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UNIVERSITI TEKNOLOGI PETRONAS

CHEMICAL AND BIOLOGICAL TREATMENT OF PRODUCED WATER

by

KHONG FONG CHEE

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CHEMICAL AND BIOLOGCAL TREATMENT OF PRODUCED WATER

by

KHONG FONG CHEE

A Thesis

Submitted to the Postgraduate Studies Programme

As a Requirement for the Degree of

MASTERS OF SCIENCE

CIVIL ENGINEERING

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR,

PERAK

JUNE 2013

DECLARATION OF THESIS

Title of thesis	CHEMICAL AND BIOLOGICAL TREAMENT OF PRODUCED WATER

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LIST OF ABBREVIATIONS

ABR	Anaerobic Baffled Reactor
Ace	Acenaphthene
ACT	Automated Chemostat TreatmentTM
Acy	Acenaphtylene
ADMI	American Dye Manufacturers Institute
Ant	Anthracene
ASFF	Aerated Submerged Fixed-film
BaA	Benzo[a]Anthracenea
BAF	Biological Aerated Filter
BaP	Benzo[a]Pyrenea
BAT	Best Available Treatment
BbF	Benzo[b]Fluoranthenea
BkF	Benzo[k]Fluoranthrenea
BOD	Biological Oxygen Demand
BPer	Benzo[g,h,i]Perylen
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
Chr	Chrysenea
COD	Chemical Oxygen Demand
COG	Petronas Trading Cooperation
CUF	Centralised Utility Facilities
DbA	Dibenzo[a,h]Anthracenea
DOE	Department of Environmental
DOMSEA	Domestic East Asia Division
DS	Total Dissolved Sulphide
E&P	Exploration and Production
EEZ	Exclusive Economic Zone
EMEPMI	ExxonMobil Exploration and Production Malaysia Incorporation
F/M	Food-to-Microorganism Ratio

FA	Free Ammonia
Fla	Fluoranthene
Flu	Fluorene
FSO	Floating Storage and Offtake
FPSO	Floating Production Storage
FS	Free Hydrogen Sulphide
GAC-FBR	Granular Activated Carbon-Fluidized Bed Reactor
GPP	Gas Processing Plant
HA/BCO	Hydrolysis Acidification/ Bio-contact Oxidation System
HELCOM	Helsinki Commission (Baltic marine protection)
HRT	Hydraulic Retention Time
HUASB	Hybrid Up-flow Anaerobic Sludge Blanket
IECS	Industrial Effluent Characterization Study
Ind	Indeno[1,2,3-cd]Pyrenea
JDS	Joint Delivery System
KSB	Kemaman Supply Base
LNG	Liquefied Natural Gas
MBBR	Moving Bed Biofilm Reactor
MBR	Membrane Bioreactor
MISC	Malaysia International Shipping Cooperation Berhad
MLNG	Malaysia LNG Sendirian Berhad
MLSS	Mixed Liquor Suspended Solids
MSBR/RO	Membrane Sludge Batch Reactor/Reverse Osmosis
Nap	Naphthalene
NSO	Nitrogen, Sulfer and Oxygen
O&G	Oil and Grease
OCM	Oregon Collection of Methanogens
OGT	Onshore Gas Terminal
OLR	Organic Loading Rate
OPTIMAL	Optimal (Olefin, Gylcol, Chemical) Sendirian Berhad
OSC	Onshore Slug Catcher

OSPARCOM	Oslo and Paris Commission (Environmental Regulations for the European Community)
P-525A or B	Skimmer Tank
P-535A or B	Surge Tank
PAH	Polycyclic Aromatic Hydrocarbon
PCSB	Petronas Carigali Sendirian Berhad
Petchem	Petrochemical
PETLIN	Petlin (Malaysia) Sendirian Berhad
PGB	Petronas Gas Berhad (Gas)
Phe	Phenanthrene
PMO	Peninsular Malaysia Operation
PPMSB	Petronas Penapisan Melaka Sendirian Berhad (Refinary)
PPTSB	Petronas Penapisan Terengganu Sendirian Berhad (Refinary)
PW	Produced Water
Pyr	Pyrene
RDS	Resak Delivery System
RESAK	Petronas Carigali Resak Offshore Gas Processing Complex
SBO	Sabah Operation
SBR	Sequencing Batch Reactor
S-DS	Total dissolved sulphide
S-FS	Free hydrogen sulphide
SKO	Sarawak Operation
SRB	Sulphate reducing bacteria
SRT	Sludge Retention Time
SS	Suspended Solid
T-250	Slop Tank
TCOT	Terengganu Crude Oil Terminal
TDS	Total Dissolved Solids
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TPH	Total Petroleum Hydrocarbon

TSS	Total Suspended Solid
TW	Tap Water
UASB	Up-flow Anaerobic Sludge Blanket
USD	United State Dollar
USEPA	US Environmental Protection Agency
V-220	Flash Stabilization Vessel
V-225	Electrostatic Precipitator Cessel
V-230	Separation Vessel
VFA	Volatile Fatty Acid
VSS	Volatile Suspended Solids
WSP	Waste Stabilization Pond

LIST OF SYMBOLS

%	percent
°C	degree Celsius
µL	micro Litre
bbl	Barrel
bbl/d	Barrel per day
bbls	Barrels
B_v	Organic loading
C1	Carbon No.1 (Methane)
C13	Carbon No.13 (Tridecane)
C40	Carbon No.40 (Tetracontane)
C5	Carbon No.5 (Pentane)
C5+	Carbon No.5 plus (Pentane plus)
C9	Carbon No.9 (Nonane)
d	day
hr	Hour
kb/d	thousand barrels per day
$kg/m^3\cdot d$	kg of BOD per cubic metre per day
kWh	kilowatt hour (unit of energy equal to 1000 watt hours or 3.6 megajoules)
L	Litre
M^2/m^3	Specific surface area
mg/L	milligram per litre
MJ	Megajoules

mmscfd	million standard cubic feet per day
mstb/d	1,000 stock tank barrel per day
ng	nano gram
NH_3-N	Ammonia-nitrogen
ppm	parts per million

