horizontal separator vessels. The water removed is either re-injected into the well or discharged into the environment (water bodies). The water separated contains dispersed or free oil, dissolved oil and other dissolved organic compounds referred to as water soluble organics. Components of the wastewater are broadly classified into three categories: dissolved mineral salts, dissolved gas and, microorganism.

### **2.1.9 ADVERSE EFFECTS OF EFFLUENTS**

PRE are priority pollutants due to their high polycyclic aromatics contents, which are toxic and tend to be more persistent in the environment. They encompass a wide range of contaminants at varied concentrations that are generally harmful. Decreased productivity of algae (a very important link in the food chain) observed for PRE-receiving water bodies have been attributed to such effects. The minimum amount of dissolved oxygen necessary for normal life in an aquatic environment is about 2mg/L, and the discharge of high organic matter containing waste waters into water bodies results in the excess consumption of oxygen by the bacteria. This is in an attempt to oxidize the effluent, thus depleting oxygen from the water faster than it dissolves back into the water from the air. This problem leads to the inadequate maintenance of higher life forms. In addition, oxygen availability is important because the end products of chemical and biochemical reactions in anaerobic systems often produce aesthetically displeasing colors, tastes and odors in water. Oil and grease are sticky in nature; they tend to aggregate, clogging drain pipes and sewer lines, causing unpleasant odors and corroding sewer lines under anaerobic condition. They also interfere with unit operations in municipal wastewater treatment plants because they float as a layer on top of the water. They also stick onto pipes and walls consequently blocking strainers and filters. Phenolic compounds pose a significant threat to the environment due to their extreme toxicity, stability, bioaccumulation and ability to remain in the environment for long periods. They generally are carcinogenic, causing considerable damage and threaten the eco-system in water bodies along with human health. The nitrogen and sulphur components of the effluent are highly toxic and are represented in the form of ammonia and hydrogen sulphide (H<sub>2</sub>S), respectively. In aqueous form, H<sub>2</sub>S exists in equilibrium with bisulphide (HS<sup>-</sup>) and sulphide (S<sup>2-</sup>), and the latter sulphur contributing significantly to oxygen depletion.

### **2.2.0 EFFLUENT WATER TREATMENT FOR SECONDARY RECOVERY OF OIL (WATER INJECTION)**

Prior to injection, produced water is often treated to remove contaminants that could otherwise plug the reservoir and/ or damage injection equipment.

Hence designed to meet the high performance demands of the Oil & Gas industry:

- Efficient treatment for increased productivity
- Robust and reliable installations and processes
- Operational safety in harsh environments
- Environmental compliance through efficient removal of pollutants

### **2.2.1 EFFLUENT WATER TREATMENT FOR EFFLUENT DISCHARGE COMPLIANCE (IN ONSHORE AND OFFSHORE)**

Tests can be conducted to analyze selected physicochemical and microbiological parameters from samples of effluent collected from onshore house-boat facilities and offshore oil production platforms at the discharge point to the recipient environment. Among the parameters determined included: Total chlorine, Biochemical Oxygen demand (BOD), Total Suspended Solids (TSS), Dissolved Oxygen (DO) and Faecal coliform. The discharge loads can be evaluated and monitored for eight weeks. The faecal coliform for the onshore facilities should have a mean value which range from 4.0 to 30.1 MPN/100ml, while the offshore facilities have mean value range of 7.4 to 42.0 MPN/100ml. Most of these results are higher than limits specified by the Department of Petroleum Resources (DPR) and an indication that the recipient environment is polluted and poses a great concern. There is therefore utmost need for further treatment before discharge for those parameters that indicated higher ranges than specified for effluent discharge.

There is growing public concern as a wide variety of toxic organic chemicals are being introduced deliberately into the environment. Petroleum hydrocarbons are a common example of these chemicals, which enter the environment frequently and in large volumes through numerous routes. Our environment has been continuously subjected to the upstream activities of numerous petroleum based industries. In most cases, the aquatic environments are the ultimate receivers of spill and other discharges which results to several toxicological effects (V., 2006). Monitoring of liquid effluents is performed to meet the objectives of environmental management of aquatic systems. Environmental monitoring should be instituted for the enforcement of the provisions of the relevant status-decrees and regulations dealing with environmental pollution, prevention and control. The limitations, standards and monitoring guidelines shall regulate and control the quality and quantity of industrial effluents associated with oil operations they shall ensure that these discharges do not cause any hazards to human health and living organisms (fauna and flora) and do not impair the quality to use adjacent surface waters, land and groundwater.

### **2.2.2 ENVIRONMENTAL HAZARDS OF ORGANIC WASTEWATER**

High amount of hydrophilic organic pollutants, such as organic matters, oil could consume a large amount of soluble oxygen. The acute toxicity and high quantity of oxygen demand could worsen the water quality and lead to great damage to the aquatic ecological system. However, their bad influence towards the environment will not last long, since they could easily be degraded by microorganisms. The situation is

different for the POPs, which have low water solubility, high accumulation capacity and potential carcinogenic, teratogenic, and neurotoxic properties. For example, many of the organochlorine pesticides cited above are carcinogenic, teratogenic, and neurotoxic. The dioxins and benzofurans are highly toxic and are extremely persistent in the human body as well as the environment (Bahadori, 2014). Several of the POPs, including DDT and its metabolites, PCBs, dioxins, and some chlorobenzene, can be detected in human body fat and serum years after any known exposures. Lindane (hexachlorocyclohexane), which was used for the treatment of body lice and as a broad-spectrum insecticide, could cause very high tissue levels, and could cause acute deaths when improperly used. Many factors, such as the characters of the pollutants, the environmental factors (PH value, temperature etc.), aging process could affect the toxicity of the organic wastewater, and their long-term influence to the ecosystem deserve further investigation.

### **2.2.3 COD AND BOD IN RELATION TO HYDROCARBON CONTENT OF EFFLUENT WATER**

BOD may be defined as the rate of removal of oxygen by microorganisms in aerobic degradation of the dissolved organic matter in water over a 5-day period. Increases in BOD can be due to heavy discharge of industrial waste water effluent, animal and crop wastes and domestic sewage. BOD values have been widely adopted as a measure of pollution effect (Fahim, Al-Sahhaf, & Elkilani, 2010). It is one of the most common measures of pollutant organic material in water. It indicates the amount of putrescible organic matter present in water. Sources of BOD in aquatic environment include leaves and woody debris, dead plants and animals, animal manure, industrial effluents, wastewater treatment plants, feedlots, and food-processing plants, failing septic systems, and urban storm water runoff. According to UN Department of Technical Cooperation for Development the maximum permitted BOD content is < 100 to 300 mg/L. It is important here to note that low BOD content is an indicator of good quality water, while a high BOD indicates polluted water. BOD directly affects the amount of dissolved oxygen (DO) in rivers and streams. The greater the BOD, the more rapidly oxygen is depleted in the water. This means less oxygen is available to higher forms of aquatic life. The consequences of high BOD are the same as those for low DO: aquatic organisms become stressed, suffocate, and die. All organic compounds with few exceptions can be oxidized by the action of strong oxidizing agents under acidic condition. The Chemical Oxygen Demand (COD) determination is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. During COD determination; oxygen demand value is useful in specifying toxic condition and presence of biologically resistant substances. It is an important, rapidly measured parameter for industrial waste water studies and control of waste treatments. COD test is used to measure the load of organic pollutants in the industrial waste water (M, 2013). The COD and BOD values both are a measure of the relative oxygen-depletion effect of a waste contaminant. Both have been widely adopted as a measure of pollution effect. COD is also one of the most common measures of pollutant organic material in water. COD is similar in function to BOD, in that both measure the amount of organic compounds in water. TDS content in water is a measure for

salinity. A large number of salts are found dissolved in natural waters, the common ones are carbonates, bicarbonates, chlorides, sulphates, phosphates, and nitrates of calcium, magnesium, sodium, potassium, iron, and manganese, etc. A high content of dissolved solid elements affects the density of water, influences osmoregulation of freshwater in organisms, reduces solubility of gases (like oxygen) and utility, of water for drinking, irrigational, and industrial purposes. The amount of organic compounds in wastewater is generally evaluated by chemical oxygen demand (COD) test, biological oxygen demand (BOD) test, and (TOC) test. The basis for the COD test is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. The COD value is always measured by the acidic potassium permanganate method and potassium dichromate method, and could reflect the pollution degree of reducing matter in water, including ammonia and reducing sulfide, so in wastewater with high quantity of reducing matter, the COD value will overestimate the organic pollutants in the water (M, 2013). BOD value is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20 °C and is often used as a robust surrogate of the degree of organic pollution of water. This is not a precise quantitative test, although it is widely used as an indication of the organic quality of water. TOC value is the amount of total carbon (water soluble and suspended in water) in the water. Using combustion during the assessment, this method could oxidize all the organic pollutants, and value reflects the amount of organic matter more directly than BOD<sub>5</sub> or COD. The COD, BOD and TOC test could quickly reflect the organic pollution in the wastewater, however, they can't reflect the kinds of organic matter and composition of the water, and therefore cannot reflect the total amount of the same total organic carbon pollution caused by different consequences.

#### **2.2.4 PROCESSES FOR REDUCING TOTAL HYDROCARBON CONTENT IN EFFLUENT WATER**

Produced water is water trapped during subsurface formations which is brought to the surface along with oil or gas. It contributes the largest volume of waste stream associated with oil and gas production. Globally, 77 billion bbl of water are produced per annum. The conventional methods to handle waste stream are reinjection into the well, direct discharge or reuse in case of thermal loop. Out of these, the most efficient way of handling produced water is to re-inject it into disposal wells. The disposal cost, which includes transportation cost, capital cost and infrastructure maintenance cost, may be as much as \$4.00/bbl. On the other hand, many oil producing regions (West Texas, Middle East and the Central Asian Republics) have scarcity of potable water. An affordable water treatment process could convert produced water into an asset. The harmful effects of produced water and the depletion of usable water resources act as a driving force for the treatment of produced water. Produced water contains soluble and insoluble organic compounds, dissolved solids, production chemicals (corrosion inhibitors, surfactants etc.) and



solid particles due to leaching of rocks and corrosion of pipelines. The methods available for treating produced water are physical, chemical, biological and membrane treatment processes. Stringent water quality parameters can be achieved efficiently through membrane processes (Fahim, Al-Sahhaf, & Elkilani, 2010). The most important advantages of using membrane processes are the ease of operation and little or no requirement of chemicals. Based on pore size, the membrane processes could be classified into Microfiltration (MF), Ultrafiltration (UF) and Nanofiltration (NF). The membranes are also classified as organic, inorganic and composite membranes. The primary disadvantage of using membranes is fouling. Irreversible and reversible foulings occur while treating produced water. The usage of appropriate pre-treatment process reduces the membrane fouling to a greater extent. Commercial treatment methods based on reverse osmosis and ion exchange processes are also discussed.

