PRODUCED WATER AEROBIC TREATMENT USING SEQUENCING BATCH REACTOR (SBR)

by

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Dissertation submitted in partial fulfilment
of the requirements for the
Bachelor of Engineering (Hons)
(Civil Engineering)

MAY 2011

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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BACHELOR OF ENGINEERING (Hons)
(CIVIL ENGINEERING)

Approved by,

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May 2011

CERTIFICATION OF ORIGINALITY

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

RANAD ELRASHID ABDALLA MOHAMED

ABSTRACT

This project was undertaken to study produced water treatment using Sequencing Batch Reactor (SBR). The treatment involves both untreated produced water and anaerobic treatment effluent of the produced water. Produced water is the water extracted along with oil and gas. Different physical and chemical methods have been used for its treatment; but their initial and/or running cost are high and produce hazardous sludge. Biological treatment of oily wastewater can be a cost-effective and Eco-friendly method for produced water treatment to comply with discharge limits. The objectives of this project are to apply an aerobic treatment process using bacteria for hydrocarbons and organic matters removal and to compare the effluent quality of an aerobically treated produced water and anaerobically treated effluent followed by aerobic treatment. Therefore project scope is to apply the treatment is applied in to meet discharge limits according to standard B. To treat produced water biologically; aerobically and anaerobically treated effluent followed by aerobically treatment, while studying different biological parameters. Project methodology started with Research and data gathering for produced water, biological treatment and SBR, followed by Sampling from TERENGGANU CRUDE OIL TERMINAL (TCOT). Sludge acclimatization was then applied by diluting produced water into domestic wastewater source of the biomass Produced water characterization. Sequencing Batch Reactor (SBR) was then configured and operated using five phases cycle fill, react, settle, decant and idle. The result showed that the removal efficiency of 73.8% and 82%, BOD removal efficiency is 61.8%, 59.8%, Oil and Grease removal efficiency is 72.5%, 81.25% for anaerobically treated effluent and produced water respectively.

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List OF ABBREVIATIONS

PW	Produced Water
EPRA	Environmental Protection Agency
BTEX	Benzene, Toluene, Ethyl benzene and Xylene
PAH	Polyaromatic Hydrocarbons
SBR	Sequencing Batch Reactor
BAF	Biological Aerated Filters
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
TSS	Total Suspended Solids
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
OLR	Organic Loading Rate
HRT	Hydraulic Retention Time
TPH	Total Petroleum Hydrocarbon

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Produced water is the water trapped in underground formations which comes to the surface during oil and gas exploration and production of oil and gas. Reservoirs have a natural water layer (formation water) that lies under the hydrocarbons as shown in Figure 1.1 below. Reservoirs often contain large volumes of water, while gas reservoirs tend to have smaller quantities (Paul et al., 2005). The rocks in most oil-bearing formations were fully saturated with water before the invasion and trapping of petroleum (Amyx et al., 1960). Hydrocarbons which have less density, migrated to trap locations, displacing some of the water from the formation in becoming hydrocarbon reservoirs. Thus, reservoir rocks normally contain both petroleum hydrocarbons (liquid and gas) and water. (veil et al., 2004).

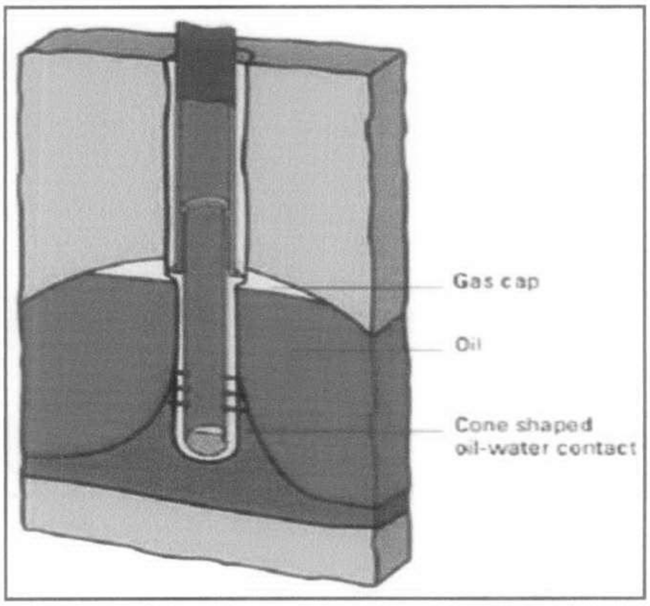

Figure 1.1: Formation Water.

Source: Research Institute of Petroleum Industry.

Produced Water quantities increase as the oil and gas fields reach maturity. Produced water comes as a by-product of petroleum production and requires to be managed efficiently (Nature Technology Solution, 2009).

Figure1.2 below shows the great increase in the water/oil ratio when the oilfield reach maturity and water by far becomes the major fraction of the production.

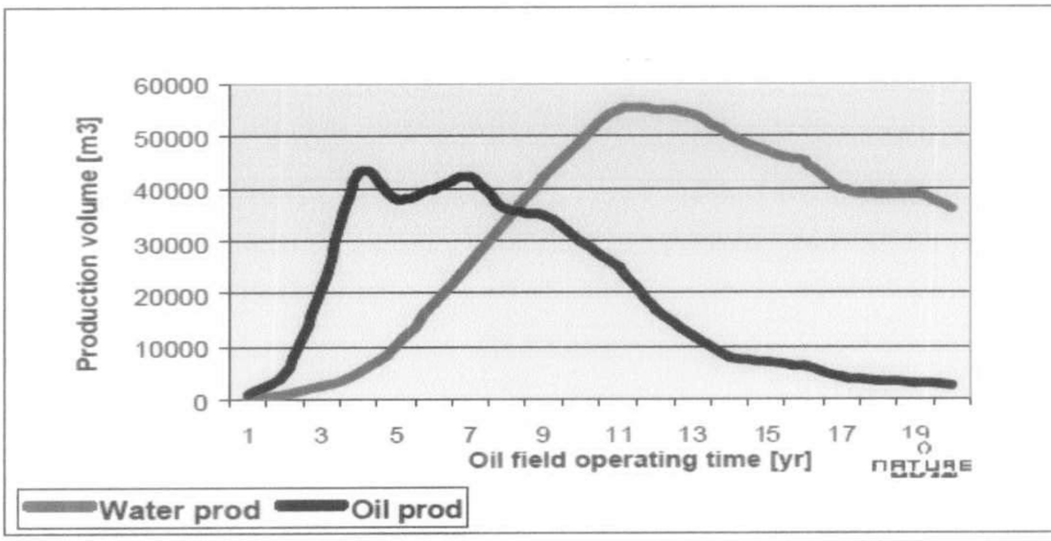

Figure 1.2: Typical production profile for an oilfield in the North East Atlantic.

Source: Nature Technology Solution, 2009.

Research has been carried out to determine the consequences of long-term exposure of produced water on the environment. It is reported that some of the toxic components in produced water may cause permanent damage to the surrounding environment. Due to this potential risk very considerable efforts are being expended by oil companies to develop new techniques for better management of produced water. (Elmara,2010).

Previously, produced water was disposed of in large evaporation ponds; nevertheless this has become an increasingly unacceptable disposal method from both environmental and social perspectives. (Moghadasi et al., 2004; Bader, 2005)

To maintain the hydraulic pressure in the petroleum reservoir, that is reduced as soon as production is started, seawater is commonly pumped into the reservoir water layer below the hydrocarbons (Figure 1.3). This pressure maintenance due to water injection causes high extensions in recoverable hydrocarbons but concurrently contributes to increased water production.

Furthermore it helps achieving maximum oil recovery additional water is often injected into the reservoirs to help force the oil to the surface. Both the formation water and the injected water are eventually produced along with the oil and therefore as the field becomes depleted the produced water content of the oil increases. (Bader, 2005)

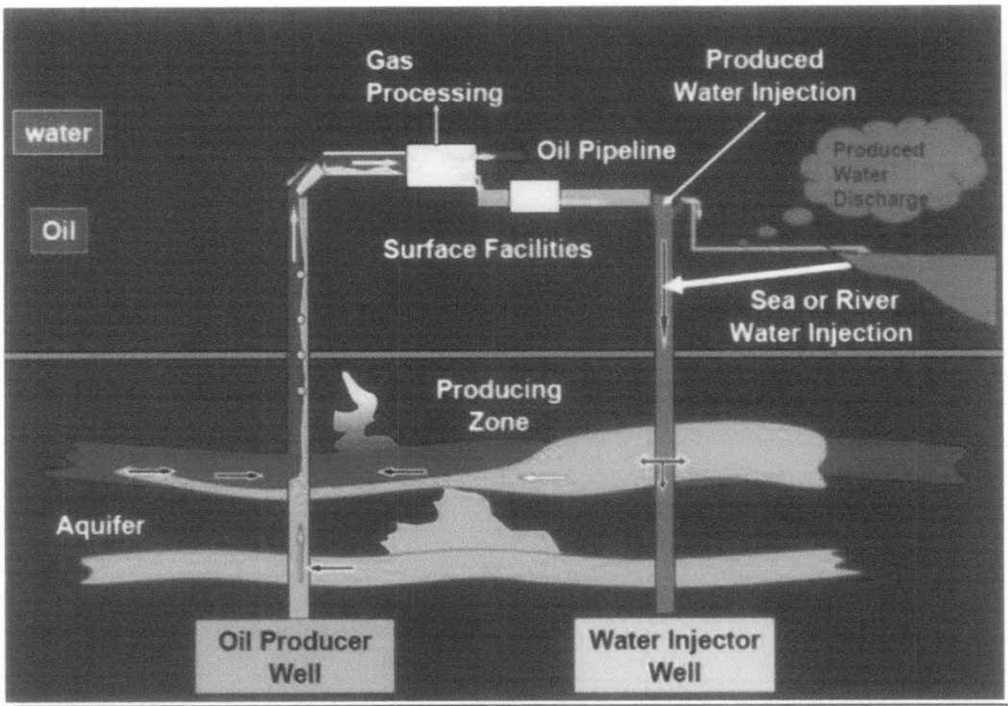

Figure1.3: Injection of separated water from an offshore installation source

1.1.1 Produced Water Origin

Produced water is the largest volume of waste generated by the oil and gas industry. These waters are produced simultaneously during crude oil and natural gas production, at both onshore and offshore operations. The amount of produced water generated is dependent upon the method of recovery, and the nature of the formation. In some formations, large volumes of water are pumped to the surface with the oil and gas in the early stages of production; in others, not until the formation has been significantly depleted.(Gilbert et al, 2002).