ABSTRACT

Produced water (PW) is the largest waste stream of hydrocarbon production. PW is present in a reservoir with hydrocarbon resource and bought to the surface with crude oil or natural gas during onshore or offshore operations. Recently, due to its fate and effect, discharging PW into water bodies has become a significant issue of environmental concern and refineries that do not meet the requirement are no longer permitted to discharge the produced water to coastal estuarine or marine water. Therefore, it is vital to deal with produced water efficiently and cost effectively to ensure compliance with the regulations. Biological treatment is an effective and economical approach to treat large water production volume from exploration activities to reduce its organic content. PW, due to its high salinity and other toxic substances, can cause inhibition and affect the metabolism of microorganisms due to plasmolysis in the presence of salt if there is no adaptation of biomass before biological (anaerobic or aerobic) treatment and thus, biological treatment of produced water is often regarded difficult. The fact that microorganisms have been shown to acclimatize well to different industrial wastewaters is the main motivation for this research. A mesophilic experimental study was conducted to evaluate the performance of Up-flow Anaerobic Sludge Blanket (UASB) and HybridUp-flow Anaerobic Sludge Blanket (HUASB) reactor in treating PW, with and without chemical pre-treatment (coagulation and flocculation using ferric chloride), at hydraulic retention time of (HRT) of 5, 4, 3, 2 and 1 d. The performance of aerobic treatment using Sequencing Batch Reactor (SBR) in treating anaerobically (UASB and HUASB) treated PW was also studied. COD reduction was found to be better at HRT of 5 d before pre-treatment with ferric chloride. This may be due to long period of acclimatization, 71 d of treatment with maximum COD removal was 67.5%, compared to after pre-treatment of ferric chloride, 38 d only of treatment with maximum COD removal was 59.92%. Longer acclimatization in HUASB reactor showed overall VFA removal was in the range of 1-10 mg/L. Naphthalene was the major constituent representing 93.0% of total 16 PAHs found in the PW. Both reactors were able to degrade PAHs almost completely with degradation efficiency greater than 99.6% at all HRTs tested. Color and turbidity were reduced by almost 98.0%. Boron was reduced to 5.5 mg/L from 13.8 mg/L and barium to 0.8 mg/L from 7 mg/L, with total of 60.1% and 88.6%, respectively of removal efficiency when pH was fixed at 10 using ferric chloride as coagulant. Ferric chloride dosage of 2197.8 mg/L with optimal pH value of 10 was chosen to pre-treat produced water sample since it gave the best yield and its final pH at 7.75 was close to the pH (6.5-7.5) to operate anaerobic treatment as post-treatment. The performance of SBR treating anaerobic pre-treated PW seems to be marginally better as the influent was change to shorter day HRT of pre-treated anaerobically treated PW effluent; the average COD removal efficiency for HUASB-SBR was performed marginally better than UASB-SBR effluent. The results indicate that in overall, anaerobic-aerobic treatment of HUASB-SBR performed better than UASB-SBR as the influent was changed to shorter day HRT from HRT of 5 d to HRT of 1 d. Ferric chloride coagulation-HUASB-SBR treatment system barely met the discharge standard. Post treatment such as membrane-coupled SBR to prevent organic shocks and retain slow growth of microorganism or, combined physical-biological-membrane (e.g.ultrafiltration-reverse osmosis) process is recommended for onshore facilities where enough space is available.

ABSTRAK

PW adalah sisa air terbesar bagi pengeluaran hidrokarbon. PW hadir dalam takungan dengan sumber hidrokarbon dan dibawa ke permukaan dengan minyak mentah atau gas asli semasa operasi carigali. Impak dan kesan membuang PW ke dalam sungai atau laut, telah menjadi satu isu besar kepada alam sekitar. Kilang penapisan yang tidak memenuhi syarat tidak lagi dibenarkan untuk membuang sisa PW ke muara pantai atau ke laut. Oleh yang demikian, ia adalah penting ketika mengendalikan sisa air dengan cekap dan kos efektif untuk memastikan ia telah memenuhi piawaian dan undang-undang. Rawatan biologi merupakan satu pendekatan yang berkesan dan ekonomi untuk merawat jumLah pengeluaran air yang berkuantiti besar daripada aktiviti carigali untuk mengurangkan kandungan bahan organik. PW yang mengandungi kandungan garam/masin yang tinggi serta lain-lain bahan toksik yang boleh memjejaskan metabolisme mikroorganisma justeru merencatkannye plasmolysis mikroorganisma dalam kehadiran garam jika tiada adaptasi sebelum rawatan biologi (anaerobik dan aerobik). Motivasi utama menjalankan rawatan biologi kadang kala dianggap sebagai sukar, tetapi pada hakikat, mikroorganisma telah menunjukkan bahawa mereka dapat menyesuaikan diri dengan baik kepada sisa air ini. Eksperimen mesopilik telah dijalankan untuk menilai prestasi rawatan anaerobik Aliran-Atas Selimut Enapcemar anaerobik (UASB) dan Hibrid Aliran-Atas Enapcemar Selimut anaerobik (HUASB) dalam merawat PW dengan dan tanpa pra-rawatan kimia (pembekuan dan pemberbukuan menggunakan klorida ferric) pada masa tahanan hidraulik (HRT) 5 hari, 4 hari, 3 hari, 2 hari dan 1 hari . Rawatan prestasi aerobik menggunakan SBR dalam merawat sisa air anaerobik (UASB dan HUASB) juga dikaji. Pengurangan COD dilihat lebih baik pada HRT 5 hari sebelum pra-rawatan dengan klorida ferric. Ini mungkin disebabkan tempoh penyesuaian yang panjang, 71 hari (maksimum penyingkiran COD adalah 67.5%), berbanding dengan selepas pra-rawatan klorida ferric, 38 hari sahaja (pengurang COD maksimum adalah 59.9%). Adaptasi yang lama terutama pada HUASB reaktor menunjukkan keseluruhan pengurangan VFA adalah dalam julat 1-10

mg / L. Naftalena adalah konstituen utama yang mewakili 93.0% daripada jumLah 16 PAH yang ditemui dalam influen. Kedua-dua reaktor dapat mengurangkan PAH shampir sepenuhnya dengan degradasi melebihi 99.6% di semua HRTs yang diuji. Kandungan warna dan kekeruhan Berjaya dikurangkan sebanyak 98.0%. Kandungan boron telah berkurang sebanyak 60.1% daripada 5.5 mg/L dari 13.8 mg/L. Kandungan barium pula berjaya dikurangkan sebanyak 88.6% kepada 0.8 mg/L daripada 7 mg/L. Apabila pH telah ditetapkan pada 10 menggunakan ferric klorida sebagai koagulan pada dos