### **2.2.5 CHARACTERISTICS OF PRODUCED WATER**

The physical and chemical properties of produced water depend on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. The main constituents of produced water are as follows:

- dissolved and dispersed oil compounds
- dissolved formation minerals
- production chemical compounds
- production solids (formation, corrosion, scale, bacteria, waxes, and asphaltenes)
- dissolved gases

Produced waters discharged from gas/condensate platforms are about 10 times more toxic than the produced waters discharged from oil wells, but, the volumes from gas production are much lower; hence the total impact may be less.

### **2.2.6 CONSTITUENTS IN PRODUCED WATER**

**1. Dispersed oil:** Oil is an important contaminant in produced water since it can create potentially toxic effects near the discharge point. It can significantly contribute to Biological Oxygen Demand (BOD) and hence affects the aquatic or marine ecosystem (H, 2014). Usually the size of dispersed oil droplets would be 4-6 microns, but it may vary from 2- 30 microns. The current treatment systems could recover oil droplets of size up-to 10 microns.

**2. Dissolved Organic Compounds:** They include organic acids, polycyclic aromatic hydrocarbons (PAHs), phenols and volatiles. Volatile hydrocarbons can occur naturally in produced water. Concentrations of these compounds are usually higher in produced water from gas-condensate producing platforms than in produced water from oil producing platforms.

**3. Treatment Chemicals:** They include biocides, reverse emulsion breakers, and corrosion inhibitors. Corrosion inhibitors can form stable emulsions. Some chemicals are highly toxic even at low concentrations such as 0.1 ppm.

**4. Produced Solids:** They consist of precipitated solids (scales), sand and silt, carbonates, clays, corrosion products and other suspended solids produced from the formation and from well bore operations.

**5. Bacteria:** Anaerobic bacteria present in produced water may lead to corrosion.

**6. Metals:** Zinc, Lead, Manganese, Iron and Barium are the metals usually present in produced water. They are in general less toxic when compared to organic constituents. But they may precipitate to form undesired solids which hinder the treatment processes

## **2.3 TREATMENT METHODS**

### **2.3.1 PHYSICAL TREATMENT**

#### *Physical adsorption*

Activated carbon, organoclay, copolymers, zeolite, resins are widely used to treat produced water.

- The combination of activated carbon and organoclays proved to be more efficient in removing total petroleum hydrocarbons (TPH).
- Copolymers reduce the oil content up to 85%.
- Zeolites are efficient in removing BTEX compounds. A multi-stage adsorption and separation system was developed, for example, by EARTH Canada Corporation to recover dispersed oil droplets in water, whose size is greater than 2 microns.

### **2.3.2 Sand Filters**

They are generally used to remove metals from produced water. Process requires series of pre-treatment steps such as pH adjustment, an aeration unit and a solid separation unit. The removal efficiency is as high as 90%.

### **2.3.3 Cyclones**

A compact floatation unit (CFU) could remove dispersed oil from 50% to 70% using a centrifugal force. The major drawback of using a cyclone is its low efficiency and inability to remove dissolved components.

### **2.3.4 Evaporation**

Evaporation does not require chemical treatment which eliminates the risk of secondary sludge handling. It also does not require highly skilled labor. On the other hand, the requirement of energy is very high which increases the operating cost. The energy consumption could be brought down by reusing hot vapor to heat the fresh feed.

### **2.3.5 Dissolved Air Precipitation (Dap)**

In this process, water at 500 kPa (for example) is saturated with air in a packed column separator. The pressure is released into the water column which causes the formation of air bubbles. It induces the flotation of aliphatic and aromatic hydrocarbons, and removes the aliphatic compounds more efficiently than aromatic compounds.

### **2.3.6 C-Tour**

It is a patented technology that uses liquid condensate to extract dissolved components from produced water. In field trials, the removal efficiency of dispersed oil was found to be 70%.

### **2.3.7 FREEZE-THAW/EVAPORATION**

This technology uses the principle of solubility dependency on temperature. When the solution is cooled below the freezing point of the solvent but not below the depressed freezing point of the solution, relatively pure crystals of solvent and unfrozen concentrated solutions are obtained. If we couple this process with conventional evaporation, large volumes of clean solvent could be obtained. The process is capable of removing 90% of Total Recoverable Petroleum Hydrocarbons (TRPH). But it has several limitations like the requirements of sub-zero ambient temperatures and large land surface.

## **2.4 CHEMICAL TREATMENT**

### **2.4.1 Chemical Precipitation**

The suspended solids and colloidal particles could be removed by coagulation and flocculation. Several coagulants like modified hot lime, FMA (a mixed metal polymer), Spillsorb, calcite and ferric ions were used as coagulant to treat produced water. The disadvantages of this process are its ineffectiveness for dissolved components and the increased concentration of metals in the sludge formed.

### **2.4.2 Chemical Oxidation**

It uses a combination of strong oxidants (e.g: O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>), irradiation (e.g: UV) and a catalyst (e.g: photocatalyst), and oxidizes the organic components to their highest stable oxidation states.

### **2.4.3 Electrochemical Process**

Almost 90% of BOD and COD could be removed from produced water in a short time (of the order of 6 minutes) by using an active metal and graphite as an anode and iron as a cathode. During the process, Mn<sup>2+</sup> is formed, which oxidizes and coagulates the organic contaminants.

## **2.5 PHOTOCATALYTIC TREATMENT**

The pH of the solution is increased to a value of 11 by adding soda. The photochemical reaction was then carried out on the supernatant obtained from the flocculation unit. Titanium dioxide is usually used as photocatalyst. The COD removal efficiency and toxicity reduction were found to be higher in photoelectrocatalysis than that in photocatalysis.

### **2.5.1 Fenton Process**

Nearly 95% of COD and dispersed oil content can be reduced by combining flocculation with the Fenton oxidation adsorption process. The flocculent used is poly-ferric sulfate.

### **2.5.2 Treatment With Ozone**

Sonochemical oxidation could destroy BTEX compounds but the addition of hydrogen peroxide does not improve the efficiency. The process requires high initial and operating cost.

### **2.5.3 Room Temperature Ionic Liquids**

The hydrophobic room temperature ionic liquids remove certain soluble organic components efficiently, but not much of the other contaminants. Hence, the screening of ionic liquids depends on the constituents of produced water.

### **2.5.4 Demulsifiers**

Some surfactants used as production chemicals are responsible for the stabilization of oilwater emulsions. They reduce the oil-water interfacial tension. Demulsifiers are surfaceactive agents that would disrupt the effects of surfactants. But a number of solids like silts, iron sulphide and paraffin, etc., present in the crude oil complicate the process.

## **2.6 BIOLOGICAL TREATMENT**

The produced water could be treated with aerobic as well as anaerobic microorganisms. The microorganisms disintegrate the organic and ammonia compounds, but could not treat dissolved solids. The COD removal efficiency increased up to 90% while treating produced water with *Bacillus* sp.

## **2.7 MEMBRANE TREATMENT PROCESSES**

Conventional treatment methods are capable of removing suspended particles with particle size of 5.0 or above. The disposal and reinjection regulations are becoming more stringent and the conventional methods are not able to treat produced water which can meet these regulations (Hidney & Parrish, 2006). The general specification for acceptable quality of oil-fields produced water for discharging into surface water (or re-injection) are less than 42 mg/L of oil/water, and less than 10 mg/L of Total Suspended Solids (TSS). Conventional treatment processes are not able to meet these water effluent standards. New

technologies should be utilized to separate both fine particles and dissolved components. Membrane processes are a rather new separation process for treatment of produced water. Membrane separation processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), are able to treat produced water and generate water with high standards to meet regulations. The driving force of the above mentioned membranes processes is pressure gradient.

### **2.7.1 ADVANTAGES OF MEMBRANE TECHNOLOGY**

Membrane technologies have some advantages that make them popular for produced water treatment processes:

- sludge reduction
- high quality of permeate
- smaller space needed
- ease of operation
- minimal impact on permeate quality with variation in feed water quality
- little or no chemicals required
- possibility for recycling of waste streams
- possibility for having an automated plant
- moderate capital costs
- ability to be combined easily with other separation processes
- low energy consumption
- continuous separation

But there may be some drawbacks for using membrane processes including concentration, polarization/membrane fouling, low selectivity or low flux and low membrane lifetime.

According to the above mentioned advantages, that membrane separation processes can, in some circumstances, be viable for treatment of produced water.

### **2.7.2 MEMBRANE PROPERTIES**

There are different types of membrane processes, membrane materials, and feed water compositions, but the main goal of preparing the membranes is the same. An ideal membrane should:

- be mechanically resistant
- have a high permeate flowrate
- have a high selectivity for a specific component

Having high permeate flowrate means having large pore sizes. A high level of selectivity for a certain component is achievable with small pore sizes and the range of pore sizes should be narrow (Kohl & Nielson, 1997). The last two parameters present a dilemma, as one is in conflict with the other. The membrane mechanical resistance depends on the membrane thickness. Therefore the membrane should have a thin layer of material (the selective layer), narrow pore sizes, and high porosity. According to the

type of materials and mechanism of separations, membranes may be categorized as porous or dense. Separation of dense membranes is based on physicochemical interaction of permeate and the membrane material. Separation mechanism of porous membranes is based on the mechanical separation by size of permeates and pore sizes of membrane (sieving).