Water is very often found together with petroleum in the reservoirs where the water, as a result of higher density than oil, lays in huge layers below the hydrocarbons in the porous reservoir media. This water, which occurs naturally in the reservoir, is commonly known as Formation Water. After oil and gas production for quite longer time, the Formation Water will reach the production wells and water production will initiate. The well water-cuts will normally increase throughout the whole oil and gas field lifetime, such that when the oil production from the field is shut down, the oil content can be as low as a couple of percent with ninety eight percent water. Until now, the majority of the oilfield-produced water in especially in East Asia was injected into the stratum without being treated properly, which could cause a variety of damages to the stratum. (Moghadasi et al., 2004; Bader, 2005). Therefore, the impact of untreated produced water discharged from world oil and gas operations on shallow water coastal wetlands has lately become an issue of considerable environmental concern (Rayle and Mulino, 1992).

1.2 Problem Statement

Produced water is typically treated through different physical, chemical, and biological methods. In offshore platforms, compressed physical and chemical systems are used. Though, current technologies cannot remove small-suspended oil particles and dissolved elements. Besides, many chemical treatments, whose initial and/or running cost are high and produce hazardous sludge. In onshore facilities, biological pre-treatment of oily wastewater can be a cost-effective and Eco-friendly method.

"Oil/water separation technology traditionally used offshore is sensitive to variations in water quality, and some of the technologies are also sensitive to large variations in flow conditions and content of solids. Predictable conditions are often needed for optimum performance of several of the technologies applied. Operational aspects are important for the performance. Integration of oil operating conditions (production chemicals, recirculation of rejects, scale control programs, operation of separators, etc.) with the produced water treatment is important for the performance of the treatment technology." (Vik, 2007).

Since Produced Water has high salt concentration and variations of influent characteristics, it is appropriate to integrate a physical treatment; hence, major research efforts in the future could focus on the optimization of current technologies and use of combined physico-chemical and/or biological treatment of produced water in order to comply with reuse and discharge limits. Produced Water became a global challenge of oil production.

Different methods have been used for Produced Water Management such as reuse in oil and gas operations – Treat the produced water to meet the quality required to use it for drilling, stimulation, and workover operations.(Elmara,2010)

"Consume in beneficial use – In some cases, significant treatment of produced water is required to meet the quality required for beneficial uses such as irrigation, rangeland restoration, cattle and animal consumption, and drinking water for private use or in public water systems."(Daniel et al., 2005)

Operators of industrial facilities are required to submit testing data to the Department of Environment for wastewater discharge from their facilities into any inland waters to demonstrate compliance with the permissible limits as stated in Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979. The table consist of two standards, namely Standard A and Standard B and its stipulated permissible limits for the twenty three parameters that operators of industrial facilities must comply. Table 1.1 describes the parameter limits of effluent discharge. Standard B is a legal requirement for TCOT.

Table 1.1: Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979. Maximum Effluent Parameter Limits Standards A and B. Source: Department of Environment (DOE), Malaysia.

	Parameter	Unit	Standard	
			A	B
	(1)	(2)	(3)	(4)
i.	Temperature	^oC	40	40
ii.	pH Value	–	6.0-9.0	5.5-9.0
iii.	BOD_5 at 20oC	mg/L	20	50
iv.	Suspended Solids	mg/L	50	100
v.	Mercury	mg/L	0.005	0.05
vi.	Cadmium	mg/L	0.01	0.02
vii.	Chromium, Hexavalent	mg/L	0.05	0.05
viii.	Chromium, Trivalent	mg/L	0.20	1.0
ix.	Arsenic	mg/L	0.05	0.10
x.	Cyanide	mg/L	0.05	0.10
xi.	Lead	mg/L	0.10	0.5
xii.	Copper	mg/L	0.20	1.0
xiii.	Manganese	mg/L	0.20	1.0
xiv.	Nickel	mg/L	0.20	1.0
xv.	Tin	mg/L	0.20	1.0
xvi.	Zinc	mg/L	2.0	2.0
xvii.	Boron	mg/L	1.0	4.0
xviii.	Iron (Fe)	mg/L	1.0	5.0
xix.	Silver	mg/L	0.1	1.0
xx.	Aluminium	mg/L	10	15
xxi.	Selenium	mg/L	0.02	0.5
xxii.	Barium	mg/L	1.0	2.0
xxiii.	Fluoride	mg/L	2.0	5.0
xxiv.	Formaldehyde	mg/L	1.0	2.0
xxv.	Phenol	mg/L	0.001	1.0
xxvi.	Free Chlorine	mg/L	1.0	2.0
xxvii.	Sulphide	mg/L	0.50	0.50
xxviii.	Oil and Grease	mg/L	1.0	10
xxix.	Ammoniacal Nitrogen	mg/L	10	20
xxx.	Colour ADMI*		100	200

Table 1.2 shows Terengganu Crude Oil Terminal (TCOT) Produced Water characteristics, this is a typical data from the field; verity parameters have exceeded standard B discharge limits, since it the required standard in TCOT.

Table 1.2: Produced Water characteristics.

Source: Terengganu crude oil terminal (TCOT)

No.	Parameter	Unit	*W-1	W-1	W-1	W-1	[redacted]
1	Biochemical Oxygen Demand (BOD)	mg/L	731	767	844	666	[redacted]
2	Suspended Solids(SS)	mg/L	21	44	31	24	[redacted]
3	Mercury (Hg)	mg/L	0.005	0.003	0.007	0.010	[redacted]
4	Cadmium (cd)	mg/L	<0.005	<0.005	<0.005	<0.005	[redacted]
5	Chromium, Hexavalent (Cr 6+)	mg/L	<0.01	<0.01	<0.01	<0.01	[redacted]
6	Chromium, Trivalent (Cr 3+)	mg/L	<0.01	<0.01	<0.01	<0.01	[redacted]
7	Arsenic (As)	mg/L	<0.005	<0.005	<0.005	<0.005	[redacted]
8	Nickel (Ni)	mg/L	<0.005	<0.005	<0.005	<0.005	[redacted]
9	Tin (Sn)	mg/L	<0.004	<0.004	<0.004	<0.004	[redacted]
10	Zinc (Zn)	mg/L	<0.005	<0.005	<0.005	<0.005	[redacted]
11	Flouride (F)	mg/L	0.90	1.00	0.90	1.40	[redacted]
12	Phenol	mg/L	13.20	3.80	9.20	3.40	[redacted]
13	Free Chlorine (Cl_2)	mg/L	<0.01	<0.01	<0.01	<0.01	[redacted]
14	Sulphide (S 2-)	mg/L	10.4	15.6	13.2	12.8	[redacted]
15	Oil and Grease (O& G)	mg/L	13	12	15	13	[redacted]
16	Ammoniacal Nitrogen (NH3-N)	mg/L	10.8	8.6	8.1	11.4	[redacted]
17	Color	ADMI	63	80	146	70	[redacted]
18	Chemical Oxygen Demand (COD)	mg/L	1479	1647	1835	1329	[redacted]
19	Chloride (Cl-)	mg/L	7878	8232	8055	7967	[redacted]
20	Hardness (CaCO3)	mg/L	825	913	831	650	[redacted]
21	pH		7.2	7.22	6.89	6.97	[redacted]
22	Temperature	°C	48.2	51.5	42.3	40.9	[redacted]

*W-1: Well catogory

Based on the Table1.2, the influent contain relatively high organic load (COD, BOD) which would contribute to environmental pollution if discharged directly into surface waters.

1.3 Objectives

The objectives of this project are:

i. To apply an aerobic treatment process using sequencing batch reactor (SBR) and bacteria for hydrocarbons and organic matters removal.

ii. To compare the effluent quality of an aerobically treated produced water and anaerobically treated effluent followed by aerobic treatment.

The treatment is applied in to meet discharge limits according to standard B.

1.4 Scope of Study

This project is intend to treat produced water biologically; aerobically and anaerobically treated effluent followed by aerobically treatment, while studying different biological parameters, to achieve the required limits of discharge. The scope of the study covered the characterization of produced water and monitoring of sequencing Batch Reactor (SBR) performance base on COD, BOD as mean organic load parameters and pH.

CHAPTER 2
LITERATURE REVIEW

Currently, Environmental standards have led to greater efforts being made to treat Produced Water. Several technologies have been developed for the removal of petroleum pollutants, biological oxygen demand (BOD) and chemical oxygen demand (COD), including flotation (Ebrahimi et al., 2010), chemical precipitation (Doyle and Brown, 2000), chemical oxidation (Bessa et al., 2001), and biological treatment (Lu et al., 2009).

2.1 Overview of Produced Water Treatment Methods

Produced Water can be treated using a variety of technologies; however, the choice depends on its cost, the quality of water required, and local legislation. Among the technologies that have been tested are separation by hydrocyclones (Lohne, 1994), microfiltration (Campos et al., 2002) ultrafiltration through polymer membranes (Cheryan and Rajagopalan, 1998) and more recently electrodialysis (Dallbauman and Sirivedhin, 2005). Biological treatment systems that were examined include activated sludge (Tellez et al., 2002), air lift attached growth (Campos et al., 2002) aerated lagoons (Beyer et al., 1979), wetlands (Ji et al., 2002 and Rambeau et al., 2004), and the Upflow Anaerobic Sludge Blanket (UASB) (Rincon et al., 2003).

Among these technologies, biological treatment is frequently used for the treatment of oilfield produced water because of its high effectiveness and economical feasibility. Biological treatment is an effective and economical concept that can be used in oil de-emulsification and wastewater treatment (Campos et al., 2002). Petroleum hydrocarbon-degrading microorganisms, such as bacteria and fungi have been reported as oil degraders since it can grow using crude oil as a source of carbon and energy. (Atlas, 1981; Wammer and Peters, 2005; Verma et al., 2006).

Numerous laboratory- and pilot-scale experiments have been performed under aerobic conditions, such as stabilization ponds (Shpiner et al., 2009), biological aerated filter (Su et al., 2009), and sequencing batch reactor (SBR) systems (Freire et al., 2001).

In recent years, interest in biological treatment, especially to remove the petroleum-derived compounds in Produced Water, has increased due to more stringent environmental standards and the desire/need to reuse the increasing amounts of water rather than pumping them at high pressure back down the aquifers which is energy intensive and expensive.

2.2 Chemical treatment

2.2.1 Treatment with ozone

Ozonolysis were used for for decomposing dissolved organic compounds in produced water (Morrow, et al, 1999). A study has been conducted for the destruction of soluble organics in synthetic and real produced water by sonochemical oxidation and ozone. Sonochemical oxidation could destroy some compounds such as BTEX, but the combination of ozone and hydrogen peroxide did not improve the oxidation of organics to CO_2. Their experiment showed that during 3 days of exposure to ozone nearly all extractable organics could be destroyed. (Klasson, et al, 2002.)