2197.8 mg/L, untuk merawat pra-sampel air yang dihasilkan kerana ia memberikan hasil yang terbaik dan pH terakhir pada 7.75 adalah dekat dengan pH (6.5-7.5) untuk mengendalikan rawatan anaerobik sebagai rawatan selanjutnya. Prestasi Purata pengurangan COD untuk HUASB-SBR telah menunjukkan prestasi yang lebih baik daripada UASB-SBR. Hasil keputusan menunjukkan bahawa secara keseluruhan, rawatan anaerobik-aerobik HUASB-SBR menunjukkan prestasi yang lebih baik daripada UASB-SBR apabila influen telah ditukar kepada HRT lebih pendek dari HRT 5 hari untuk HRT 1 hari. Rawatan kimia menggunakan ferric klorida-HUASB-SBR rawatan menghampiri kepada standard B. Penambahan membran selepas rawatan SBR dapat mengelakkan kejutan organik dan mengekalkan pertumbuhan perlahan mikroorganisma. Gabungan proses fizikal-biologi-membran (osmosis egultrafiltration-terbalik) sekiranya mempunyai ruang yang luas.

CHAPTER 1

INTRODUCTION

This chapter highlights the introduction of Peninsular Malaysia Operation - Terengganu Crude Oil Terminal (PMO-TCOT), the current issues of produced water at TCOT and the regulation governing the disposal of produced water. Also, objective and the scope of this study will be discussed.

1.1 Background

PETRONAS Carigali Sdn. Bhd. (PCSB) [1] is a wholly-owned subsidiary of PETRONAS (PETROLIAM NASIONAL BERHAD). The company was incorporated on 11th May, 1978. PCSB was formed to augment the exploration and development activities of foreign oil companies and through its participation, to enhance the pace of development of the upstream sector in the country. PCSB operates in three regions within Malaysia viz:-

a) Peninsular Malaysia Operations (PMO)
b) Sabah Operation (SBO)
c) Sarawak Operation (SKO)

1.1.1 Peninsular Malaysia Operation (PMO)

Effective 1st April, 2002, these regional operations were put under PCSB's Division called Domestic and South East Asia Division (DOMSEA) [2]. This study relates to PMO. PMO started its operation in April, 1984 (the first production division in PCSB) with the commencement of gas production from the Duyong field. Its main office is located at PETRONAS Office Complex in Kerteh about 110 km south of Kuala

Terengganu. PMO is supported by Kemaman Supply Base (KSB) in terms of warehousing and logistic activities, Kerteh Helibase for helicopter services, Onshore Gas Terminal (OGT) and Onshore Slug Catcher (OSC) at Paka for gas receiving facilities, and Terengganu Crude Oil Terminal (TCOT) at Paka for crude receiving facilities. There are a total of thirty three platforms, two Floating Production, Storage and Offloading facilities (FPSO), and OGT. TCOT, OGT and OSC act as the gatekeeper for upstream operations (or E&P business) at onshore side on behalf of PETRONAS prior to the massive value-chain process downstream business namely Refining (PPTSB and PPMSB), Gas (PGB), Petchem (Vinyl/ Petlin/ Ammonia/ Acetyl/ CUF/ Optimal), Marketing (COG), LNG (MLNG) and Shipping (MISC). Figure 1.1 represents the Peninsular Malaysia Upstream Crude Production Network; blue represents ExxonMobil Exploration and Production Malaysia Inc. (EMEPMI) fields and green represents PCSB fields.

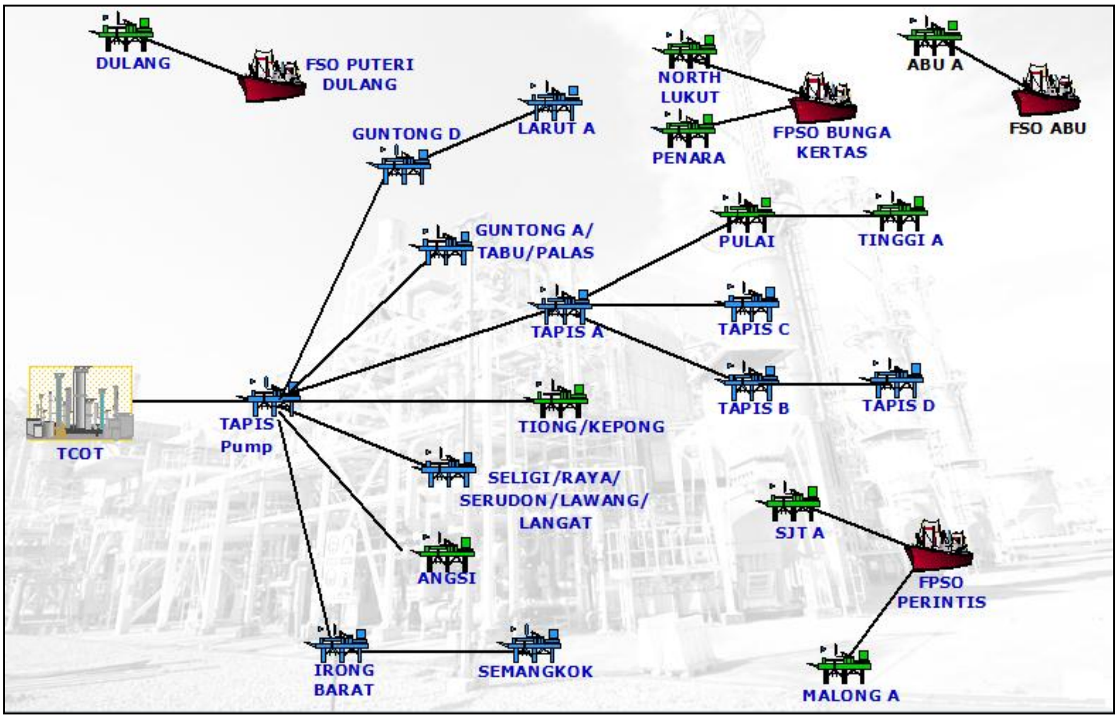


Figure 1. 1: Peninsular Malaysia Upstream Crude Production Network

1.1.2 Terengganu Crude Oil Terminal (TCOT)

TCOT operatorship was transferred to PCSB on 1st July, 2008. TCOT's function is to separate crude, gas and produced water to the required specifications:

a) Crude-separation using process vessels such as flash separation and electrostatic precipitation, store stable crude, pump and metered, and ready to export to either PPTSB or Tankers
b) Gas-compression and export GPP
c) Produced water-treat and allow to settle and then discharge to beach front to meet DOE requirements

Most of the crude from PMO is evacuated through the 24″ Tapis line system (Tapis Pump and Tapis Trunkline) to TCOT. Total crude transferred through Tapis Line to TCOT is approximately 230 mstb/d (gross) or it is worth of USD 11 million/d. Total crude produced at FSOs and FPSOs is approximately 60 mstb/d (gross) collected from four different offshore terminals which are Perintis, Abu, Bunga Kertas and Dulang. The incoming crude is mixed with associated gas and water. Table 1.1 shows TCOT infrastructure and current production rate.

Table 1. 1: TCOT infrastructure and current production rate

	Infrastructure	**Current Production Rate**
Crude Handling	2-Train crude stabilization plant. 385,000 bbl/day	Incoming: 280 kb/d
Gas Handling	Turbo Booster Compressor (20 mmscfd) Vapour Recovery Compressor (32 mmscfd)	Total offgas: 26-28 mmscfd
Produced Water Handling	30,000 bbl/day	25-30 kb/d
Storage Capacity	Crude: 2,500,000 bbls Condensate: 600,000 bbls	Data not available

The received live crude from Tapis line is pumped into the slop oil tank (T-250) at 25 ℃ and preheated for 24 hours at 40 ℃. After that, the temperature is ramped up to 180 ℃ in a close system. Slop tank’s function is to break hydrocarbons and water emulsion to free phase hydrocarbons and water, then remove all as much water as possible from the hydrocarbon. [3]. The oil/gas/water mixture is processed through separation devices to separate the three phases from one another. Chemicals may be added to the process stream to improve the efficiency of oil/ gas/ water separation. The crude is pumped into flash stabilization vessel (V-220) where a manipulation of oil pressure and temperature is applied to separate gas/oil/water. The gas is then pumped for purification and the oil is further separated by electrostatic precipitator vessel (V-225) to separate oil/ water. The oil from V-230 is flashed in V-230 to recover final gas/oil/water. The wastewater from separation processes (V-220, V-225 and V-230) is produced water (PW). PW is pumped into settling tank. A skimmer (P-525A or B) is placed to remove remaining oil droplets of greater than 100 micron [4] and filters to remove oil and grease from PW; a range between 10-20 ppm (highest approval to discharge is 100 ppm). Water is then pump into surge tank to accommodate pressure change before P-535 A or B upon discharged into coastal sea. Figure 1.2 shows TCOT general overview and process.

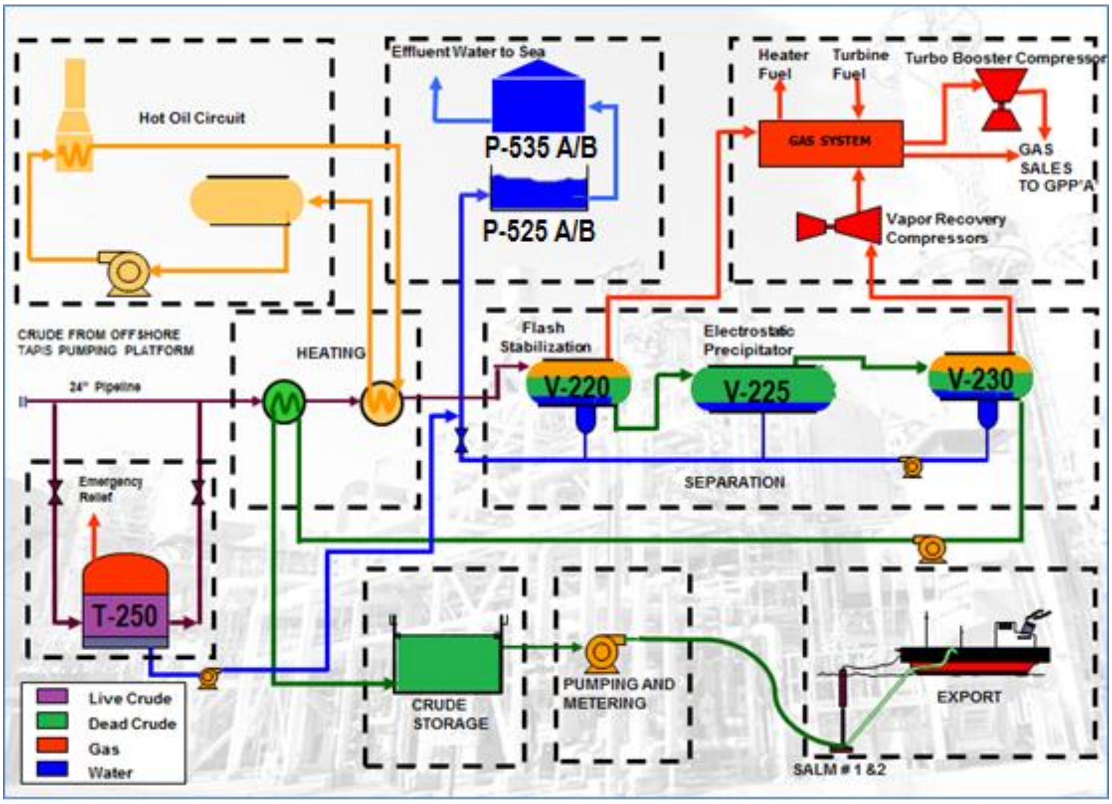


Figure 1. 2: TCOT General Overview & Process

No advance equipment available in the market is able to separate oil/water with 100 percent efficiency. Treated PW that is discharged to the ocean often contains small amounts of hydrocarbons, other organic chemicals, dissolved salts, and metals.