## 2.8 TYPES OF MEMBRANES

Membranes can be generally classified based on their structure or morphology. Symmetric and asymmetric membranes are two classes. Symmetric membranes have different types including isotropic microporous, nonporous dense membrane, and electrically charged membranes. Asymmetric membranes are divided into Loeb-Sourirajan anisotropic, thin-film composite anisotropic, and supported liquid membranes. Membranes can also be classified based on the type of materials like ceramic, inorganic, and composite membranes.

### 2.8.1 POLYMERIC MEMBRANES

Polymeric membranes have some advantages including high efficiency for the removal of particles, emulsified and dispersed oil; small size; low energy requirements, and being cheaper than ceramic membranes (M, 2013). They also have some disadvantages including the inability to separate volatile and low molecular weight compounds, fouling problems due to oil, sulfide or bacteria which may be required to be cleaned daily, an inability to be used at temperatures above 50 °C, and they also create the possibility of having radioactive byproduct in the effluent and need for some pre-treatment processes.

Process	Mechanism of	Material/Type	Typical Objective
Microfiltration (MF)	Separation by sieving through macropores (>50 nm)	Polymeric and inorganic / Porous	Removal of suspended solids, large organic molecules, and large colloidal particles including microorganisms
Ultrafiltration (UF)	Separation by sieving through mesopores (2-50 nm)	Polymeric and inorganic / Porous	Removal of large dissolved solute molecules and suspended colloidal particles, including bacteria and
Nanofiltration (NF)	Separation through combination of charge rejection, solubility- diffusion	Polymeric / Dense	Removal of multivalent ions and specific charged or polar molecules

Reverse Osmosis (RO)	Separation is based on the difference in solubility and	Polymeric / Dense	Removal of low molecular weight components such as inorganic ions
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**Table 1.** Membrane processes

Polymeric membranes are prepared from materials like polyacrylonitrile (PAN) and Polyvinylidenedifluoride (PVDF). These membranes are relatively cheap. Polymeric membrane should be tested via integrity testing to be sure that they are not damaged. Their life cycle is approximately 7 years. Polymeric membranes can be used to treat feed streams containing high TDS contents. Their efficiency for dead-end and cross-flow operations are 85% and 100%, respectively.

## 2.8.2 INORGANIC MEMBRANES

Inorganic membranes have better chemical and thermal stability than polymeric membranes. There are four different types of inorganic membranes, such as ceramic membranes, glass membranes, metallic membranes (including carbon), and zeolitic membranes are utilized in MF and UF processes (Manning, Thompson, Manning, & Buthod, 1991). Metallic membranes are prepared from metal powders like stainless steel, tungsten or molybdenum. Ceramic membranes are synthesized from a combination of metals like aluminium, titanium, silicium, or zirconium with non-metals like oxides, nitrides, or carbides. Aluminium oxide ( $Al_2O_3$ ) and zirconium oxide ( $ZrO_2$ ) are the most important materials for ceramic membranes. Glass membranes (silica or  $SiO_2$ ) can also be considered as ceramic membranes. Zeolite membranes are new set of membranes.

### 1) CERAMIC MEMBRANES

Ceramic membranes are prepared from nitrides, oxides, or carbides of metals like zirconium, titanium, or aluminum. Tubular modules have been the most widely used, and in which the feed flows inside the membrane channel. Tubular membranes consist of a porous support layer (typically-alumina), one or more decreasing pore diameter layers and an active layer responsible for separation alumina, zirconia, etc.). Ceramic membranes have some advantages including higher flux due to their higher porosity, more hydrophilic surface than organic membranes, better recovery performance of the membrane due to better resistance against mechanical, thermal, and chemical stress than organic membranes. The main advantage of ceramic membranes is its capability to meet the current water treatment effluent standards with no chemical pre-treatment. Ceramic membranes have some disadvantages including sealing problems because of thermal expansion of ceramic membrane, and module housing. Ceramic membranes should be handled carefully as they are brittle. Another advantage of ceramic membranes is a greater removal of the

particles at higher flux than polymeric membranes due to well-defined pore distribution of the ceramic membranes. Membrane fouling is one of the problems associated with usage of membranes in produced water treatment processes, but the high chemical and thermal stability of the ceramic membranes will make the chemical and thermal cleaning methods possible; this is not the case for the polymeric membranes. Thermal and chemical stability of mullite ceramic membranes are very high compared to other ceramic membranes. They are very cheap as they can be produced by extruding kaolin clay. Organic matter, oil and grease, and metal oxides can be removed using ceramic membranes but dissolved ions and dissolved organics cannot be separated and some pre-treatment processes like pre-coagulation, straining or cartridge filtration should be utilized (Mokhatab, Mak, Valappil, & Wood, 2014). Feed streams containing high amount of total dissolved solids (TDS) can be treated using ceramic membranes, but high ion-concentration may cause irreversible fouling. Based on several studies, it was concluded that ceramic membranes have better performance, lower energy requirement, longer life cycle (more than 10 years), but it requires higher capital cost, than polymeric membranes. effluent of Tehran refinery. Effects of the transmembrane pressure (TMP), cross flow velocity (CFV) and temperature on permeate flux; total organic compound (TOC) and fouling resistance (FR) were investigated. The recommended working conditions were 1.25 bar for the transmembrane pressure (TMP), 2.25 for the cross flow velocity (CFV) and 32.5 °C for temperature. Backwashing was stated to be useful to prevent the declination in permeate flux. Oil and grease content was reduced to 4 mg/L therefore meeting the National Discharge Standard, and total organic compound removal efficiency was more than 95%. These systems were recommended to replace the conventional wastewater treatment method. In a different study, ceramic microfiltration was used for treating produced water from two onshore and two offshore pilot plants. Dispersed oil and suspended solids concentration were less than 5 mg/L and 1 mg/L, respectively, in permeate stream. Produced water was pretreated to avoid membrane fouling. At suitable membrane pore size and cross velocity, flux was increased up to 1750 gal/ft<sup>2</sup>D.

## **2) ZEOLITE MEMBRANES**

Zeolite membranes have attracted much research in separation of ions from aqueous solutions by reverse osmosis. The separation mechanism includes electrostatic repulsion (Donnan exclusion) at intercrystalline pore entrances and size exclusion of hydrated ions. These special kinds of separations have made the zeolite membrane a unique separation process for the removal of organics and electrolytes from water by RO processes. Zeolite membranes are mostly used in composite structure due to their high fragility. Composite zeolite membranes consist of a thin film of zeolite supported on a porous material like ceramics, metal glasses, and porous alumina. Among different support materials, alumina is the most widely used. Some studies for zeolite composite membranes will be presented in the following section.



### 3) COMPOSITE MEMBRANES

Fouling resistance of hydrophilic NaA membrane was better than tubular ceramic membrane. In general, zeolite membranes are cheaper than ceramic membranes. Silica and alumina reagents like TEOA and sodium aluminate may be used for preparing inexpensive zeolite membranes. The energy-intensive sintering process, which is widely used for preparing ceramic MF membranes, is not needed for preparing zeolite membranes. Zeolite membranes demonstrated good stability against oil fouling and caustic cleaning solutions. Oil rejection efficiency and flux were more than 99%, and  $85 \text{ Lm}^{-2}\text{h}^{-1}$  flux was obtained for water containing 100 mg/L oil. Backwashing with hot water and alkali solution did not affect the membrane performance. It is used as inorganic nano-sized alumina particles for the modification of tubular UF module equipped with Polyvinylidene difluoride (PVDF) membranes. The PVDF- $\text{Al}_2\text{O}_3$  membrane was used to treat oily wastewater from an oil field. Chemical oxygen demand and total organic carbon retention efficiencies were 90% and 98%, respectively. The type of process was cross-flow. It was seen that permeation performance was improved and flux was increased to twice that of unmodified one (Manning, Thompson, Manning, & Buthod, 1991). The antifouling performance of modified membrane was favorable and flux recovery ratio increased to 100% by washing with 1 wt% (commercial) OP-10 surfactant solution. The permeation water quality met the requirement for oil field injection or drainage. Oil content and suspended solids content were both 1 mg/L after membrane treatment, and was therefore demonstrated that PVDF- $\text{Al}_2\text{O}_3$  composite membrane can be used in oily wastewater treatment. Four commercial thin-film composite polyamide membranes including RO membrane, two ultra-low pressure RO membranes, and one NF membrane were used for treatment of produced water to reach the standards of potable and irrigation waters. Produced water from sandstone aquifers was treated using a two-stage membrane unit. TOC concentration was less than 200 mg/L. The system can recover 60-80% iodide which causes the final concentration of iodide in retentate to be more than 100 mg/L and can be used for commercial iodide recovery purposes. Molecular sieve zeolite membranes were prepared on the inner surface of tubular -alumina substrate, and produced water was treated in a RO separation process. Good ion rejection and chemical and mechanical stabilities led to the conclusion that molecular sieve zeolite membrane can be used in produced water purification, while polymeric membranes have many problems with fouling and structure instability. The overall ion rejection was 98.4% for synthetically produced water, the separation of NaCl solutions in presence of counter-ions or at increased pressure and concentration from produced water employing a pure silicate zeolite membrane synthesized on a commercial tubular -alumina substrate (PALL, pore diameter= 2m). Ion and water transport are highly dependent on the operating pressure, feed ion concentration and solution chemical composition. Exponential increase of ion flux was due to increasing feed ion concentration. Reductions in ion rejection rate and water flux were seen in

the presence of high valence cations. It was suggested that the MFI-type zeolite membrane can be used for the desalination of produced water.

#### **4) MEMBRANE BIOREACTOR (MBR)**

A membrane bioreactor (MBR) has two steps including the activated sludge process in which produced water is treated biologically and the membrane filtration process which biomass (activated sludge) is separated from treated water using the membrane. MF and UF are used for the separation process. Better effluent quality will be obtained using an MBR compared to conventional activated sludge process (Kohl & Nielson, 1997). Use of membrane bioreactors has some advantages over conventional methods for treating produced water which includes lower energy costs, compactness, no need for chemical additives, low sludge production, high loading rate capacity and high quality of the treated water. There are few studies available for treatment of produced water using an MBR.