In addition to the low removal efficiency of chemical oxidation products, high running costs due to the high demand of energy and consumption of chemicals are disadvantages of these methods (Renou et al., 2008).

2.2.2 Demulsifier

In the alkali/surfactant/polymer (ASP), flooding process large quantities of alkali, surfactants, and polymer chemicals are used. During the production process, residual chemicals enter to Produce Water. Surfactants are mainly responsible for the stability of oil droplets, reducing oil–water interfacial tension, and zeta potential on the surfaces of the oil droplets (Deng, et al, 2005).

The 'skin' surrounding the tiny droplets in the oil–water emulsion prevents the water droplets from uniting and the emulsion remains stable. Demulsifiers are surface active agents that are effective in disrupting the effects of natural emulsifiers present in the oil. In most crude oils, solids such as iron sulfides, silts, clay, drilling mud, paraffin, etc. complicate the demulsification process (Holloway, 1977).

2.2.3 Chemical precipitation

Coagulation and flocculation can is used to remove suspended and colloidal particles, but are not effective for removing dissolved constituents. Lime softening is the usual process for water softening. In the modified hot lime process produced water containing 2000ppm hardness, 500ppm sulfides, 10,000ppm TDS, and 200ppm oil could be successfully converted to steam generator quality feed-water. In this process, alkali consumption and sludge production could be reduced by 50% in comparison with conventional hot lime (Garbutt, 1999).

FMA is an inorganic mixed metal (Fe, Mg, and Al) polynuclear polymer. This chemical had good coagulation, de-oiling and scale inhibition properties particularly in produced water of high SS levels of 50–400mg/L FMA. SS and oil can be removed to levels >92% and 97%, respectively (Zhou, et al, 2000). On the other hand, calcite, and lime have been used to remove heavy metals from produced water. Results showed that lime heavy metals removal efficiency is greater (>95%) than with others and that it was an economical chemical (Houcine, 2002.)

In a study on treatment of oil and gas fields produced water, an oxidant, ferric ions, and flocculants were used to remove hydrocarbons, arsenic, and mercury. In this process, the oxidation–reduction potential of the wastewater was controlled by oxidant addition to allow the required arsenic oxidation to occur while maintaining the mercury in elemental form. Results showed that effluent streams had less than about 10 parts per billion (ppb) of mercury (calculated as Hg), less than about 250 ppb, and preferably less than 100 ppb of arsenic (calculated as As), and less than about 40ppm of TPH (Frankiewicz and Gerlach, 2000). Disadvantages of the process are generation of sludge and increased concentration of metals in effluents.

2.3Physical treatment

2.3.1 Sand filters

This required three steps of pre-treatment before sand filtering for removing metals from Produced Water. The system consisted of the following:

- pH adjustment: to initiate oxidation reaction,
- Aeration unit: to increase oxygen concentration for reaction,
- Solid separation unit: sufficient retention time for settling of precipitated solids,
- Sand filtration: removing fine solids that could not settle.

Results of different runs by the system showed that more than 90% iron could be removed. (Adewumi et al, 1992).

2.3.2 Evaporation

Evaporation methods have been proposed to treat saline wastewater containing oil components (Bertness, and Lipoma, 1989). Vertical tube, falling film, and vapour compression evaporation are effective methods for produced water treatment because they:

1. Eliminate physical and chemical treatments so no chemical sludge is produced, and costs of waste and life cycle are lowered.
2. Require less maintenance materials and maintenance labor.
3. Reduce the amount of produced water de-oiling equipment required.

Nevertheless, due to presence of high impurity levels of solid salts the reuse of these materials is impossible (Lefebvre, R.Moletta, 2006). Becker [57] proposed wastewater distillation using two proprietary new designed systems (PNDS) that recover over 95% of the energy required to distil water as follows:

1. New mechanical vapor recompression (MVR) system to recycle produced water into distilled water.
2. Waste steam to accomplish the same. In commercial scale applications, more than 95% of the operating cost of distillation is energy. Thus the proposed PNDS reduces the total operating cost by 90 %.(Becker, 2000.)

2.3.3 Electrodialysis (ED)

Dissolved salts in water are cations and anions. These ions can attach to electrodes with an opposite charge. In ED, membranes are placed between a pair of electrodes.

The membranes allow either cations or anions to pass through. (J. Arthur, et al, 2005). This method is suitable for produced water recovery with low TDS concentrations. Recent results point out that this approach might be suitable for reclamation of produced water with relatively low TDS loads but is unlikely to be cost-effective for treatment of concentrated produced waters. (Dallbauman and Sirivedhin, 2005).

2.4 Biological treatment

Aerobic and anaerobic microorganisms were used in studies of biological treatment of produced water. In aerobic treatment, researchers used activated sludge, trickling filters, sequencing batch reactors (SBRs), chemo-state reactors, biological aerated filters (BAF), and lagoons (Fakhrul et al., 2009) . Four sources of microorganisms were studied in biological treatment:

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

Activated sludge is the usual method for treating wastewater. In a continuous-flow pilot plant, an oil skimmer was used to remove oil before treatment in an activated sludge system. Naturally occurring microbial growth was used in an aeration tank. The activated sludge treatment unit could maintain a total petroleum hydrocarbon (TPH) removal efficiency of 98–99% at a solids retention time of 20 days (Tellez et al., 2002).

Activated sludge is the typical method for treating wastewater. In a continuous-flow pilot plant, an oil skimmer was used to remove oil before treatment in an activated sludge system. Naturally occurring microbial growth was used in an aeration tank. The activated sludge treatment unit could maintain a total petroleum hydrocarbon (TPH) removal efficiency of 98–99% at a solids retention time (SRT) of 20 days (Tellez et al., 2002). Experiments were conduct to study COD removal efficiency of acclimated sewage sludge in SBR with different percentages of produced water and sewage. In 45% and 35% (v/v) mixtures of wastewater, COD removal efficiencies varied from 30% to 50%, (Freire et al., 2001). On the other hand, in a study to compare total influent organic carbon (TOC) removal efficiency of produced water with acclimated microorganisms in 180 mg/L NaCl, three biological systems including SBR, trickling filters and chemostate reactors were studied as follows:

- 2-L SBR with 24-h cycle (1 h for feed, 20 h for reaction, 2 h for settling, and 1 h for withdrawal).
- A trickling filter equipped with annular plastic supports with packing volume of 1.7 L and hydraulic load of 3m3/m2 h.
- A 1-L chemostate reactor with 8 days hydraulic retention time.

TOC removal efficiency of SBR was higher than that of the trickling filter or of the chemostate but continuous operation of SBR could lead loss of biomass (Baldoni et al, 2006).

It was found out that salinity did not have significant effect on COD removal of mixed wastewater, only recalcitrance of organic compounds affected biological treatment; (Freire et al., 2001). In addition, when Cl− concentration was increased from 2000 to 36000 mg/L, inhibitory effect of the high salinity on composite microbial culture was negligible, (Wei, et al, 2003). Nevertheless, some bacterial consortia degrade crude oil of 80,000 mg/L effectively; (Dfaz et al, 2000). However, when salinity increased to 100,000 mg/L, the biodegradation rate fell dramatically because high concentration of sodium chloride causes environmental stress, microbial less effect, and promotes loss of biomass (Tellez et al, 2002). In the aeration tank of salty wastewater treatment plants, slow growth rod-shaped microorganisms dominate the microbial community (Ng, et al., 2005). In addition to cell less effect, reduction of filamentous bacteria can affect the integrity of the flocs and raise the turbidity of effluents in biological treatment of salty wastewaters (Lefebvre and Moletta, 2006).

Using of rotating biological surfaces (biodisks) to treat oilfield-produced water. The biodisks were seeded by bacterial sludge from sewage treatment plant microorganisms. BOD and O&G removal efficiency of the plant were 94% and 74%, respectively, (Palmer et al, 1981).

In biological oxidation, harmless bacteria, algae, fungi, and protozoa convert dissolved organics and ammonia compounds into water and CO_2, nitrates/nitrites, respectively (Palmer et al, 1981). A study was carried on a two-stage pilot lagoon in series consisting of 80m^3 plastic-lined steel tanks each filled with 60m^3 of fluid. The primary tank was for oxidizing suspended oil and dissolved organic compounds and the second lagoon was designed for oxidizing dissolved ammonia compounds (Beyer et al, 1979) ; however, in another study, one-stage biological oxidation was used for removing ammonia and phenols from produced water (Palmer et al, 1981).

Different types of wetland-like free-water surface (FWS) and subsurface flow (SSF) pilot plants were designed, constructed, and tested to treat oilfield-produced water. Results showed that SSF wetland removed more COD than FWS wetland did (Jackson and Myers, 2003). Although the wetland is a cost-effective method, the temperature dependence of the system is not a desirable factor. Besides, if these wetlands are not lined, groundwater contamination is not prevented.

Activated sludge has the property of adsorbing and occluding not only soluble but also insoluble materials. Bacteria produce surface-active compounds such as surfactants (biosurfactants) and emulsifiers (bioemulsifiers) that enhance the local pseudo-solubility of hydrocarbons and thus improve mass transfer to biodegrading bacteria (Hommel, 1990).

Biodegradation of less complex oil components, e.g., normal alkanes is easier than of complex and large molecules. Less biodegradable oil molecules attached to microorganisms will remain in the aeration tank. These components are removed along with sludge in excess-sludge removal processes. The mixture of hydrocarbons and microorganisms are a source of hazardous material which has to be disposed. When raw wastewater is concentrated, anaerobic degradation of pollutants would be a cost-effective alternative (Metcalf and Eddy, 2003).

A research has been carried out to study biodegradation of organic acids in simulated produced water under anaerobic conditions in the presence of naphthenic acids in a 0.59 L fixed-film bioreactor. Microbial seed used was from the sludge in a produced water holding-pond of the anaerobic digester of a municipal treatment system. Results showed that naphthenic acids were not reduced in anaerobic conditions (Gallagher, 2001).

Reed beds technology is using a plant for bioremediation of wastewater. Reed beds can remove hydrocarbons and heavy metals. In a study, an 800-m2-reed bed with Phragmites australis plant was used to treat 20m3/day of produced water; results showed that more than 98%ofhydrocarbonswere removed (Gurden and Cramwinckel, 2000). In a similar pilot plant, 3000m3/day of produced water was treated to reduce total hydrocarbon concentration by an average of 96%. Metal concentration decreased by 78% for Al, Ba, Cr, Cu, and Zn, up to 40% for Fe, Li, Mn, Pb, As, Cd, Co, Mo, Ni, Se, Tl, and V [96]. Although this system is a cost-effective method, the effluent has to be refined and requires a lot of land (Al Mahruki and Alloway, 2006).