1.1.3 Onshore Sludge Catcher (OSC)

OSC handles gas from most of the EMEPMI operated fields, and Angsi (PCSB operated) fields, supplying about 1500 mmscfd of gas to GPP. OGT handles gas received from two lines, RDS (Resak Delivery System) and JDS (Joint Delivery system). Both plants handle about 700 mmscfd gas in total to GPP. Figure 1.3 represents of Peninsular Malaysia Upstream Gas Production Network; blue represents EMEPMI fields and green represents PCSB fields.

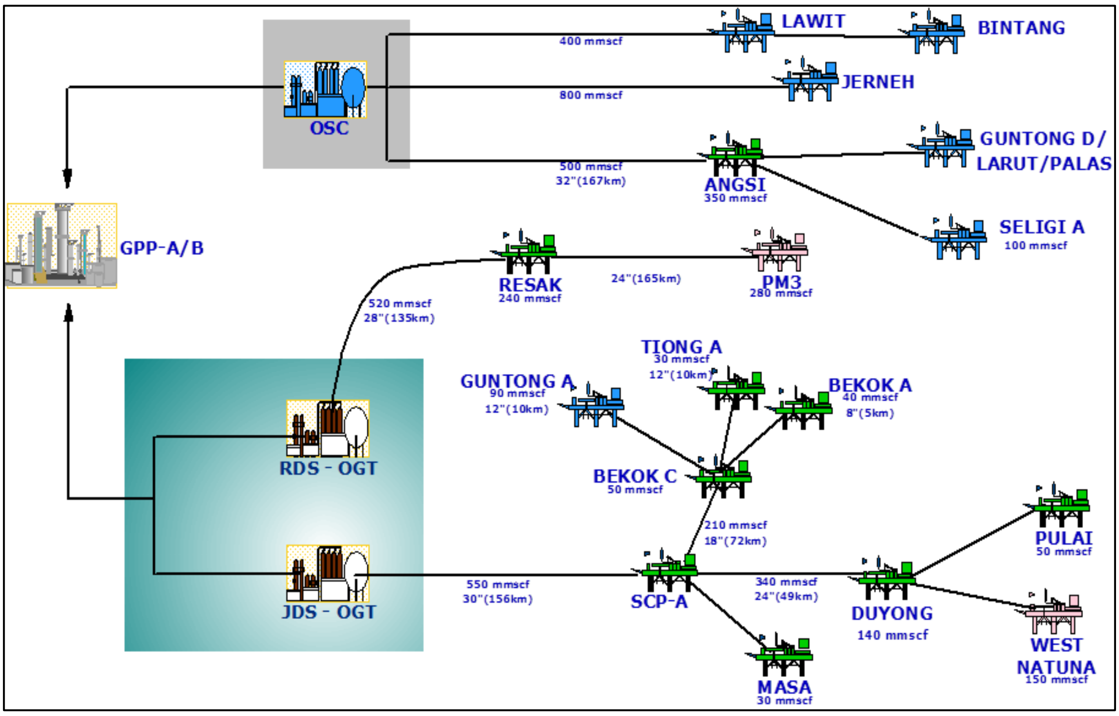


Figure 1. 3: Peninsular Malaysia Upstream Gas Production Network

Both OSC and OGT function is to handle gas processing and the difference between OSC and OGT is the capacity to handle and the source of the gas; source for OSC is from Angsi and other Exxon operated locations; source for OGT are from the JDS (gas from Duyong, Bekok, Masa) and RDS (gas from Resak and PM 3).

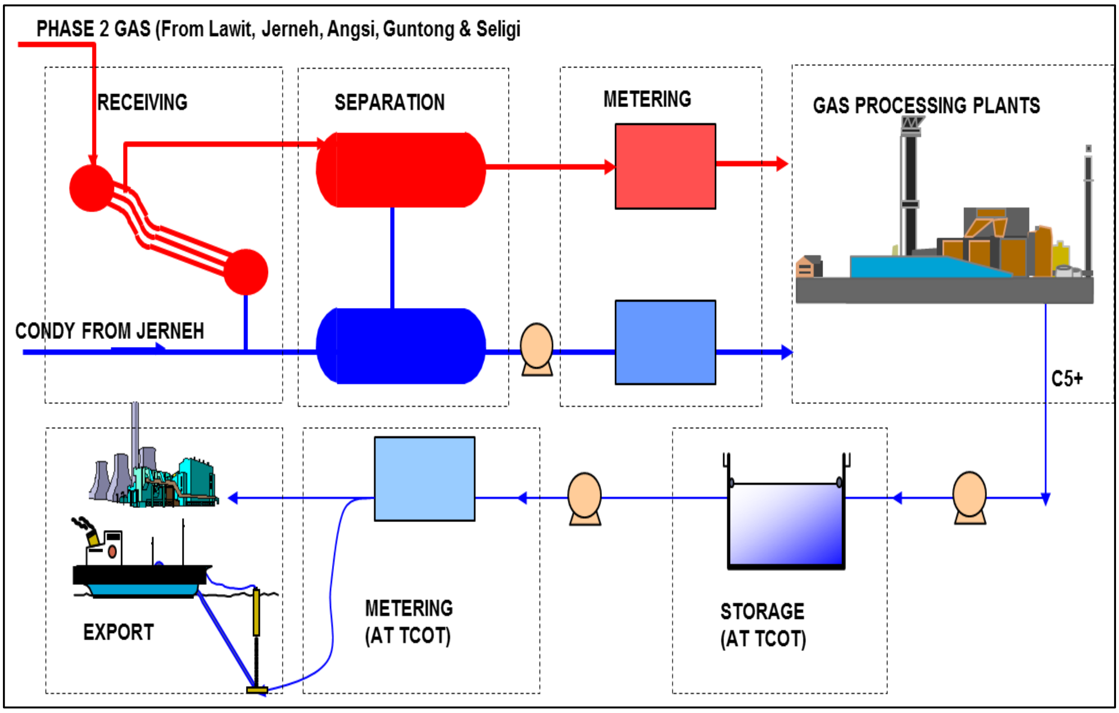


Figure 1. 4: OSC General Overview & Process

Gas received from upstream location, will be send to separation process to separate gas and liquid, and later to metering and subsequently, the output will be gas sales to GPP. Figure 1.4 shows the OSC general overview and process.