#### **5) MEMBRANE DISTILLATION**

Membrane distillation (MD) is a separation process based on a thermally driven membrane. Vapour pressure gradient is the driving force for mass transfer through the membrane. MD is the only membrane separation process where the performance does not change with changing of feed TDS content. Operating cost of MD is lower than conventional distillation processes. The following materials are typically used for MD: Polyvinylidenedifluoride (PVDF), Polypropylene (PP), and Polytetrafluoroethylene (PTEE). Flat-sheet and hollowfiber are two typical modules for MD. Direct contact MD (DCMD), vacuum MD (VMD), seeping gas MD (SGMD), and air gap MD (AGMD) are four different methods of MD operation. Direct contact membrane distillation (DCMD) separation process utilizes a hydrophobic microporous membrane which in one side has a hot brine feed and on the other side a cold distillate stream (Stewart & Arnold, 2011). Water vapor passes through the membrane pores from the hot brine section. For treating hot brines, if reverse osmosis (RO) process was to be used, the feed should first be cooled which requires some energy, but DCMD process can treat hot feed streams without cooling which is an advantage of DCMD over RO process. Furthermore, the application of DCMD process above 100°C eliminates porous substrates which are required for low temperatures. Produced water feeds with TDS content of more than 35000 mg/L can be processed using MD and all non-volatile solutes (like Na, B and heavy metals) are rejected with a theoretical efficiency of 100%, but the diffusivity of compounds having higher volatility than water, diffuse faster through the membrane. As a pre-treatment, pre-filtration of feed is required to remove all compounds which may wet the hydrophobic surface of the membrane. MD systems have larger footprint than nanofiltration or reverse osmosis systems.

### **2.8.3 COMMERCIAL TREATMENT PROCESSES**

#### **Reversed Osmosis based processes**

These are the various types of reversed osmosis processes;

##### **1) CDM Technology**

CDM Smith produces a technology that is a combination of three major processes such as ion exchange process, reverse osmosis and evaporation. It is mostly used to treat high TDS coal bed methane (CBM) produced water (A.H, 2004). UV disinfection is also included to reduce the bacterial activity. The total cost of treatment per barrel of produced water was found to be \$0.30. The inclusion of pretreatment processes reduced the membrane fouling to a great extent, and water recovery ranged from 50% to 90%.

##### **2) Veolia: OPUSTM – Optimized pre-treatment and separation technology**

It is designed to treat sparingly soluble solutes (e.g., SiO<sub>2</sub>, CaSO<sub>4</sub>, and Mg(OH)<sub>2</sub>), organics, and boron. The raw produced water is acidified and degasified. It is followed by Multiflo<sup>TM</sup> chemical softening, which is a series of coagulation, flocculation and sedimentation. Decant from sedimentation is fed into packed-bed media filtration column. The microorganisms present would be removed by IX resin (A.H, 2004). Water is then pressurized and treated by BWRO (Brackish Water Reverse Osmosis) membrane at high pH. The entire process system could fit on a cargo trailer. Produced water recovery is estimated to be greater than 90%.

##### **3) Eco-sphere: Ozonix<sup>TM</sup>**

Ozonix<sup>TM</sup> is primarily used for the treatment of frac flow-back water, but it could also be used for produced water treatment. The feed water is mixed with supersaturated ozonized water in a reaction vessel. The hydroxyl radicals, formed from ozone, readily oxidize metals, and decompose soluble and insoluble organic compounds and microorganisms (A.H, 2004). The reaction vessel had two electrodes to induce precipitation of hard salts. Water is then treated with activated carbon cartridge filter and a RO membrane. Water recovery approaches 75%.

##### **4) GeoPure water technologies**

The GeoPure desalination process is a combination of pre-treatment, ultrafiltration and reverse osmosis. This technology was developed for the treatment of oil and natural gas produced waters. Water recovery was reported to be 50%.

#### 2.8.4 BENTONITE

Bentonite is an absorbent aluminium phyllosilicate, which is essentially impure clay consisting mostly of montmorillonite. There are different types of bentonite, each named after the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca) and aluminium (Al). Experts debate a number of nomenclatorial problems with the classification of bentonite clays. Bentonite is usually formed from weathering of volcanic ash, most often in the presence of water. However, the term bentonite, as well as a similar clay called tonstein, has been used to describe clay beds of uncertain origin. Bentonites have excellent rheological and absorbent properties. For industrial purposes, two main classes of bentonite exist: sodium and calcium bentonite. Sodium bentonite expands when wet, absorbing as much as several times its dry mass in water. Because of its excellent colloidal properties, it is often used in drilling mud for oil and gas wells and for geotechnical and environmental investigations. Calcium bentonite is a useful adsorbent of ions in solution, as well as fats and oils, and is a main active ingredient of fuller's earth, probably one of the earliest industrial cleaning agents (G.R, August/september 1996). Calcium bentonite may be converted to sodium bentonite (termed sodium beneficiation or sodium activation) to exhibit many of sodium bentonite's properties by a process known as "ion exchange". Bentonites are environmentally safe providing dust abatement procedures which are used in processing and handling. Bentonite also has the interesting property of adsorbing relatively large amounts of protein molecules from aqueous solutions. Therefore, it is uniquely useful in the process of wine making, where it is used to remove excessive amounts of protein from white wines. Were it not for this use of bentonite, many or most white wines would precipitate undesirable flocculent clouds or hazes upon exposure to warmer temperatures as these proteins become denatured. It also has the incidental use of inducing more rapid clarification of both red and white wines. Bentonite can also be used as a desiccant due to its adsorption properties. Bentonite desiccants have been successfully used to protect pharmaceutical, nutraceutical and diagnostic products from moisture degradation and extend shelf life. In fact, in most common packaging environments, bentonite desiccants offer a higher adsorption capacity than silica gel desiccants. Bentonite complies with the FDA for contact with food and drugs (Food and Drug Administration 2011). As far as adsorptive properties are concerned, bentonite clay has an overall neutral charge; it has an excess negative charge on its lattice and is characterized by a three-layer structure with two silicate layers enveloping an aluminate layer. This arises from the partial replacement of tetravalent silica with trivalent aluminium that leads to the replacement of trivalent aluminium with divalent calcium. Since opposite charges attract, the negatively charged surface lattice of the bentonite clay may have an affinity for cationic dye. Thus, it could be assumed that bentonite clay may have a greater capacity to adsorb cationic dye as it exhibited high removal of cationic Basic Blue 9 and Thioflavin T dyes (Ramakrishna and Viraraghavan 1997). Bentonite has been used to remove a number of chemical species: amines (Breen 1991); organic pigments (carotenoids) (Gonzalez-Pradas et al. 1991); cations (Ni, Zn), phenol and ketones (Stockmeyer and Kruse

1991); phosphates, pesticides, chlorophyll and non-ionic contaminants. Bentonite has proven to be a promising economic material for the removal of dyes due to its abundance and availability.

## **2.9 METHODS OF DETERMINING THE TOTAL HYDROCARBON IN OILFIELD EFFLUENT WATER**

### **2.9.1 Field Measurement Methods**

While reference methods are essential for compliance monitoring, comparison of results and the development of future legislation, developments, they are not always user-friendly, and in some cases they may even be impossible to apply. Also, from an operational standpoint, one often requires results quickly. This is particularly true when a production process is being optimised. Analysis using some of the reference methods such as GC-FID and gravimetry, can be time consuming. Instruments and methods for use in the field that are easy, inexpensive and rapid, offer advantages and are often needed.

Field instruments and methods can be grouped into two major categories – laboratory bench-top and online monitors. Bench-top instruments and methods used for routine oil-in-water analysis may be correlated to the reference methods so that results can be submitted in compliance reports. Online monitors are used for process trending and detection of process deviation. They are advantageous in process optimisation.

### **2.9.2 BENCH-TOP**

There are a significant number of bench-top instruments on the market for the measurement of oil in produced water. Techniques used include the following:

- Colorimetric;
- Fibre optical chemical sensor;
- Infrared
- Horizontal Attenuated Total Reflection (HATR);
- Using S-316 as an extraction solvent;
- Using Supercritical CO<sub>2</sub> as an extraction solvent;
- Solventless;
- Using a non-conventional wavelength for detection;
- UV absorption;
- UV fluorescence.

#### **1) COLORIMETRIC**

In a colorimetric method, oil in water is determined by extracting a sample with a solvent and then directly measuring the colour in the sample extract using a visible spectrophotometer at a wavelength, for example, of 450 nm. It is critically important that the oil in the contaminated water must show colour. A

colourless oil is undetectable by this method. As a result for water samples collected from gas and gas condensate installations, such a method may not work properly. A well-established colorimetric method is provided by Hach (Hach Method 8041), which has the measurement range of 0–80 ppm. But according to a comparison study (Lambert et al. 2001), such a method is best suited for water samples containing dark coloured oil in a concentration range of between 10 and 85 ppm. The colorimetric method is widely used by Petrobras in Brazil.

## **2) FIBRE OPTICAL CHEMICAL SENSOR**

A fibre optical chemical sensor is essentially an optical fibre coated with a polymer that can absorb hydrocarbons. Such a sensor comes as a probe. When the probe is inserted into an oily water sample, hydrocarbons are absorbed by the polymer which can change its refractive index. By measuring the amount of transmitted light before and after the absorption of hydrocarbons and through calibration with known concentrations of hydrocarbons, it is possible to measure the oil concentration in an unknown water sample. In principle it should work; however, measurements will depend on the types of oils and how easily the hydrocarbons are absorbed by the polymer. It is also equilibrium based, and as a result, it can take some time before a reading is taken. The probe must be cleaned and re-zeroed after each measurement. According to the manufacturer (Saini and Virgo 2000), PetroSense PHA-100 WL systems have been used by oil operators in the Gulf of Mexico. It is uncertain how well the technology is able to cope with dispersed oil which can actually form the main phase of oil in produced water derived from oil and gas installations.