2.5 Sequencing Batch Reactor (SBR)

SBR treats wastewater in an activated sludge system within an aerobic condition. Oxygen is bubbled through the produced water to reduce biochemical oxygen demand (BOD) and chemical oxygen demand (COD); the resulting effluent is low in turbidity and nitrogen levels.

SBRs could achieve nutrient removal using alternation of anoxic and aerobic periods (Rim, et al,1997). Nitrification and denitrification are achieved in a SBR by mentioned periods, while the separation of treated wastewater and microorganisms is accomplished by ceasing aeration and/or mixing at the end of process cycle (Irvine, et al, 1971).

Sequencing Batch Reactor (SBR) become one of the most likely used alternatives for wastewater treatment, because of its simple configuration, since all necessary processes are taking place in a single tank based on timed cycle, (Lamine et al, 2006) As a result of its operational flexibility, it can be simply to increase its efficiency of the treatment by changing the duration of each phase instead of adding or removing tanks in continuous flow systems.

2.5.1 SBR Operating Principles

Separate tanks are required in conventional activated sludge systems for the unit processes of biological reactions (aeration of mixed liquor) and solids-liquid separation (clarification) and also require process mixed liquor solids (return activated sludge) to be returned from the final clarification stage to the aeration tanks. In contrast,

SBR technology is a method of wastewater treatment in which all phases of the treatment process occur sequentially within the same tank. Hence, the main benefits of the SBR system are less civil structures, inter-connecting pipe work, and process equipment and the consequent savings in capital and operating costs (Nigel, 2006)

SBR operation is on a time-based process cycle to achieve the process conditions necessary for carbonaceous oxidation, nitrification, de-nitrification and biological phosphorus removal. In addition, solids-liquid separation, treated effluent removal, and solids wasting are also incorporated to complete the process cycle. The various phases in a typical SBR process cycle usually comprise the following:-

1. **Fill:** Wastewater enters the SBR tank and mixes with activated sludge mixed liquor solids within the tank. Influent wastewater and activated sludge are mixed together to produce anaerobic / anoxic conditions in biological nutrient removal (BNR) systems.
2. **React:** Aeration of the tank contents. Biological reactions occur until the desired degree of treatment has been achieved.
3. **Settle:** Aeration is stopped and the activated sludge solids settle to form a blanket on the base of the reactor vessel, leaving an over-layer of treated effluent.
4. **Decant:** Clarified treated effluent (supernatant) is removed (decanted) from the tank without disturbing the sludge blanket.
5. **Idle:** Unexpired time between cycles. Wasting of excess activated sludge occurs.

Completion of these phases constitutes a cycle, which is then repeated. The operation process cycle is illustrated in Figure 2.1 (Environmental Protection Agency (EPA), 1999).

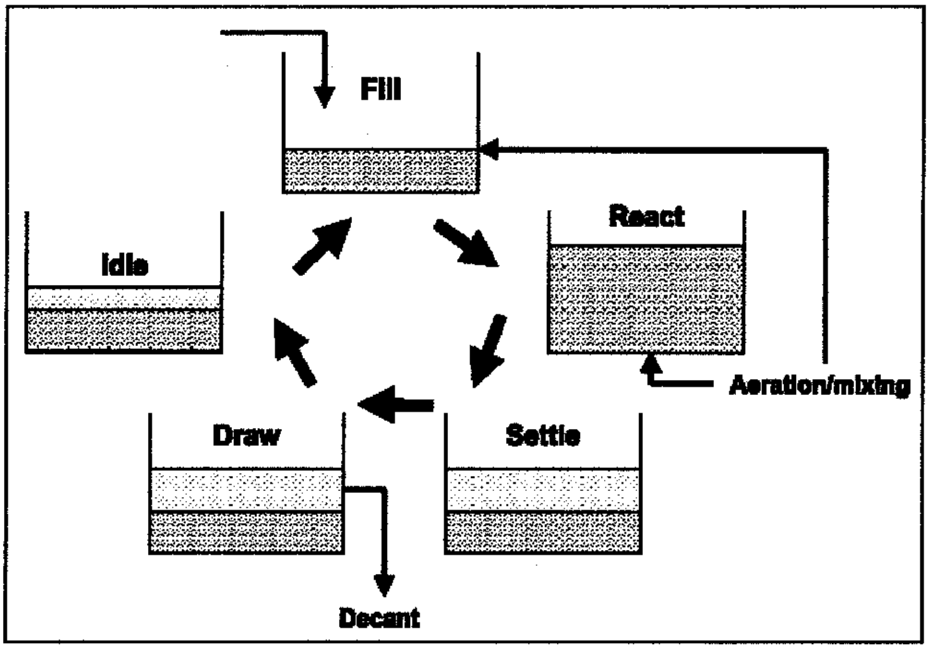

Figure 2.1: SBR operation process cycle

Source: Environmental Protection Agency (EPA)

SBR technology has the advantage of being much more flexible than conventional activated sludge processes in terms of matching reaction times to the concentration and degree of treatment required for a particular wastewater. For example, the SBR process allows for the following adjustments to be made in addition to those (such as sludge age and operating mixed liquor solids concentration) that can be made in an equivalent conventional process:

- Total cycle duration
- Duration of each phase within the process cycle
- Pattern of inflow
- Dissolved oxygen profile during aeration
- Operating top water level
- Operating bottom water level

Hence changes in wastewater characteristics over time may be readily accommodated in the SBR process (EPA, 1999).

In the SBR process a tank is never completely emptied, rather a portion of settled solids are left to seed the next cycle (Henry and Heinke, 1996). This allows the establishment of a population of organisms uniquely suited to treating the wastewater (Buchanan and Seabloom, 2004).

By subjecting the organisms to periods of high and low oxygen levels, and to high and low food availability - the population of organisms becomes very efficient at treating the particular wastewater (Henry and Heinke, 1996).

Fine bubble flexible membrane diffusers provide high efficiency in terms of process oxygen per unit of energy and also allow the flow of air to be interrupted during process air off (settling and decanting) phases without fouling of the diffusers or flooding the air distribution pipework. Removable fine bubble aeration equipment may be used to facilitate maintenance of the diffusers, where the tank cannot easily be drained. (Nigel, 2006)

2.5.2 ADVANTAGES AND DISADVANTAGES

As these systems have a relatively small footprint, they are useful for areas where the available land is limited. In addition, cycles within the system can be easily modified for nutrient removal in the future, if it becomes necessary. This makes SBRs extremely flexible to adapt to regulatory changes for effluent parameters such as nutrient removal. SBRs are also very cost effective if treatment beyond biological treatment is required, such as filtration. (EPA, 1999). Advantages and disadvantages of SBRs are listed below:

Advantages:

- Equalization, primary clarification (in most cases), biological treatment, and secondary clarification can be achieved in a single reactor vessel.
- Operating flexibility and control.
- Minimal footprint.
- Potential capital cost savings by eliminating clarifiers and other equipment.

Disadvantages:

- A higher level of sophistication is required (compared to conventional systems), especially for larger systems, of timing units and controls.
- Higher level of maintenance (compared to conventional systems) associated with more sophisticated controls, automated switches, and automated valves.

- Potential of discharging floating or settled sludge during the DRAW or decant phase with some SBR configurations.
- Potential plugging of aeration devices during selected operating cycles, depending on the aeration system used by the manufacturer.
- Potential requirement for equalization after the SBR, depending on the downstream processes.

CHAPTER 3
METHODOLOGY

Throughout this project, the following procedures ware considered. This is to ensure that the project was accomplished within the given timeframe.
Based on the objectives of the project, two samples ware used. The first sample was Produced Water and the second sample was the effluent of an anaerobically treated Produced Water, and this has been collected by collecting the effluent of anaerobic produced water treatment running experiment in the laboratory.

3.1 Data research and gathering

Elements of projects involved in this stage include the study of produced water characteristics and its contaminants, SBR efficiency and sludge acclimatizing technique. Researches about biological treatment were conducted and SBR was found to be the most effective and has high efficiency relatively.

3.2 Experimental method selection

The treatment process will be a combination of different treatment methods such as physical, chemical and biological. Therefore the most effective combination will be taken as the main process. SBR has been selected to be the essential treatment option.

3.3 Preparation for experimental work

Produced water sample was to be collected and its characteristics ware identified. Treatment stages are to be prepared according to the desired contaminant to be removed first, as well as aerobic bacteria selection and breeding since it will be used for aerobic biological treatment stage.

3.4 Produced water samples characterization

In this stage, the collected data will be used to specify the required tests; therefore the experimental part of the project would be carried out accordingly. Results will be disused later in chapter four results and discussion.

The tests will include the fundamental tests and measurements such as BOD, COD, TSS, MLVSS, TKN, pH, NH_3, TP, and NOx.

Water sampling for COD was carried out every day. Sampling for other measurements was carried out at irregular intervals. The wastewater quality parameters were monitored according to standard methods. COD was determined by filtering with a 0.45-mm filter and then oxidation with potassium dichromate under strongly acidic conditions and at an elevated temperature for 2 h. The oil content in the wastewater was determined by using an infrared spectrophotometry oil-measuring instrument .NH3-N was determined by Nessler's reagent colorimetry. The content of phosphorus was determined by the ascorbic acid method. Additionally, temperature, dissolved oxygen, and pH were routinely monitored with probes. Generally, samples were drawn at the end of each tank.

3.5 Tools

Environmental Engineering laboratory equipments and facilities was used to conduct all the experiments.

3.6 Sludge acclimatization

Since its an activated sludge system, sludge should be ready to be used in the system directly, but the used sludge it a domestic wastewater sludge from Univesiti Teknologi PETRONAS (UTP) Sewage Treatment Plant (STP), hence the organic matters should be acclimatized to adopt the new environment which is produced water. This can be done by diluting the produced water and add it to the domestic wastewater, and increase the produced water fraction in dilution through the acclimatization period. Sludge acclimatization was first applied by diluting both samples in domestic wastewater from STP_UTP using ratios of 12.5%, 25%,50%,75% and finally 100% of samples for its respective reactors. Microorganisms feeding was carried on average of 5 days/ cycle.

3.7 Sampling

Sample was collected from Terengganu Crude Oil Terminal TCOT, Kertih, Malaysia. Sampling point was directly after settling tank at the site. The Sample was about 300 liters maintained in specific containers and stored in the environmental laboratory sample storage cooling room.

3.8 SBR configuration and operation

A sequence batch reactor of Plexiglas material having a total volume of 5 L capacity ware used for experiment. The reactor will be operated in suspended growth configuration in a temperature of (25°C-28°C). Sequence batch reactor (SBR) for laboratory scale ware used for this project. SBR which are shown in Figure 3.1 below , were operated on five steps basis; fill the sample, react using aeration and mixing, settle the solids, decant the effluent and idle while waiting for filling by a new sample to start the process again. Data was collected on daily basis.