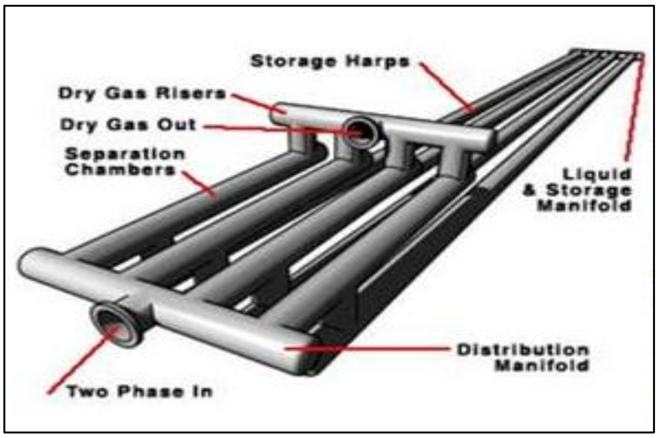


Figure 1. 5: Sludge Catcher Anatomy

The separator/sludge catcher consists of several modules from distribution headers, separation chambers, dry gas risers, storage harps and liquids and sludge manifolds as shown in Figure 1.5. The distribution manifold takes the incoming gas/liquid stream, slow it down, and splits it into several smaller streams to allow uniform flow into separation chambers. In the separation chambers, the majority of the gas liquid separation is accomplished. The required length, size and number of these chambers is a combined function of gas flow, gas chemistry and other known conditions. The primary function of the gas risers is to deliver dry gas back into the system. As some secondary separation occurs here, their sizing is important. Since GPP only handle gas from methane to pentane (C1-C5), and does not have condensate (also known as pentane plus, C5+) processing capabilities, thus condensate will be returned to TCOT for separation (same process as crude separation which begin with T-250, V-220, V-225 and finally V-230), storage and export later. OSC and OGT are estimates generating 1-2 kb/d of produced water daily.

1.2 Regulation for Produced Water Disposal

Generally, there is no single consistent format for produced water regulatory requirement around the world to follow. National or regional agencies of each country have set limits on the concentration of petroleum hydrocarbons (or total oil and grease) that can remain in produced water destined for ocean disposal based on several key international agreements on “completion fluids overboard discharge limits” shown in Table 1.2 [5] and worldwide produced water overboard discharge limits in Appendix A [6].

Table 1. 2: Produced Water Regulatory Requirements around the World.

Agreement	Oil in Water Limit	Other
OSPARCOM (North Sea Countries)	40 mg/L-current; 30 mg/L-by 2006	Pre-approval of chemical additives
Baltic Sea Convention and HELCOM standards	15 mg/L; 40mg/L if BAT cannot achieve 15 mg/L	Pre-approval of chemical additives
Kuwait Convention and Protocols (Red Sea Region)	40 mg/L; 100 mg/L max	-
Barcelona Convention and Protocols (Mediterranean countries)	40 mg/L; 100 mg/L max	-

1.3 Problem Statement

PW is the largest waste stream from hydrocarbon production. Previously, shore-side treatment facilities i.e. onshore recovery by gravity separation of crude oil, gas or water was designated and extraction of water is permitted for territorial sea discharge [7]. The Malaysia EEZ (Exclusive Economic Zon) Act 1984 required all aqueous effluent from process units and operational discharges to be treated prior to discharge to the marine environment. The 100 ppm oil limit stipulated under this act therefore applies to drilling mud/ cutting, produced water and drainage discharges from offshore installation [8].

Recently, due to its fate and effect, discharging PW into water bodies has become a significant issue of environmental concern. The Department of Environment (Malaysia) has now stipulated compliance with Standard B of the Environmental Quality Act 1974 under Environmental Quality (Industrial Effluents) Regulations, 2009 (Table 1.3) [9] and refineries that do not meet the requirement are no longer permitted to discharge produced water to coastal estuarine or marine water. TCIT IECS result in table 1.3 shows that few parameters from TCOT current wastewater effluent do not comply with DOE standard B limits i.e. COD, boron, phenol and, oil and grease. Hence, TCOT wanted to evaluate the effectiveness of biological treatment, particularly anaerobic treatment, in treating PW to be able to discharge the effluent inland or the nearest stream which is the Kertih River. Therefore, it is vital to deal with produced water efficiently and cost effectively to ensure compliance with the discharge standards.

Biological treatment is an effective and economical approach to treat large water production volume from exploration activities to reduce its organic content. PW, due to its high salinity and other toxic substances, can cause inhibition and affect the metabolism of microorganisms due to plasmolysis in the presence of salt if there is no adaptation of biomass before biological (anaerobic and aerobic) treatment and thus, biological treatment of produced water is sometimes regarded as difficult. The fact that microorganisms have been shown to acclimatize well to different industrial wastewaters is the main motivation for this research.