## **3) INFRARED – HORIZONTAL ATTENUATED TOTAL REFLECTION (HATR)**

In a conventional infrared method, oil concentration is quantified by measuring infrared absorbance after transmitting an infrared light through a cuvette containing sample extract. With HATR, infrared light is reflected at a crystal surface above which a layer of oil is deposited once the solvent has evaporated from the sample aliquot. At each reflection, infrared light is absorbed in a similar way as in the conventional infrared analysis. Therefore by calibration and comparing the absorbance obtained from a sample extract to that obtained from calibration standards with known concentrations, the oil concentration in the sample is determined. This is a well-established technology with portable instruments available from Wilks Enterprise, Inc. These instruments are believed to be widely used by the offshore oil and gas industry. According to Wilks Enterprise, the measurement range is 4–1000 ppm. The sample extract requires evaporation before measurement. It is inevitable that some of the volatile components in the sample extract will be lost during the evaporation process. Therefore, such a method may be less suited for samples taken from gas and gas condensate installations, which may contain a significant amount of volatile hydrocarbons.

#### **4) HORIZONTAL ATTENUATED TOTAL REFLECTION (HATR)**

This is a semi-automatic version of a conventional infrared analysis method. Small volumes of water sample and extraction solvent S-316 are injected into the Horiba instrument. Extraction and separation are then carried out automatically, and a portion of the extract is diverted to a measurement cell. Oil concentration is obtained by measuring the infrared absorbance. This is believed to have been well established and widely used, especially in Asian countries. Although the measurement process is essentially the same as a conventional infrared-based reference method, it is not a reference method. According to the instrument supplier, Horiba, the measurement range is 0 – 200 ppm. Key issues are the use of S-316, which is a CFC, and more importantly, the expenses as discussed in the early sections.

#### **5) INFRARED – USING SUPERCRITICAL CO<sub>2</sub> EXTRACTION**

In this method, one uses supercritical CO<sub>2</sub> as an extraction solvent to extract the oil from water samples. Infrared quantification is then carried out on the supercritical CO<sub>2</sub> that contains the extracted oil just like a conventional infrared method. In theory it is easy to understand. In practice, however, the technology is more complicated as it involves pumping liquid CO<sub>2</sub> into a high pressure metal vessel in which a sample bottle is placed until it reaches a supercritical state. On reaching the supercritical state, a portion of the supercritical CO<sub>2</sub> (now containing oil) is diverted to a high pressure infrared cell for quantification. After analysis is carried out, CO<sub>2</sub> is vented directly to the atmosphere. This interesting technology does not require the use of CFC. Although CO<sub>2</sub> has its health and safety issues, the technology does not produce CO<sub>2</sub>, therefore one can claim that it is environmentally neutral and friendly. The author has tested such an instrument (Yang 2003) and found the results similar to those using other solvents, e.g. tetrachloroethylene. However, for water samples containing heavy oil, it was found that cleaning of the high pressure vessel after extraction can be time consuming.

#### **6) INFRARED – SOLVENTLESS APPROACH**

Recently a solventless approach has been developed. A sample of oil in water is filtered through a special membrane which can retain oil (dispersed). The membrane is dried before it is placed into the instrument, and infrared quantification is done just like a conventional infrared reference method. The key element is the membrane, which apparently can transmit infrared light. The technology is still being perfected before entering the market. One of the key issues will be the effect of solid particles that are often present in a produced water sample. Other issues are related to sample size, and the possible loss of oil (as oil can stick to the internal surface of an injection syringe). According to the supplier, a detection range from 3 to 200 ppm is covered (Smith and Martin 2008). Also it is believed that the supplier of the technology is working towards a single-laboratory validated method acceptable to ASTM.

## 7) INFRARED – USING A NON-CONVENTIONAL WAVELENGTH FOR DETECTION

This is a new technology based on Quantum Cascade Laser Infrared (QCL-IR) technology in which an oily water sample is extracted by a cyclic hydrocarbon, such as cyclohexane or cyclopentane. Quantification is then carried out by measuring absorbance at a wavelength in the region of 1350–1500  $\text{cm}^{-1}$  using mid-infrared spectroscopy that employs a Quantum Cascade Laser as a light source. By exploring the difference and through calibration, one can calculate the oil concentration in a water sample. The technology is new. There is now an instrument available called “Eracheck” which according to the supplier has a measurement range of 0.5–1000 ppm. 5.1.8 UV Absorbance like aliphatic hydrocarbons which absorb infrared at certain wavelengths, aromatic hydrocarbons absorb ultraviolet (UV) light. Therefore by measuring the UV absorbance of a sample extract in a similar fashion to the reference infrared method, but using UV spectroscopy, one can quantify aromatic hydrocarbons in an oily water sample (Devold, 2006). Provided that the ratio of aromatic hydrocarbon content to that of the total hydrocarbon content remains relatively constant, the total hydrocarbon content can be obtained via calibration. The UV absorbance technique has not been widely used for oil in produced water measurement.

## 8) UV FLUORESCENCE

When aromatic hydrocarbons absorb UV light, they emit fluorescent light at a longer wavelength. By measuring the intensity of the UV fluorescence light, one can determine the amount of aromatic hydrocarbons, which can be related to the total amount of hydrocarbons providing that the ratio of aromatics to total hydrocarbons remains relatively constant. UV fluorescence instruments have been widely used by the oil and gas industry for the measurement of oil in produced water. Portable instruments are available on the market, for example, the TD-500 from Turner Designs Hydrocarbon Instruments (Brost 2008) and Fluorocheck from Arjay Engineering (Reeves 2006). Both of these are handheld and easy to use. The UV fluorescence technique is the second most widely used and accepted after infrared. It is very sensitive and requires no use of CFC solvents, but it is important to remember that should the ratio of aromatic to aliphatic (or aromatic to total hydrocarbons) change due to, for example, the inclusion of new oil streams from different fields, then a new calibration should be established before a measurement is carried out.

## 9) ONLINE

There are many techniques that can be used for online oil in water monitors. A list of these techniques is given below.

- . Focused ultrasonic acoustics



- . Fibre Optic Chemical Sensors
- . Image analysis
- . Light scattering and turbidity
- . Photoacoustic sensor
- . UV fluorescence including Laser-Induced Fluorescence (LIF).

## **2.9 DEFINITION OF ADSORPTION AND ITS APPLICATION**

### **2.9.2 ADSORPTION**

This is a phenomenon commonly used in the gas phase, but can effectively be used for water and waste water treatment. Adsorption has a great advantage over other methods of water and wastewater treatment, especially when biomass is used. The major disadvantage in this process is its non-selective (i.e. it cannot isolate each pollutant and get it removed independently of one another) all contaminants are getting concentrated on the surface of adsorbent. Unlike ion exchange the processes are selective to the ions it needs to adsorb by selecting the ion in such a way that it is having affinity only that ion. Adsorption is understood to be a process involving interface accumulation or concentration of substances at a surface of the material. Adsorption is a phenomenon which normally takes place in an interface of any two surfaces, such as gas-liquid, gas-solid, liquid-liquid or liquid-solid interface. Meanwhile on the process of adsorption, absorption can also take place, and is a process by which molecules or atom of one phase interpenetrates nearly uniformly in to another phase to form a solution<sup>13</sup>. Important models used in this system are adsorption isotherm which describes the adsorption behavior at equilibrium. Point of saturation is normally attained when no further adsorption can take place. Typically, the mathematical correlation, play an important role towards the operational design, modeling and practical application of the adsorption systems (G.R, Environmental solutions, 1996). Recently, researchers have shown an increased interest in the use of adsorption reaction models to describe the kinetic process of the systems. Studies on the use of biomaterials such as adsorption of copper by Spent yeast<sup>15</sup>, biointerface of copper, zinc, cadmium and lead<sup>16</sup>, adsorption of Cu<sup>2+</sup> from aqueous solution onto iron oxide coated egg shell powder<sup>17</sup>, have yielded positive kinetic results with good correlations. The results of investigation by Ali et al<sup>18</sup> and Arief et al<sup>19</sup>, show that, modified Oil Shale Ash and Ceratonia Siliqua Bark are promising adsorbent for removal of heavy metals with high correlation values which obey pseudo second order kinetic models. Biosorption of heavy metals from aqueous solutions generally, is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluent.

### 2.9.3 ADSORPTION ON CLAYS AND CLAY MINERALS ADSORBENTS

Several adsorbents were used for the removal of these pollutants. One of an effective and low cost adsorbents is clays and clay minerals. Natural clay minerals due to their high surface area and molecular sieve structure are very effective sorbents for organic contaminants of cationic or polar in character. Natural and modified clay minerals and zeolites are good adsorption technique for the Removal of Organic Pollutants from Water and Wastewater candidates for improving activated carbon(AC) performance, because they have large surface areas for retention of pollutants. Adsorbent prepared from organoclays and activated carbons were shown to remove a variety of organic contaminants. Montmorillonite was applied as adsorbent for the removal of cationic surfactants, while the hydrophilic surface of montmorillonite was modified and used as adsorbent. Calcined hydrocalcites was prepared and used to remove organic anionic pesticides from polluted water. Vesicle clay complexes in which positively charged vesicles composed of didodecyldimethyl- ammonium bromide (DDAB) were adsorbed on montmorillonite and removed efficiently anionic (sulfentrazone, imazaquin) and neutral (alachlor, atrazine) pollutants from water. These complexes (0.5% w:w) removed 92-100% of sulfentrazone, imazaquin andalachlor, and 60% of atrazine from a solution containing 10 mg/L. A synergistic effect on the adsorption of atrazine was observed when all pollutants were present simultaneously (30 mg/L each), its percentage of removal being 85.5. Column filters (18 cm) filled with a mixture of quartz sand and vesicle.clay (100:1, w:w) were tested. For the passage of 1 L (25 pore volumes) of a solution including all the pollutants at 10 mg/L each, removal was complete for sulfentrazone and imazaquin, 94% foralachlor and 53.1% for atrazine, whereas removal was significantly less efficient when using activated carbon. A similar advantage of the vesicle.clay filter was observed for the capacities of removal. Mesoporous silica materials is performed using self-assembling micellar aggregates of two surfactants: cetylpyridinium bromide (CPB) and cetyltrimethylammonium bromide (CTAB). The retention properties have been studied of these two kinds mesoporous silicas towards environmental pollutants (mono-, di-, tri-chloroacetic acid, toluene, naphthalene and methyl orange). The effect of the composition (presence and absence of surfactants, different kinds of surfactants) on the sorption performance has been considered. They found that materials show excellent retention performance toward chloroacetic acids, toluene, naphthalene and methyl orange. The materials without surfactants does not show, if any, affinity for ionic and non-ionic analytes. The applicability of mesoporous aluminosilica monoliths with three-dimensional structures and aluminum contents was studied as effective adsorbents of organic molecules from an aqueous solution. Mesocage cubic aluminosilica monoliths were successfully fabricated using a simple, reproducible, and direct synthesis. The acidity of the monoliths significantly increased with increasing amounts of aluminum species in the silica pore framework walls. The batch adsorption of the organic pollutants onto (10 g/L) aluminosilica monoliths was performed in an aqueous solution at various temperatures. These adsorbents Modified clays were used as adsorbents for the removal of organic pollutants from wastewater.