Figure 2.1: Sequencing Batch Reactor

3.9 Produced water characterization and testing

Produced water sample is to be collected and its characteristics are to be identified. Treatment stages are to be prepared according to the desired contaminant to be removed first, as well as aerobic bacteria selection and breeding since it will be used for aerobic biological treatment stage.

3.10 Standard tests and measurement required

In this stage, the collected data will be used to specify the required tests; therefore the experimental part of the project could officially starts. The tests will include the fundamental tests and measurements such as BOD, COD, pH, TSS, TDS, ammonium–nitrogen, nitrate, TKN, phenols content, sluphide content, oil and grease, Total phosphorus.

CHAPTER 4
RESULTS AND DISCUSSION

The results were continuously updated. Produced water characteristics have been studied as it's required for comparison of the data before and after the treatment of the sample, as well as for choosing the most suitable methods of carrying out the tests.

4.1 Produced Water Characteristics Results

Produced water characteristics were determined for BOD, COD, TKN, pH, Ammonia-Nitrogen, Nitrite, Nitrate, Sulfate, Sulfide, MLVSS, TSS, Total Phosphorous and color. Results are listed in Table 4.1.

4.2 Produced Water Treatment Results

The treatment has been carried out in term of cycles in both reactors, domestic wastewater sludge was used and it has been acclimatized to Produced Water medium gradually. Acclimatization was done by diluting the produced water and the anaerobically treated produced water effluent into domestic waste water; produced water and the anaerobic treatment effluent portions was increased by the time, each time a new cycle starts.

Two reactors were used; named A and B; for the anaerobic treatment effluent and the produced water respectively. So far seven cycles have been applied as show in Tables 4.2 and 4.3 for Reactors A and B respectively.

Table 4.1: Produced Water sample and Anaerobically treated effluent characteristics.

Produced Water characteristics													
Sample	COD	pH	Sulfate SO_4^{2-} mg/L	Sulfide S^{2-} mg/L	Nitrogen Ammonia NH_3-N µg/L	Nitrite NO^-_2-N mg/L	Nitrate NO_3^--N mg/L	TKN	Total Phosphorous PO_4^{2-} mg/L	Color ptco	MLVSS mg/L	TSS mg/L
PW sample	1422	7.47	775	2053.33	16.6333	0.033	6.8	32.1267	2.1867	23.333	0.08316	0.1358
Anaerobically treated effluent	686.3	8.57	–	–	10.375	0.05	0.0005	71.170	3.29	–	–	–

Table 4.2: Anaerobically treated Effluent Reactor cycles

Anaerobically treated Effluent Reactor				
Cycle no.	PW (L)	WW (L)	pH	Remarks
1	0.5	3.5	6.16	PW
2	0.5	3.5	6.73	PW
3	1	3	7.99	PW
4	1	3	8.53	PW
5	2	2	8.6	effluent
6	4	1	8.45	effluent
7	4	1	8.36	effluent
8	4	0	8.85	effluent
9	4	0	8.74	effluent
10	4	0	8.68	effluent

Table 4.3: Produced Water Reactor cycles

Produced Water Reactor			
Cycle no.	PW (L)	WW (L)	pH
1	0	4	4.9
2	0	4	4.83
3	1	3	7.77
4	1	3	8.48
5	1	3	8.37
6	2	2	8.37
7	2	2	8.57
8	4	0	8.47
9	4	0	8.54
10	4	0	8.57

Considering that environmental adaptability of microorganisms and biodegradation ability can be enhanced by the addition of conventional nutrients such as di-potassium Hydrogen Phosphate and Ammonium Chloride. The proper addition of appropriate nutrient is necessary to maintain good performance of the treatment system.

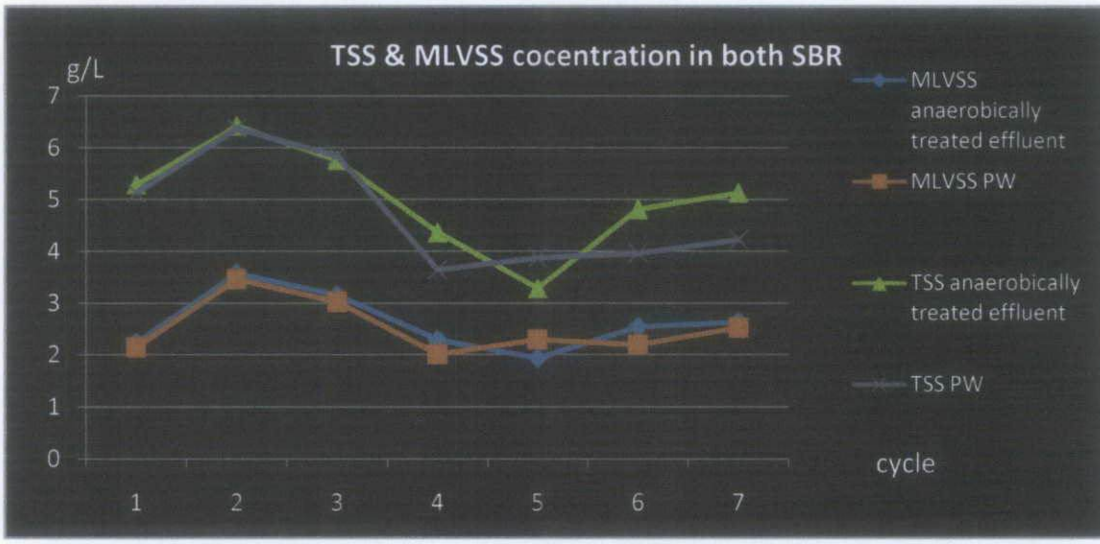

Figure 4.1: Total Suspended Solids and Mixed Liquor Volatile Suspended Solids concentration

Figure 4.1 indicates that's there was instability in solid growth and that's due to that biomass was still under acclimatization duration. Variation in COD removal is due to human errors while conducting the test, change in organic loading due to sample taking during SBR operation and lake of nutrients. In reactor A after using produced water anaerobic treatment effluent the removal efficiency is more stable.

In anaerobically treated effluent SBR, the initial high COD removal is due to that activated sludge is still under acclimatizing period, and on the same time produced water was only 12.5%, while in Produced water SBR, produced water amount was initially 25%.