Table 1. 3: TCOT effluent in compliance with Environmental Quality Act 1974 under Environmental Quality (Industrial Effluents) Regulations, 2009 (Standard B)

	Parameter	**Unit**	**Standard B**	**TCOT Effluent**
i.	Temperature	^oC	40	40.9-53.7
ii.	pH Value	–	5.5-9.0	6.89-7.29
iii.	BOD_5 at 20^oC	mg/L	50	666-1210
iv.	COD	mg/L	200	1329-3594
v.	Suspended Solids	mg/L	100	21-51
vi.	Mercury	mg/L	0.05	0.005-0.255
vii.	Cadmium	mg/L	0.02	< 0.005
viii.	Chromium, Hexavalent	mg/L	0.05	< 0.01
ix.	Chromium, Trivalent	mg/L	1.0	< 0.01
x.	Arsenic	mg/L	0.10	< 0.005
xi.	Cyanide	mg/L	0.10	< 0.02
xii.	Lead	mg/L	0.5	< 0.01
xiii.	Copper	mg/L	1.0	< 0.005
xiv.	Manganese	mg/L	1.0	< 0.001
xv.	Nickel	mg/L	1.0	< 0.005
xvi.	Tin	mg/L	1.0	< 0.004
xvii.	Zinc	mg/L	2.0	< 0.005
xviii.	Boron	mg/L	4.0	7.8-10.0
xix.	Iron	mg/L	5.0	0.190-0.586
xx.	Silver	mg/L	1.0	< 0.005
xxi.	Aluminium	mg/L	15	0.64-0.90
xxii.	Selenium	mg/L	0.5	< 0.01
xxiii.	Barium	mg/L	2.0	2.13-3.30
xxiv.	Fluoride	mg/L	5.0	0.80-1.40
xxv.	Formaldehyde	mg/L	2.0	< 0.05
xxvi.	Phenol	mg/L	1.0	3.4-13.2
xxvii.	Free Chlorine	mg/L	2.0	< 0.01
xxviii.	Sulphide	mg/L	0.50	10.4-16.4
xxix.	Oil and Grease	mg/L	10	10-15
xxx.	Ammonia Nitrogen	mg/L	20	6.0-10.8
xxxi.	Color	ADMI*	200	63-147

*ADMI: American Dye Manufacturers Institute

1.4 Objectives of the Study

1. To evaluate the performance of anaerobic treatment of PW by Up-flow Anaerobic Sludge Blanket (UASB) and Hybrid Up-flow Anaerobic Sludge Blanket (HUASB) reactors.
2. To study the effect of chemical pre-treatment (coagulation and flocculation using ferric chloride)on anaerobic treatment of PW.
3. To evaluate the performance of post-treatment of anaerobically (UASB and HUASB) treated PW by aerobic Sequencing Batch Reactor (SBR).

1.5 Thesis Organization

Chapter 1 contains the introduction of Peninsular Malaysia Operation - Terengganu Crude Oil Terminal (PMO-TCOT), the current issues of produced water at TCOT and the objectives of the study. Chapter 2 This chapter provides an introduction to produced water and its treatment. Also, highlights the paradigm shift towards biological treatment of produced water treatment. Specifically, UASB, HUASB and SBR are discussed in detail. Section 2.1 to 2.3 describe produced water including the definition, current treatments methods for produced water and biological options. Section 2.4 and 2.5 discuss the principle of anaerobic (UASB, HUASB), aerobic treatment (SBR), and also summarizes common problems encountered during anaerobic and aerobic treatment during the treatment. Section 2.6 discuss on the originality and significance of the study. Chapter 3 discuss the methodology of the study which involved two phases. The first phase was to evaluate the performance of anaerobic treatment to treat raw PW by UASB and HUASB reactors under mesophilic condition at HRT of 5, 4, 3, 2 and 1. A pre-treatment (ferric chloride as coagulant) by coagulation and flocculation techniques was studied to compare its effect on PW treatment using UASB and HUASB reactors. Phase two was to observe the performance of aerobic treatment by SBR as post-treatment of effluent from UASB and HUASB reactors. Chapter 4 will give an analysis of the results and discussion. Chapter 5, discuss the conclusion and recommendation.

CHAPTER 2

LITERATURE REVIEW

2.0 Chapter Overview

This chapter provides an introduction to produced water and its treatment. Also, highlights the paradigm shift towards biological treatment of produced water treatment. Specifically, UASB, HUASB and SBR are discussed in detail. Section 2.1 to 2.3 describe produced water including the definition, current treatments methods for produced water and biological options. Section 2.4 and 2.5 discuss the principle of anaerobic (UASB, HUASB), aerobic treatment (SBR), and also summarizes common problems encountered during anaerobic and aerobic treatment during the treatment. Section 2.6 discuss on the originality and significance of the study.

2.1 Produced Water

Produced water (PW), formation water, connate water or oilfield brine, is defined as any water that is present in a reservoir with hydrocarbon resource and bought to the surface with crude oil or natural gas during onshore or offshore operations. Oil and gas are forced into production wells by pumping the water back into the reservoir to maintain reservoir pressure [10].

2.1.1 Sources of Produced Water

PW is the largest waste stream of hydrocarbon production [11]. It is estimated that daily water production volumes significantly exceed that of oil, to the extent that 211-250 million barrels of water are produced by the industry daily compared to 77-85 million barrels of oil [12]; making the water to oil ratio to be around 3:1 or water cut is 70% [13]. Due to the continuous rise of global water cut, PW treatment market is expected to worth US$ 4.3 billion for the next five years [14]. The amount and quality of PW generated is dependent upon the nature of formation and the recovery method.

2.1.2 Produced Water Characteristics

PW properties and volume can vary throughout the lifetime of a reservoir. Besides the large number of barrels of water, it contains naturally-occurring chemicals i.e. salinity, inorganic ions, metals, radioisotopes, organic acids, total organic carbons, phenols, petroleum hydrocarbons, volatile hydrocarbons, aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and other organic components and production chemicals [15]. PW characteristics vary considerably depending on the geographic location of the field, the geological formations with which PW has been in contact and the type of hydrocarbon product being extracted. [13]. All formation waters contain dissolved solids, primarily sodium chloride. The water sometimes is called brine or salt water. However, oilfield brines bear no relationship with seawater, either in the concentration of solids or in the distribution of ions present [16]. Table 2.1 [15] contrasts sea-water and PW characteristics. Table 2.2 is a summary of a range of produced water characteristics in different oilfields reported in various papers and works.