#### **2.9.4 CLAY AND ORGANICALLY MODIFIED CLAY**

A relatively new technology for the retention and adsorption of organic pollutants involves the use of, organically modified clays. The accessible surfaces within the crystalline structure of clay minerals are chemically modified with organic derivatives such as alkyl ammonium ions. This clay modification imparts an organophilic character to the clay. The clay surface is thus rendered suitable to adsorb organic molecules. Clays such as bentonite have been used for many years as Pond and landfill liners because of their low permeability to water (G.R, American water works Association, 2002). The low permeability of these clays has been shown to be affected adversely by fluids containing organics. Organically modified clays allow an extension of clay barrier technology into organic systems. As a result of the affinity between organically modified clays and organic pollutants, applications for their use in waste treatment and remediation have evolved. These applications include:

- 1) Waste stabilization - organically modified clay is mixed with organic wastes and then cementing agents to produce a solidified matrix, resulting in reduced leachability of the organics from the stabilized matrix.
- 2) Water treatment - organically modified clay is used for treatment of ground and surface water to remove organic constituents within the waste stream.
- 3) Spill control - organically modified clay can be distributed on water or soil surfaces to sorb organic liquids as necessary for spill control.
- 4) Tank farm liners - organically modified clay can be used in liner systems for fuel oil storage tanks.
- 5) Hazardous waste liner systems - organically modified clay can be used as a barrier layer component within liner systems for hazardous waste storage and disposal sites.

The use of organically modified clays in hazardous waste management applications offers a significant new and untapped potential. These clays may be used in the stabilization of organic wastes and organically contaminated soils, for waste water treatment, for oil spill control, for liner systems beneath fuel oil storage tanks, and as a component within liner systems of hazardous waste storage treatment and disposal facilities. Organically modified clays (organophilic clays) may be employed in each of these systems to adsorb organic waste constituents, enhancing the performance of these applications. This paper first describes the nature of organophilic clays, and then discusses their application in each of the five areas.

#### **2.9.5 ORGANIC MODIFICATION OF CLAYS**

The investigation of clay organic interactions began over 50 years ago. An early study reacted organic bases and their salts with montmorillonitic clays and presented evidence that an ion exchange reaction had occurred. Similar early experiments using organic chemicals in montmorillonitic clay demonstrated that the exchangeable inorganic cations could be replaced by organic cations, and that uncharged polar compounds could enter the inner layer region without the was also found that bentonite, after reaction with certain organic compounds, gains the properties of swelling and dispersing in organic fluids. These studies describe the clay-organic interactions which impart the organophilic characteristics upon the modified

clay. Since that time, these interactions have proven to be effective and, in many cases, commercially viable in transforming a naturally hydrophilic clay into an organophilic clay.

### **2.9.6 RELEASE OF CATIONS.**

A number of chemical interactions between the clay and organic compound were identified in the organic modification of clays. The primary reactions which occur are adsorption, intercalation, and cation exchange. Additional reactions include ion exchange, anion exchange, protonation of organic molecules at the clay surface, hemisalt formation, ion-dipole coordination, hydrogen bonding, pi-bonding, entropy effects, and covalent bonding. It is beyond the scope of this paper to discuss in detail these reactions, which influence the organic modification of clays. To produce an organically modified clay, an unmodified clay mineral is reacted with an organic compound. In this process, a cationic surfactant, such as quaternary ammonium, replaces the exchangeable inorganic sodium, calcium and/or magnesium ions on the negatively charged surface of the clay. In this reaction, the clay's nature is converted from a hydrophilic to an organophilic condition. Reaction of the clay with the appropriate organic cation will result in a modified clay which will swell and disperse in the presence of a variety of organic liquids. The organic compounds most commonly used to modify clays are quaternary ammonium salts. A quaternary ammonium salt is a form of an organic nitrogen compound in which the molecular structure includes a central nitrogen atom joined to four organic groups along with an acid radical. They are all considered cationic, surface active coordination compounds and tend to be adsorbed on surfaces, thus the term surfactants. The most commonly employed types of quaternary ammonium compounds used to modify clays are dimethyl ammonium, methyl benzyl ammonium, dibenzyl methyl ammonium, and benzyl dimethyl ammonium quats. In the dry process, limited amounts of water are first added to the unmodified clay. The clay is then reacted with the organic compound in a mixer, pug mill or extrusion device. Finally, the reacted material is dried and ground. Since centrifugation is not performed in the dry process, some impurities still exist in the finished clay product. Additional detail regarding the clay manufacture can be found elsewhere. Adsorption on organophilic clays are suitable media for the adsorption of soluble organic compounds from dilute aqueous solutions. This adsorption occurs through electrostatic hydrogen bonding forces at the hydrophilic sites, and by van der Waals forces at the organophilic sites of the organophilic clay. The following factors affect the adsorption of organic compounds from dilute aqueous solutions by organophilic clays:

- a) the nature of the adsorption sites,
- b) the nature of the organic molecules to be adsorbed,
- c) thermodynamic Quantities, and spatial considerations,
- d) Manufacture of Organically
- e) solubility of the adsorbate

### **2.9.7 MODIFIED CLAYS IN THE SOLVENT .**

Portions of the organically modified clays surface which were not are manufactured using either a dry process or a wet process. In a wet process, the unmodified clay is mixed with water, forming a slurry. The resulting slurry is centrifuged to remove inert, non-clay minerals. The supernatant, which contains ultra-pure clay, is then reacted with the specified organic compound. The mixture is filtered, dried and ground. Modified during the organic modification process are still hydrophilic. As a result, adsorption by electrostatic hydrogen bonding with the hydrophilic portion of the adsorbate molecule occurs at these hydrophilic clay sites. On the remainder of the clay surface, which is organophilic, van der Waals bonding occurs. Since adsorption occurs at both types of sites on the clay surface, a balance between the organophilic and hydrophilic clay sites optimizes the adsorption capacity of the clay.

### **2.9.8 ADSORPTION ON CLAYS AND CLAY MINERALS ADSORBENTS**

Several adsorbents were used for the removal of these pollutants. One of an effective and low cost adsorbents is clay and clay minerals. Natural clay minerals due to their high surface area and molecular sieve structure are very effective sorbents for organic contaminants of cationic or polar in character. Natural and modified clay minerals and zeolites are good Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater candidates for improving activated carbon(AC) performance, because they have large surface areas for retention of pollutants. Adsorbent prepared from organoclays and activated carbon were shown to remove a variety of organic contaminants. Montmorillonite was applied as adsorbent for the removal of cationic surfactants, while the hydrophilic surface of montmorillonite was modified and used as adsorbent. Calcined hydrocalcites was prepared and used to remove organic anionic pesticides from polluted water. Vesicle–clay complexes in which positively charged vesicles composed of didodecyldimethyl- ammonium bromide (DDAB) were adsorbed on montmorillonite and removed efficiently anionic (sulfentrazone, imazaquin) and neutral (alachlor, atrazine) pollutants from water. Organic pollution is the term used when large quantities of organic compounds contaminate human resources. It originates from domestic sewage, urban run-off, industrial effluents and agriculture wastewater. Sewage treatment plants and industry including food processing, pulp and paper making, agriculture and aquaculture. During the decomposition process of organic pollutants the dissolved oxygen in the receiving water may be consumed at a greater rate than it can be replenished, causing oxygen depletion and having severe consequences for the stream biota. Wastewater with organic pollutants contains large quantities of suspended solids which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the river bed, rendering it an unsuitable habitat for many invertebrates (G.R, American water works Association, 2002). Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates. Toxic organic pollutants cause several

environmental problems to our environment. The most common organic pollutants named persistent organic pollutants (POPs). POPs are compounds of great concern due to their toxicity, persistence, long-range transport ability and bioaccumulation in animals, travel long distances and persist in living organisms. POPs are carbon-based chemical compounds and mixtures (twelve pollutants) that include industrial chemicals such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and some organochlorine pesticides (OCPs), such as Hexachlorobenzene (HCB) or dichloro-diphenyl-trichloroethane (DDT), dibenzo-p-dioxins (dioxins) and dibenzo-p-furans (furans). PCDD/Fs are released to the environment as byproducts of several processes, like waste incineration or metal production. Many of these compounds have been or continue to be used in large quantities and due to their environmental persistence, have the ability to bioaccumulate and biomagnify.

### **2.9.9 USES AND BENEFITS OF ORGANOPHILIC CLAY**

Organophilic clays find a diverse range of applications in, for example, cosmetics, inks, polishes, chromatography (Klemm *et al.*, 1980), dispersions of hydrophilic polymers in oil, and catalysis (Cornelis & Laszlo, 1982). In this review, four areas of largest application are considered in more detail: i.e. drilling fluids, paints, greases and fibreglass resins. It will be useful at this point to introduce the concept of 'polar activator'. For an organophilic clay to swell in an organic solvent, it is usually necessary for small amounts of polar molecules to be present--typically to the extent of 10-50 wt% based on organophilic clay. If they are not present naturally in the solvent system, the required quantity of, e.g., methanol, acetone or propylene carbonate may need to be added. This concept is developed later.

#### **1) DRILLING FLUIDS**

Circulating drilling fluids have been in use since the mid 1800s. The drilling fluid removes drill cuttings, stabilizes the hole, prevents blow-outs, supports the drill string and casing, transmits hydraulic power to the bit, and lubricates the drill string and bit. Most muds are chosen to be pseudoplastic or thixotropic--the advantages being maximized cutting carrying capacity at low flow rates, slow settling of weighting compounds (e.g. baryte) if drilling stops, relatively easy pumping and separation of solid cuttings, and slow penetration into porous rock formations.