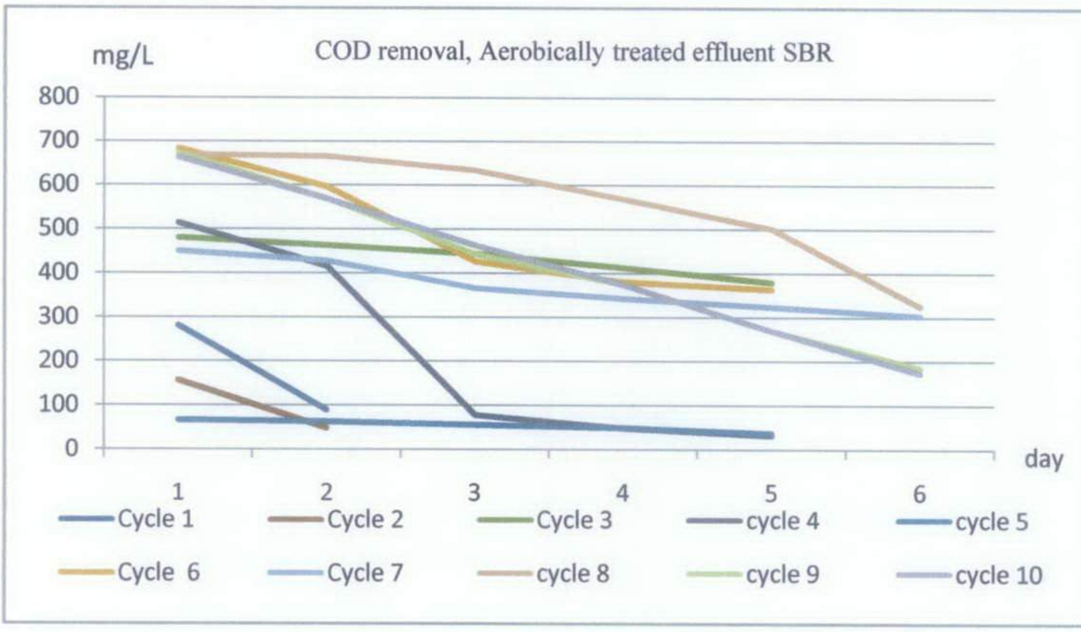

Figure 4.2: Anaerobically treated Effluent Reactor COD removal

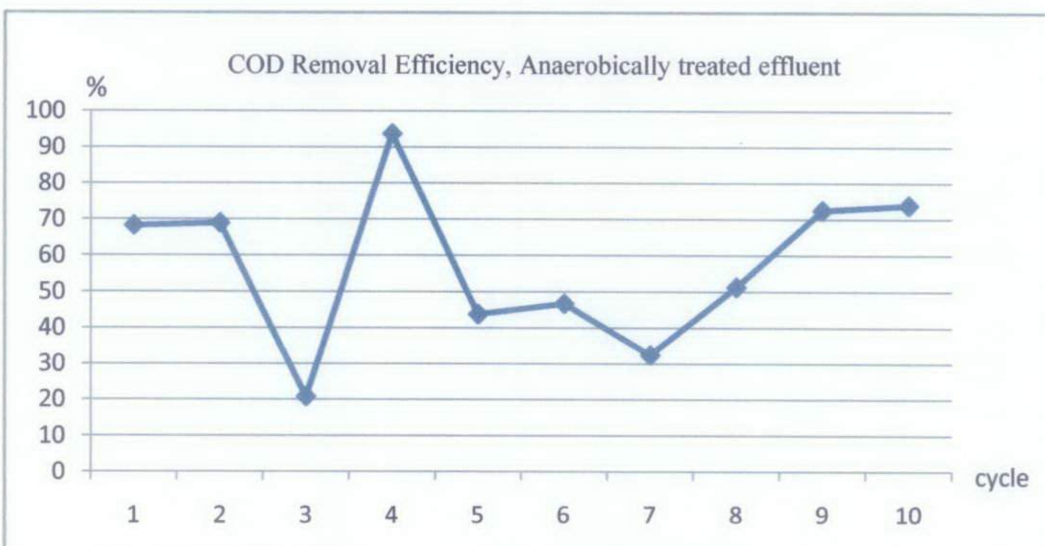

Figure 4.3: Anaerobically treated Effluent Reactor COD removal Efficiency

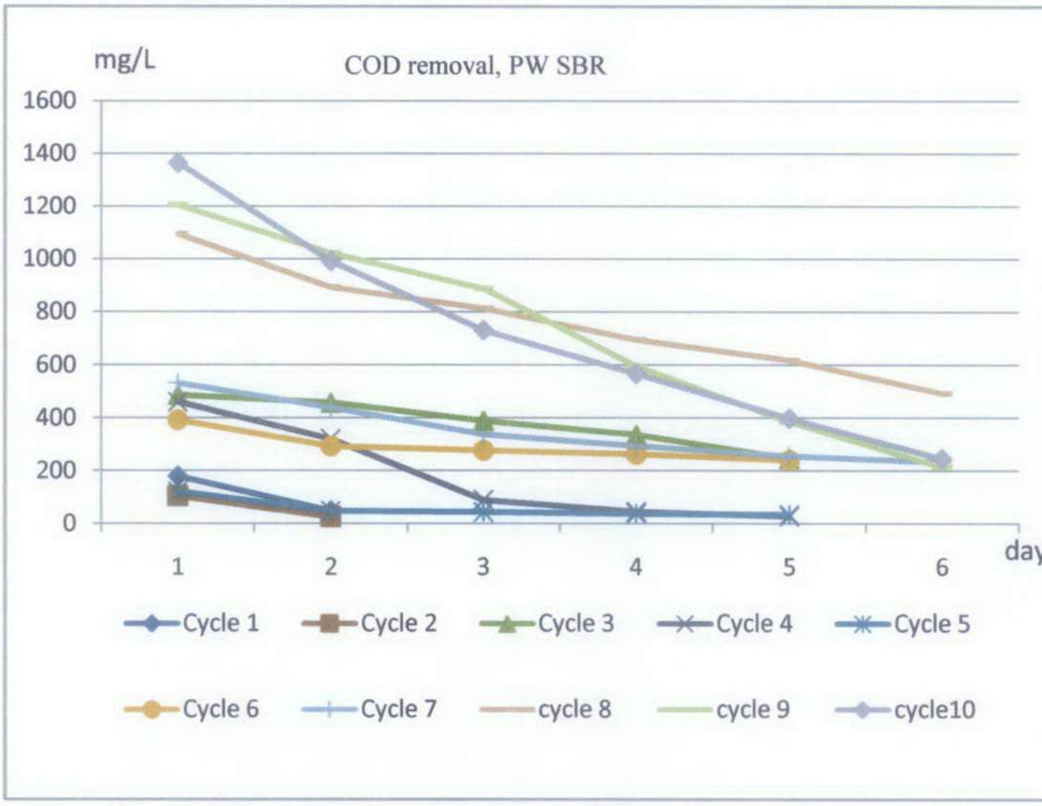

Figure 4.4: Produced Water SBR COD Removal

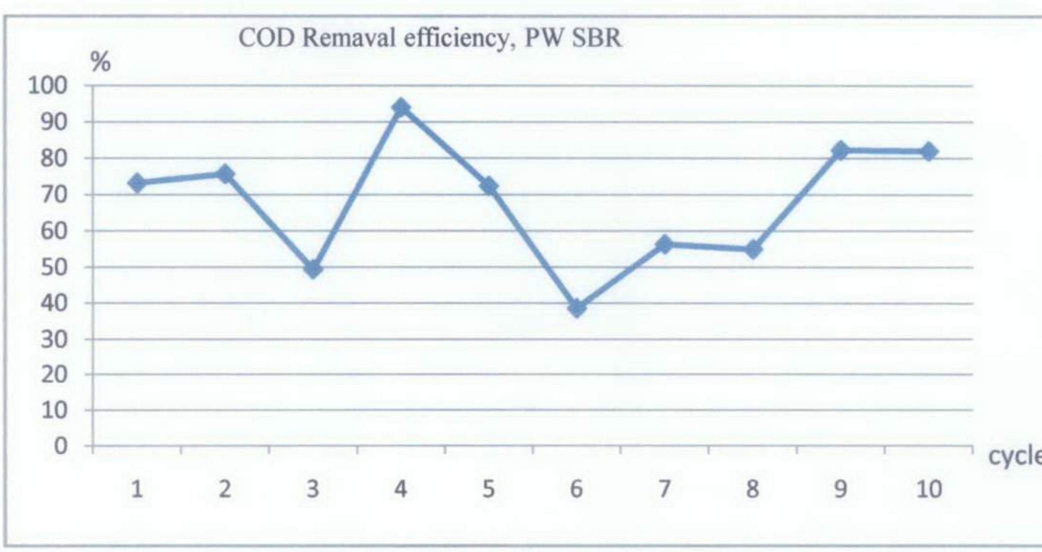

Figure 4.5: Produced Water SBR COD Removal Efficiency

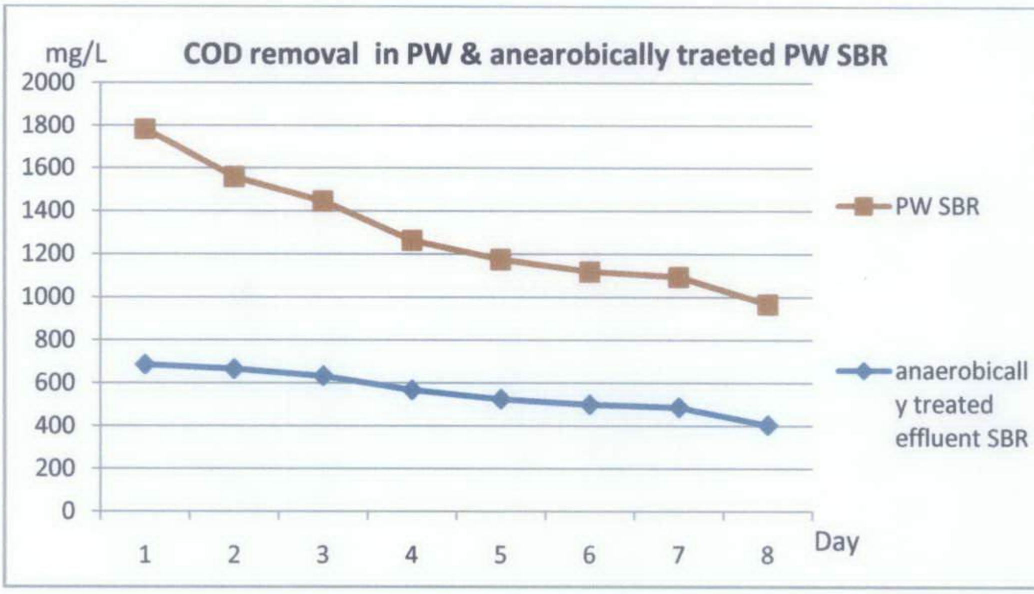

Figure 4.6: COD removal Efficiency

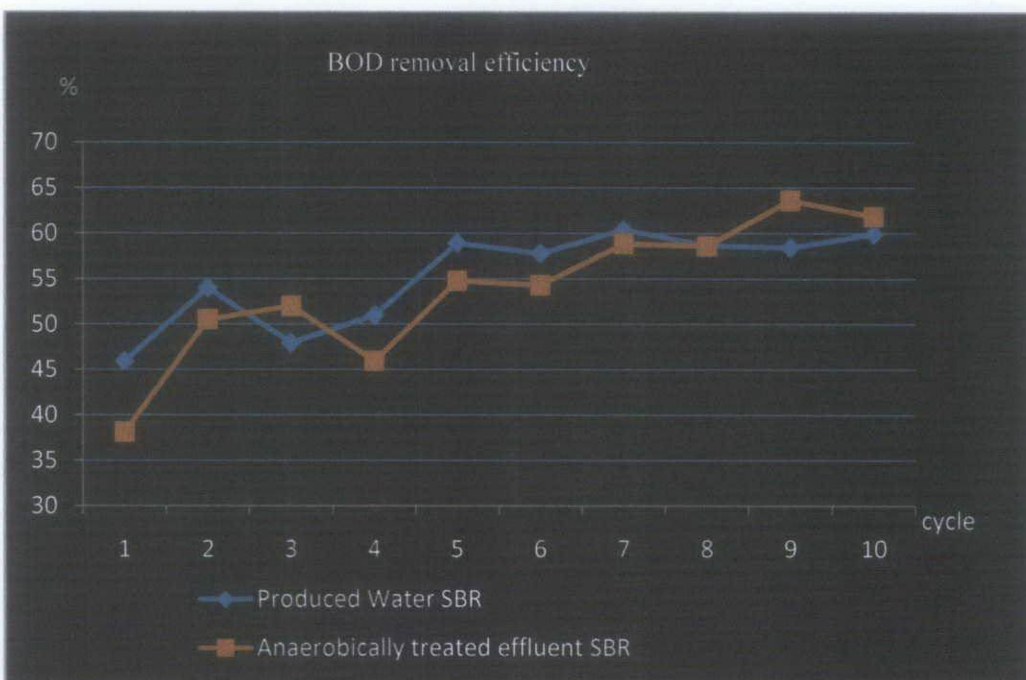

Figure 4.7: BOD removal Efficiency

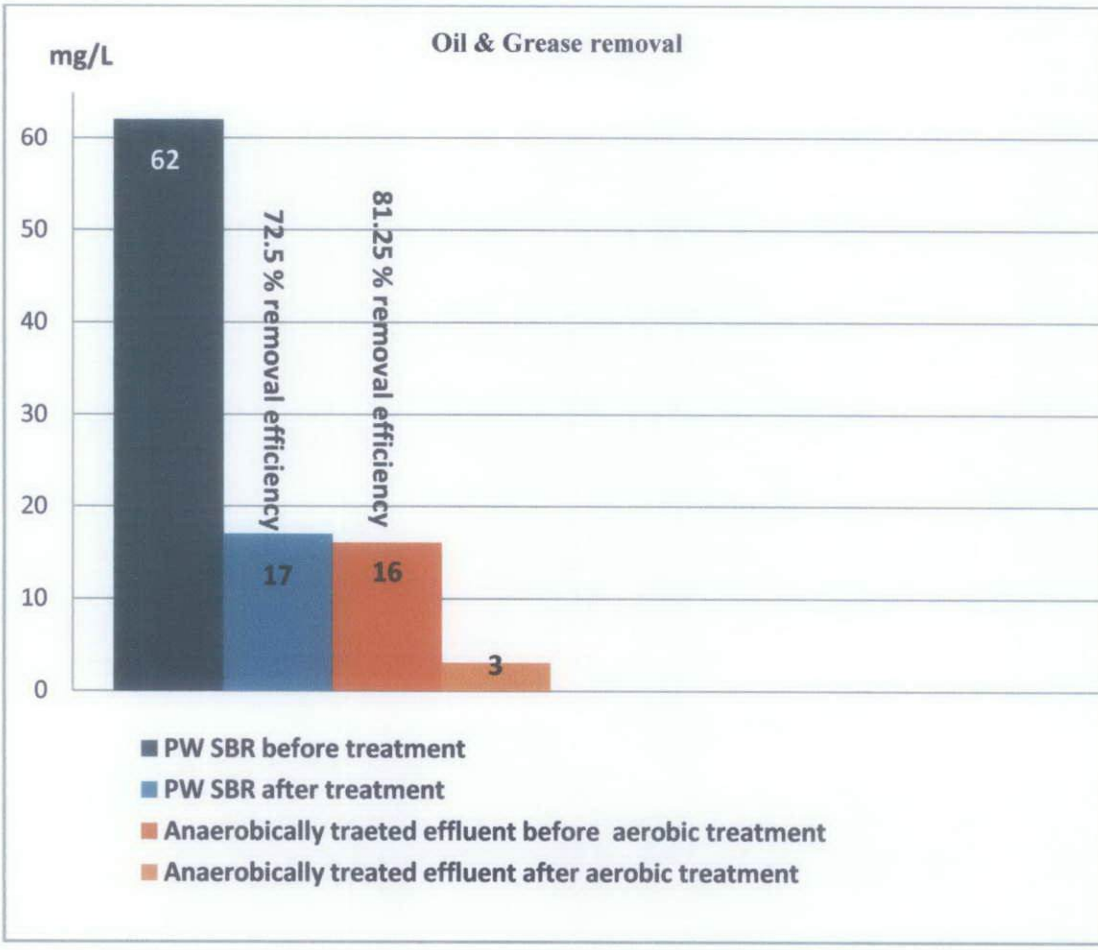

Figure 4.8: Oil & Grease Removal

Monitoring was continued on daily basis. BOD, COD, Nitrite, Nitrate, Ammonia-Nitrogen, O&G, Total phosphorous and solids are the main parameters ware observed.

CHAPTER 5
CONCLUSION

As Produced Water issue has a high concern in oil and gas sector, finding out the most optimum, realistic, higher efficiency and cost effective treatment scheme is wide range searching area. Sequencing Batch Reactor (SBR) can meet all this required criteria as its low cost in investment, in term of economical construction, low operation cost, minimum number of personnel is required for operating, as well as it has optimal mixing and aeration adjustable according to the variation of treatment quality desired and ease of maintenance.

Its recommended that project to be continued studying different Hydraulic retention times (HRT), and different Organic Loading Rates (OLR) using the same both produced water and produced water anaerobic treatment effluent.