Drilling fluids are usually water-based, but in deep-well drilling (greater than 4000 m) oil-based muds have certain advantages and are being increasingly used despite their considerably higher initial cost. The advantages of oil-based muds are apparent in water-sensitive formations (e.g. swelling shales), in soluble salt formations, and at high temperatures. These muds are also useful for drill-stem lubrication, particularly in drilling curved or 'deviated' wells, and for corrosion protection (e.g. against salts, carbon dioxide and hydrogen sulphide), and have the further advantage of being reuseable. An oil-based mud is a

complicated colloidal system. It is an emulsion of water in diesel oil (a typical ratio would be 15:85 by volume) with organoclay dispersed in the oil phase.

Oil- and water-soluble surfactants help to stabilize the emulsion and render the cuttings oil-wettable. The water phase may contain high concentrations of salt, and oil-soluble polymers may be present to control the filtration properties of the mud. In addition, the driller requires stable rheological and colloidal properties up to depths of 5000 m where the pressure could be 10 s Pa and the temperature 230~ A good organoclay mud satisfies these requirements, provided that the other components of the system are correctly chosen. The water and the organoclay are strongly synergistic in their viscosifying effect, which shows how the yield point of colloidal mixtures of diesel fuel/water/organophilic clay\* varies with water and clay content. A very viscous form of oil-based drilling mud is used as a 'packer fluid' in Arctic production wells. It is pumped into the annulus between concentric casing pipes, and serves to insulate the permafrost from the warm oil. Packer fluids are also used, between the casing and the rock, to protect the casing from corrosive groundwaters and from seismic shock. However, this application is coming under increasing objection from an environmental point of view.

## 2) PAINT

Like drilling muds, paints are an extraordinarily complex colloidal system, and it is a tribute to the formulators that a tin of paint can remain on the shelf for years, and still be suitable for immediate use. Conversely, the chemistry can go away resulting in a dense sediment, flocculation, separation of liquid components or solidification. In oil-based paints, organoclays, although present in minute doses, play a vital role in stabilizing the colloidal system by preventing pigment settling, reducing separation of liquid components, enhancing application properties and controlling absorption into porous substrates. The thixotropic properties of the paint can be accurately controlled by adjusting the type and quantity of organoclay. During application, the high apparent viscosity falls rapidly, enabling a thin film to be readily formed. Once applied, the film must regain viscosity sufficiently rapidly to minimize sagging, but not so rapidly that brushwork imperfections do not smooth out. Which shows the effect of increasing organoclay dose on the sag of various thicknesses of paint film on a vertical surface. demonstrate the high degree of thixotropy resulting from only 0.5 wt% organophilic clay in the paint formulation. Recent years have seen a rapid increase in the variety of solvents used in paint. For instance, ketones and esters are used in synthetic resin-based paints and 'high solids' paints are essentially liquid resins which contain a minimum of volatile solvents. Aerosol paints need to be very fluid, yet the heavy pigment particles should not settle in the can to give a hard, compact sediment. The newer organophilic clays can ensure that the pigment settles to a soft voluminous sediment, which is easily redispersed. greases with increasing organoclay content; acetone was used as the polar activator. The yield-point onset is clearly seen. The standard industrial test method for greases is to drop a cone into the grease, and measure its ultimate penetration. The latter depends on the viscosity/shear rate profile of the grease, but is mainly a measure of the gel strength. Many other chemicals are added to greases, such as antioxidants, rust inhibitors, film

strengthening agents, and extreme pressure agents. Sometimes additives can destroy the gel structure if they are not compatible with organophilic clays.

### **3) FIBREGLASS RESIN**

Fibreglass resin is a 50 wt% solution of low-molecular-weight unsaturated polyester in styrene. By adding an initiator (e.g. an organic peroxide) and a catalyst (e.g. a metal soap) the styrene cross-links the polyester to give a tough thermoset plastic. The liquid resin needs to be thixotropic in order to:

- (i) suspend additives and fillers during prolonged storage,
- (ii) prevent the separation of fibreglass while the resin is curing,
- (iii) prevent sagging while the resin is curing on an inclined mould and
- (iv) enable easy pumping and spraying of the liquid resin.

Fumed silica is the most widely used thixotropic agent, but recent advances in organophilic clay technology, especially in the USA, has seen increasing use of clay-based thixotropes for this purpose.

Polar activators are not needed, since the organophilic clay is able to swell and disperse completely in commercial styrene. The thixotropic properties are similar to those required for paints

The Deer rheometer (concentric cylinder) and Brookfield viscometer (rotating disc) were used. Since the resin has a low apparent viscosity at high shear rates, it is easily sprayed on to the mould. The rate of recovery of apparent viscosity after cessation of shear is important since, as with paints, this affects spreading, sagging and separation of fibreglass. It is generally accepted that approximately two minutes is the optimum time for viscosity recovery. The rate of recovery of apparent viscosity was determined using the Deer rheometer. The cup was rotated with an applied shear stress of 15.3 Pa for 60 s and the shear stress was suddenly reduced to 0.0324 Pa. The rotation rate was then monitored as a function of time. Rapid recovery occurs over the first two minutes. It is evident that the low shear viscosity of a resin system can vary by a factor of 50, depending on the shear history of the sample. This must be taken into account when comparing different viscometers and when comparing different gellants. It is interesting to note that in this recovery experiment the Deer rheometer measures the shear rate at a constant applied torque; consequently the shear rate at which apparent viscosity is measured decreases as recovery proceeds.

### **4) WASTE STABILIZATION**

The remediation of organically contaminated soils and wastes employing stabilization and solidification techniques has become increasingly widespread. The stabilization process is designed to maximize shear strength and minimize the rate of leaching of hazardous constituents from the stabilized matrix into the environment. Conventional stabilization techniques, such as cement and flash, are usually limited to inorganic, metal-bearing wastes. For organic wastes, modified clays have been employed to adsorb organic constituents. Preliminary laboratory data indicate that organophilic clays are effective as stabilization agents. When used in conjunction with conventional cement-based or pozzolanic additives,



organically modified clays are effective in reducing the mobility of organic constituents from the stabilized matrix. Reductions in the mobility of organics has been demonstrated and is the subject of several patents. Organically modified clays are first mixed with the waste to adsorb the organic constituents. In this manner, the organics are chemically bound within the organoclay, thereby reducing the organic interference with the normal cement reactions and lattice formation. The clay, with organic contaminants bound within the clay structure, is then macroencapsulated in a cementitious matrix formed by a cement or pozzolan. This technique, which utilizes an organophilic clay in conjunction with a cement product, is employed by the Silicate Technology Corporation of Scottsdale, Arizona for the stabilization of organic hazardous wastes. In this technique, the leaching potential of the organic constituents is decreased through the use of organophilic clays as compared to techniques using only cement or pozzolan in the stabilization process.

## **5) WATER TREATMENT**

Organically modified clays are used to treat organically contaminated waste water. In this process, the aqueous solution is filtered through organically modified clay and the organic contaminants are adsorbed by the clay. Unlike activated carbon, which adsorbs organic contaminants through surface related phenomena, organically modified clays swell as the organic contaminants are sorbed into the clay structure. Thus, the organic molecules of the contaminant preferably partition into the organic phase of the organoclay instead of the aqueous phase poorly adsorbed, whereas oils and greases are readily adsorbed as a result of their differing partition coefficients, organically modified clays are typically used along with other water treatment technologies.

### **2.9.8 PROPERTIES OF ORGANOPHILIC CLAYS**

Many investigators have reported on the interaction between amines and layer-silicates. Each combination of amine (e.g. primary, quarternary, long-chain, short-chain, poly- amines) and layer-silicate (e.g. montmorillonite, mica, vermiculite) yields a complex with its own unique characteristics, so care must be taken when attempting to interpret the industrial applications of organophilic clays in terms of structures and properties described in the literature.

### **2.9.9 STABILITY OF ORGANOPHILIC CLAYS**

Quaternary ammonium ions are adsorbed highly preferentially on to the cation exchange sites of montmorillonites. Thus solvents do not significantly dissolve amine from the clay, and the structure is stable in the presence of high concentrations of metal cations. The stability of quarternary ammonium montmorillonite complexes has been attributed (Theng et al., 1967) partly to the van der Waals attraction of the hydrocarbon chain with its neighbouring chains and with the clay surface (this effect increases rapidly with increasing chain length), and partly to a thermodynamic stabilization of the quaternary

ammonium ion at the clay surface compared with the same ion hydrated in aqueous solution (Maes et al., 1977). Thus organophilic clay gels are relatively heat stable, and can be used at temperatures up to 250~ This is particularly useful in drilling muds, heatcured paints, and greases. It has also been speculated that water improves gel strength by contributing to edge-edge and edge-face hydrogen bonding in the dispersed clay platelets (Powell, 1982). In most cases, shear forces are required to break up aggregates of clay particles and to ensure that the centre of each aggregate is exposed to solvent. This is particularly important with viscous solvents such as the base oil for grease. Organoclay greases are made under very high shear in a colloid mill. Once a gel has been formed, it is normally stable indefinitely. Occasionally, interactions with other components of the formulation can occur to give flocculation and loss of gel strength. For instance, this can occur in polyester/styrene resins and in greases, where metal soaps may be present. It has been postulated (Powell, 1982) that the soaps coordinate to the clay platelet edges, thus weakening the edge-edge interactions. This deleterious effect can be overcome by adding other components such as amines which preferentially hydrogen-bond with the metal soap. A similar deleterious effect is observed when excess polar activator is added. Again it has been postulated that the excess adsorbs at the clay platelet edges, breaking the edge-edge structure to give a parallel alignment of plates. In support of this, a concentrated organophilic clay gel was reported to develop dilatant characteristics at high polar activator doses (Berezov et al., 1981). This can cause particular difficulty if the solvent itself is polar, for example an ester or alcohol.