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APPENDIX 1

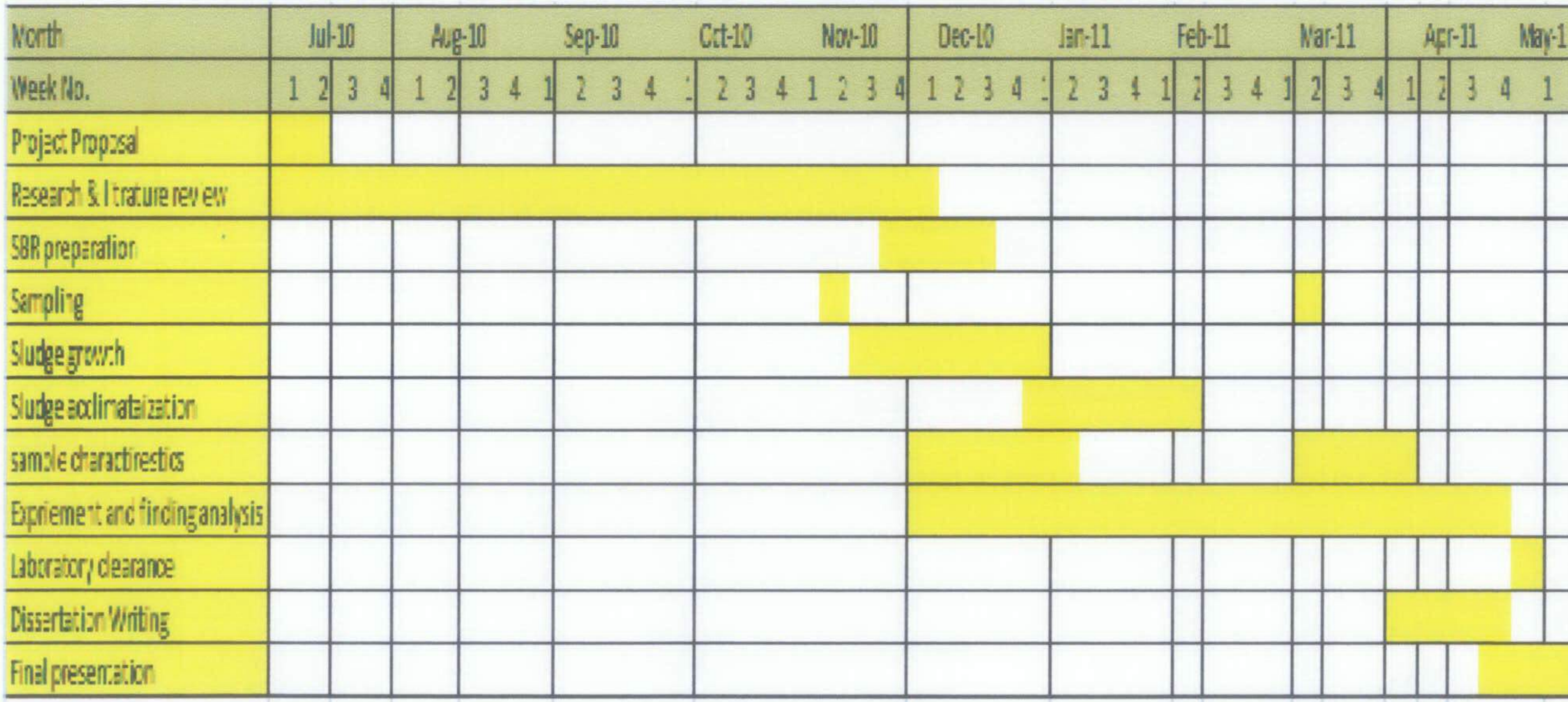

Figure 1: Project Gantt \Chart

APPENDIX 2

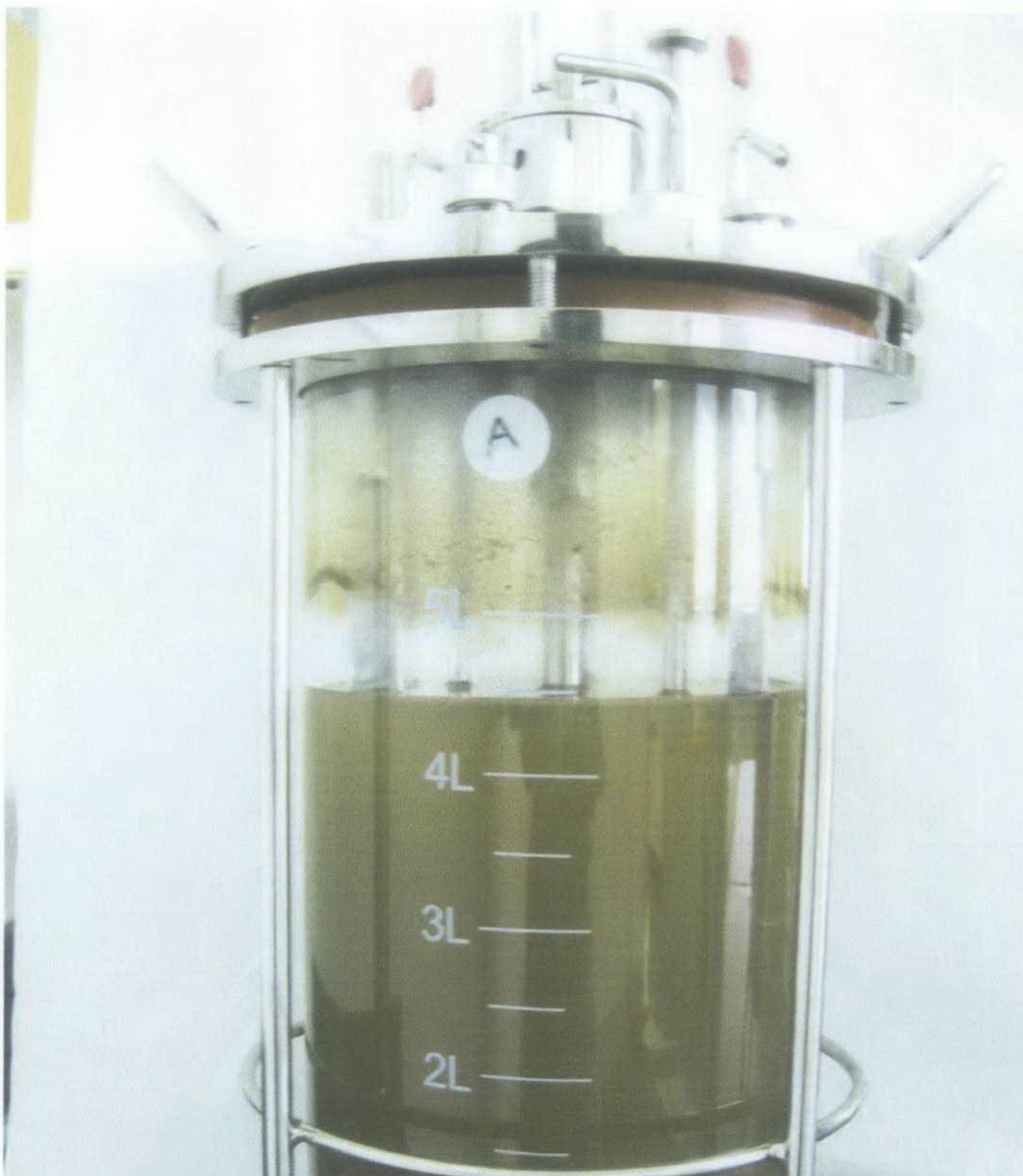

Figure 1: produced water aerobic treatment SBR

Figure 2: SBR setup and pump connection

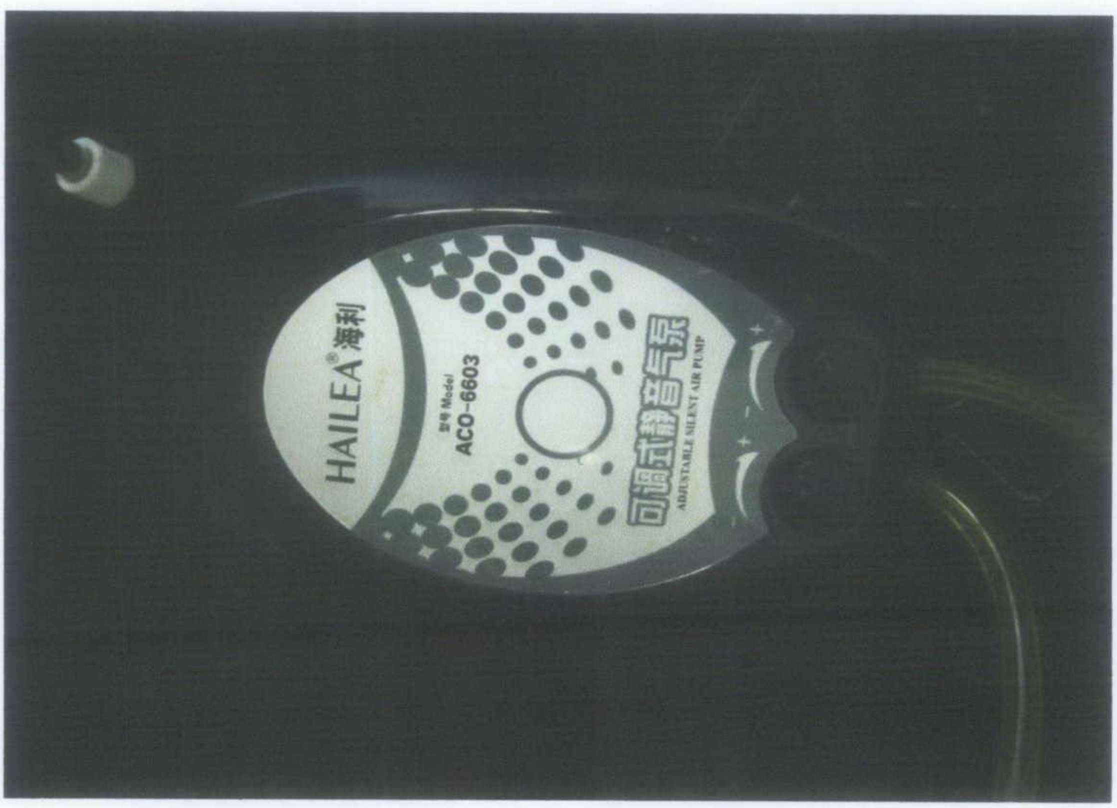

Figure 3: Aquarium pump used for aeratio

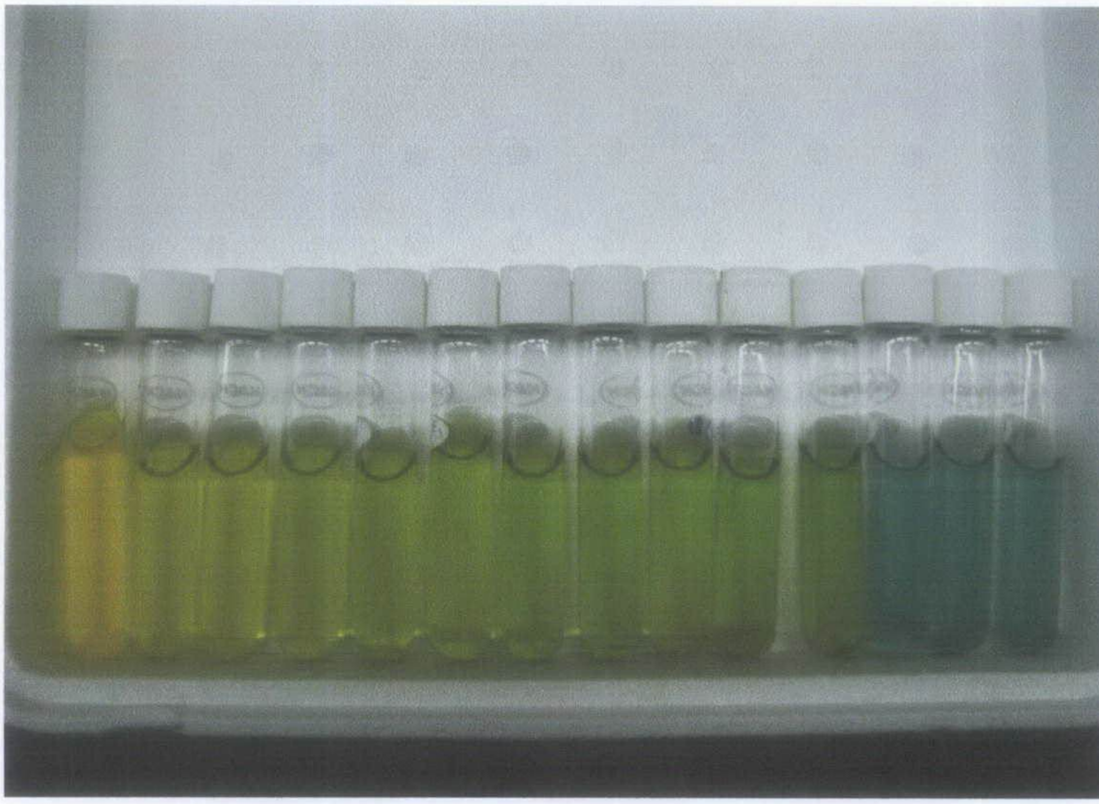

Figure 4: COD test

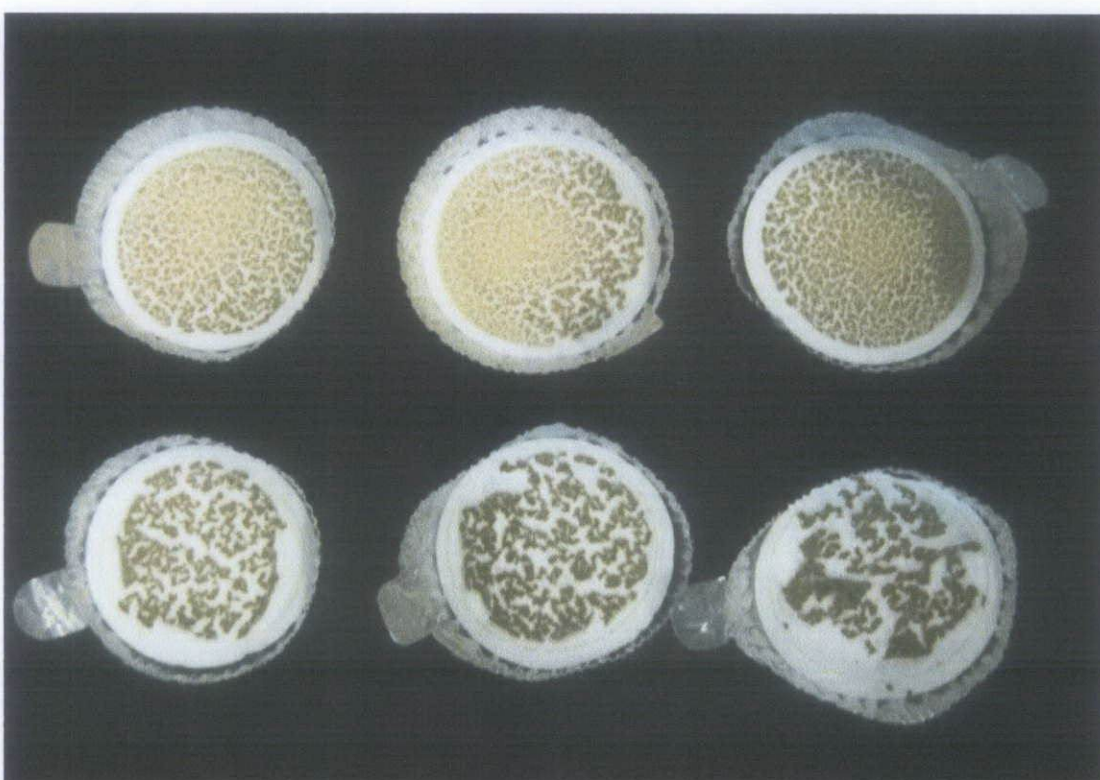

Figure 5: TSS and MLVSS test

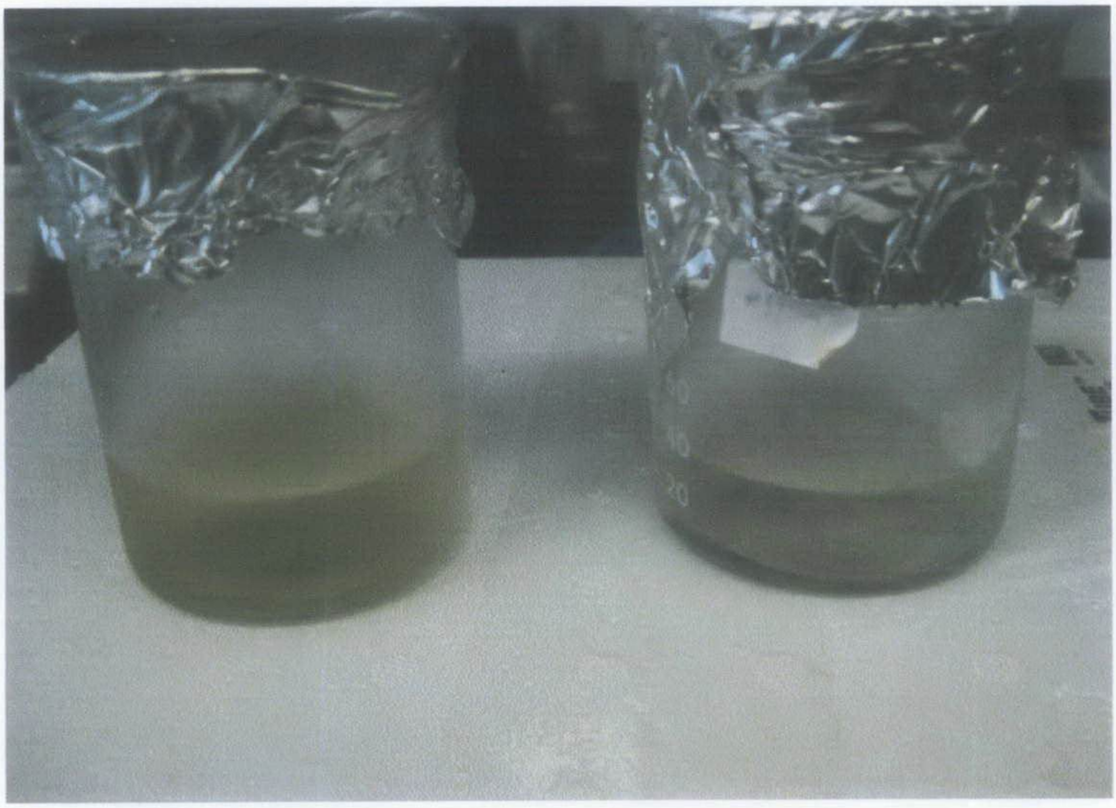

Figure 6: Produced water before and after treatment