**Gellation** The typical manufactured organophilic clay is easily wetted (and swollen to some extent) by most organic solvents. However, to be industrially useful it must consistently disperse into individual platelets, and form a gel in very dilute (e.g. 1.0 wt%) suspensions. In any application of organophilic clays, the solvent system must be given careful consideration since the clays show widely differing gelling ability in various solvents (Slabaugh & Hiltner, 1968; Void & Phansalkar, 1962). Usually it is found that the solvent must contain both hydrophobic and hydrophilic groups or molecules for successful swelling. Thus pure non-polar hydrocarbons do not swell organophilic clays because the hydrocarbon chains of the amine are not solvated to any significant extent by hydrocarbons (Krumgalz, 1982) and thus there is no energetic advantage in swelling. On the other hand, certain polar aromatic solvents such as nitrobenzene and even styrene are particularly effective swelling solvents. This may be because the phenyl group can strongly adsorb on to silicate surfaces (Burba & McAtee, 1981; Dekany et al., 1975) and act as a polar activator. As indicated earlier, polar activators are required in the majority of applications. These are molecules such as MeOH, EtOH, Me<sub>2</sub>CO or propylene carbonate which are added to the extent of 10--50 wt% based on organophilic clay. Several studies have shown that the polar activator can enter the interlayer, adsorb on the silicate surfaces and begin the expansion process. For example, Burba & McAtee (1981) recently showed that glycol can, with certain organophilic clays, actually lift up the aliphatic chain and increase the basal spacing. It appears to be a prerequisite that the aliphatic chain is already somewhat crowded or buckled and not lying flat on the surfaces. In support of this conclusion, it is commonly observed that the gelling ability of an organophilic clay is very sensitive to the amine/clay ratio. Shows how the apparent viscosity

of a hydrocarbon gel varies with this ratio. At low amine doses the clay cannot swell, possibly because the amine chains are lying flat on the silicate surfaces. It will be noted that gellation is also inhibited at higher amine doses. The reason for this is not known. It has been postulated (Powell, 1982) that polar activators also contribute to the gel structure by linking the dispersed clay particles edge-to-edge in a hydrogen-bonding matrix. Perhaps surprisingly, water in small quantities (1-2 wt%, based on organoclay) is also necessary before a gel can be formed. The role of water is uncertain, but it has been found that small amounts can increase the mobility of small quaternary ammonium ions over the surface (Gast & Mortland, 1971). Also, water profoundly affects the zeta potential of organophilic clay dispersed in organic solvents. It has been suggested (Moraru et al., 1980) that water induces dipoles at the clay surface, and perhaps dipolar repulsion is a driving force in the swelling process, after the initiating effect of the polar activator. Sometimes water is deliberately added during the manufacture of organophilic clay greases, especially if hot oil is used in the process. It is often found that methanol/water mixtures are better polar activators than methanol alone, for instance in the manufacture of paints (Lagaly, 1984).

# **CHAPTER THREE**

## **MATERIALS AND METHODOLOGY**

### **3.1 Material Requirements**

- Clay or bentonite
- Quaternary ammonium chloride
- Beakers
- Oven
- Crude Oil
- Micropipette
- Deionized water
- Produced water (with oil sheen)
- pH meter
- DR3000 Spectrophotometer (colorimetric method)
- Adsorber unit or filtration unit
- COD units
- 100X100 Mesh or
- 8 x 30 Mesh (in case granules instead of powdery organoclay are to be used)
- Stopwatch

### **3.2 METHOD**

#### **3.2.1 PREPARATION OF ORGANOPHILLIC CLAY**

If bentonite is unavailable, then the clay that is to be used has to be conditioned by dispersing 200g of it in 1000ml of hot distilled water at 70°C. The suspension will be thoroughly mixed for 90 minutes. The solid will be filtered and dried in an oven maintained at 70°C to a moisture content of < 0.05%. The quaternary ammonium salt will be dissolved in distilled water to have 1M NH<sub>4</sub>CL (90-110 mEq/100 g of a quaternary ammonium salt).

A slurry of the clay and the quaternary ammonium salt solution will be made for 5 different solid/liquid ratio, e.g. 100g clay/100ml salt, 100gclay/200ml salt e.t.c. All samples will be well labeled. Allow the slurry to settle, and then decant. The sediments from each of the slurry will be dried in an oven maintained at 70°C to a moisture content of < 0.05%. Crush to fine particles and sieve.

#### **3.2.2 SAMPLING AND PRESERVATION OF PRODUCED WATER**

- 1) 4litres of produced water will be collected in well labeled glass jars from a nearby flowstation.
- 2) The samples will be preserved below 4°C in ice packed coolers and used within 24Hrs.

### **3.2.3 EXPERIMENTAL PROCEDURE**

- 1) I will determine the total hydrocarbon content using spectrophotometer.
- 2) If the THC in the produced water is high, I will dilute it until it consists 10ppm or below.
- 3) Then I will measure the turbidity and pH value using nephelometer and pHmeter respectively.
- 4) I will measure 50ml of produced water and pass it through the adsorption unit packed with an organophillic clay sample.
- 5) I will Collect the treated produced water from the adsorption unit labeled accordingly to the clay samples.
- 6) Then I will measure the total hydrocarbon content, turbidity and pH value.
- 5) Then I will repeat step 3, 4 and 5 for all the other four(4) samples.

### **3.2.4 COLORIMETRIC METHOD**

Colorimetric method oil-in-water tests measure the absorption of energy in the visible light range. This test only works well with dark oils. The measurement is then correlated to a sample with a known concentration to determine the concentration of the test water. One major problem associated with this method is that a calibration sample of the oil is needed, and if the sampling quality or process flow changes the hydrocarbon ratio in the sample, the analysis can have a large uncertainty and degree of error associated with the final resultant oil-in-water measurement.

### **3.2.5 PROCEDURE**

1. Various samples (5) of the organoclay will be made by varying the solid/liquid ratio.
2. The samples are oven dried at 35<sup>0</sup>C, ground and filtered with 100X100 Mesh.
3. The organoclay is placed in the adsorber unit before allowing the produce water to flow through it.



The ability of clay to remove oil from waste water was studied by adding quantanary ammonium chloride 10, 20, 30, 40 and 50ml respectively to 100g of clay. The wastewater with initial THC of 133.35ppm, the absorbance of the effluent was 0.316 and was measured at 430Nm, the results of this experiment is shown in the table above.

Clay appears to have good capability for oil removal. The total hydrocarbon content of the produced water decreases rapidly from 133.35 to 130.01ppm when no quantity of ammonium chloride was added, and from 133.35 to 57.29ppm when 10ml of ammonium chloride was added, 133.35 to 35.02ppm when 20ml ammonium chloride was added, 133.35 to 25.35ppm when 30ml ammonium chloride was added, 133.35 to 12.74ppm when 40ml ammonium chloride was added and finally 133.35 to 8.96ppm when 50ml ammonium chloride was added respectively. Using quantities of ammonium chloride more than 10ml, the concentration of oil decreases slowly until it reaches 8.96ppm for 50ml.

Oil concentration was not decreased below 10Mg/L(allowable limits of oil in discharged effluent), as shown in figure above. This is because of the hydration of clay which causes that organic compounds with average molecular weights (amu) below 150 are weakly adsorbed or not absorbed by pure montronites (clay) due to their relatively large solubility in water (unless they carry a charge and can enter into an exchange reaction). The interaction forces under these conditions are the same in magnitude as hydration forces, so that competition with water molecules for solid surfaces dominates. Soluble compounds with molucular weights above 150 amu, whether or not charged are often adsorbed by montronites due to their reduced solubilty in water.

### **EFFECT OF QUANTITY OF ORGANOCCLAY ON OIL REMOVAL**

The prepared organoclays with quantanary amine weight ratios of 10,20,30,40 and 50ml/100g clay were investigated to find the quantity of organoclay required to remove the greatest amount of oil from wastewater. Figure below shows the effect of volume of ammonium chloride on the total hydrocarbon content in wastewater with initial concentration of (133.35ppm) and time 100 minutes was used.

As shown in figure, the total hydrocarbon content in wastewater samples decreased rapidly as the quantity of clay remain constant (100g), as the solid/liquid ratio moves from 100g of clay/10ml of ammonium chloride to 100g of clay/50ml of ammonium chloride the THC or oil concentration falls gently. The best quantity of organoclays was 100g clay/50ml ammonium chloride, where the lowest THC obtained from the treated water was 8.69, which represents THC removal capacity of 1.24%.

# CHAPTER 5

## CONCLUSION

- ❖ Clay has a good capacity for oil removal where decreasing the total hydrocarbon content in waste water from 133.35 to 8.96ppm using 2g/ml of organoclay.
- ❖ Spectrophotometer measurements gave good approximation for the exchange quaternary ammonium chloride in specific place of  $\text{Ca}^{++}$  at the surface of the clay to obtain organoclay.
- ❖ The quantity of quaternary ammonium chloride used in the preparation of organoclay has very appreciable effect on the removal of oil from wastewater. As the weight ratio of quaternary amine in the organoclay increases then the oil removal increases. 2g/ml of organoclay with amine ratio of 50ml/100g clay is recommended to remove oil from waste water.
- ❖ The measure of the absorbance at 430Nm of the effluent in tge spectrophotometer was 0.316, and it had considerable effect on the removal of oil from the wastewater. Total hydrocarbon content falls from 133.35ppm to 8.96ppm for operating time of 1.67hours.
- ❖ The calibration curve equation of the spectrophotometer shows that the effluent and samples A, B, C, D, E are 133.35, 57.29, 35.02, 25.02, 12.74 and 8.96 respectively.
- ❖ The PH of the vrious samples gradually decreases in acidity as it falls from 4 to 6 of samples A and E respectively.
- ❖ The degree of turbidity also decreases from 11.3 to 5NTU of samples A and E respectively, but the least degree of turbidity was for sample C with 1.2NTU.
- ❖ Organoclay prepared form clay is very effective in removing oil from wastewater. The best results obtained for the removal of oil from wastewater with THC of 8.96ppm is 2g/ml of prepared organoclay having 50ml ammonium chloride/100g clay using 300ml of wastewater for 14.08min (0.23hrs), with turbidity value of 5NTU and PH value of 6. The flowrate of produce water through the absorber was 21.4ml/min and highest THC removal capacity of 1.24%.



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## **APPENDIX**

Molecular mass of  $\text{NH}_4\text{Cl}$  =  $14+4+35.5=53.5\text{g/mol}$