Table 2. 1: Salinity (‰) and concentrations (mg/L) of selected inorganic ions in typical seawater and in produced water

Chemical	Seawater	Produced Water
Salinity (‰)	32-36	3-320
Sodium	10560	65-97000
Chloride	18900	<5-201000
Calcium	400	13-118800
Strontium	13	7-3200
Magnesium	1270	4-11700
Potassium	380	3-6500
Sulfate	880	<1-1650
Sulfide	-	0.12-256
Ammonia	-	<0.1 - 650

Table 2. 2: Summary of a range of produced water characteristics in different oilfields reported by various papers and works.

	Concentration (mg/L)													
Reference	[17]	[18]	[19]	[20]	[21]	[22]	[23]	[24]	[25]	[26]	[27]	[13]	[28]	[29]
Parameter	**World PW**	**Wyoming, Western U.S.**	**Compos Basin, Brazil**	**Egbeda, Nigeria**	**Permian Basin, New Mexico**	**T á Juana, Venezuala**	**Huabei Oilfield, China**	**Gulf of Guinea, Liberia**	**Shengli Oilfield, China**	**Shengli Oilfield, China**	**Sarawak, Malaysia**	**India**	**Henan Oilfield, China**	**TPAO Basin, Turkey**
pH	4-10	-	-	8.30	7.3	-	8.0	6	-	5.8	8.2	-	6.4	7.95
Turbidity	-	-	-	49	-	-	270	-	-	-	850	181	-	-
TDS	-	-	110244	-	35023	-	-	-	-	-	16400	-	4950	8367
BOD_5	-	-	-	282	-	-	63	219	-	72	527	-	82	-
COD	1220	588	4300	1411	431	1150	124	399	285.5	345	1240	1542	343	2371
O&G	2-565	53	229	17742	147	-	20	-	81.43	-	15	-	-	140
TOC	0-1500	-	1415	361	-	-	38	130	-	84	540	340	82	-
SS	-	-	-	-	-	-	130	379	105.8	155	168	-	-	-
TSS	1-1000	-	-	-	85	-	-	-	-	46530	-	86.5	-	58
Σ HC	-	-	-	-	126	-	-	7.4	-	23	-	117.4	24	-

* Turbidity in NTU unit; O&G= oil and grease; TOC= Total organic carbon; SS= suspended solid; TSS= total SS; ΣHC = Total Hydrocarbon; Σ P = Total Phosphorous; Mg^{2+} = Magnesium

Table 2.2: Summary of a range of produced water characteristics in different oilfields reported by various papers and works (continued)

	Concentration (mg/L)													
Reference	[17]	[18]	[19]	[20]	[21]	[22]	[23]	[24]	[25]	[26]	[27]	[13]	[28]	[29]
Parameter	**World PW**	**Wyoming, Western U.S.**	**Compos Basin, Brazil**	**Egbeda, Nigeria**	**Permian Basin, New Mexico**	**T á Juana, Venezuala**	**Huabei Oilfield, China**	**Gulf of Guinea, Liberia**	**Shengli Oilfield, China**	**Shengli Oilfield, China**	**Sarawak, Malaysia**	**India**	**Henan Oilfield, China**	**TPAO Basin, Turkey**
Σ P	-	-	-	-	-	1-9.8	0.055	-	-	0.15	-	-	0.19	0.4
Σ Phenol	0.009-23	-	6	-	-	21.5		-	-	-	0.99	-	-	-
Sulphate	-	-	-	-	-	-	26	-	-	-	665	-	36	204
Sulphite	10	-	-	-	-	-	19.7	-	0.14	-	2.2	-	1.5	-
Phosphate	24-4300	-	-	-	-	-	-	0.23	-	-	39.2	-	-	-
Calcium	13-25800	-	1054	-	-	-	82	14200	-	1600	14.2	-	165	72.4
Mg^{2+}	8-6000	-	-	-	-	-	-	1800	-	143	4.7	-	25	34.4
Barium	1.3-650	-	-	-	-	-	-	-	-	-	3.79	-	-	0.6
Chloride	80-200000	-	62170	21872	–	2780	–	155000	2910	24350	–	-	-	3861
Boron	5-95	-	-	-	-	-	-	-	-	-	-	-	-	-
Ferum	<0.1-100	-	-	0.180	-	-	-	-	0.52	-	-	-	9.5	1.0

2.2 Current Treatments Methods of Produced Water

Hughes et al. [30] recommended three methods to reduce soluble organics concentration: biological oxidation, advance chemical oxidation and source minimization.

2.2.1 Option (1)-Dissolved Air Floatation (DAF)/ Chemical Oxidation/ Metals Precipitation

DAF is a system that able to reduce residual oils to 10 mg/L and suspended solids concentration to 20 mg/L. The chemical oxidation process can reduces hydrocarbon, mainly methanol and amines by 90%. pH adjustment using hydrated lime, coagulation, flocculation and clarification, and passing through filter media further reduce metal concentration through metal sulphide precipitation. Suspended solids concentration in the filtered effluent is approximately 5 mg/L before pumped to sea for final discharge. Estimated budget capital cost Option (1) is approximately USD 14 million. In this option, all requirements of process design is satisfied with exception of arsenic, cadmium, mercury, and lead, all of which would have treated effluent concentration of 0.02 mg/L rather than the required 0.01 mg/L [30]

2.2.2 Option (2)-Option (1) plus Ion Exchange

This treatment option has all the treatment processes provided in Option (1) with additional ion exchange process for further reducing arsenic, cadmium, mercury and lead concentration. Estimated budget capital cost Option (2) is approximately USD 15 million. This option consistently satisfies the discharge requirement for all the contaminants except mercury (0.001 mg/L could be met but not on a consistent basis). Although it produces a higher effluent quality, it is not expected to satisfy all the proposed discharged permit requirement consistently [30]

2.2.3 Option (3)-DAF/ Mechanical Evaporation/Chemical Oxidation.

The wastewater steam for this method is treated in the oil/water separator and DAF unit. The wastewater is then conditioned with chemical reagents and pumped to a mechanical evaporation system. As water is evaporated in the evaporator, a reject stream consisting crystallized salts, residual suspended solids and oils is formed. The distilled water stream is condensed by heat exchange with influence stream. The condensed distillate containing residual organics is subjected to chemical oxidation to reduce methanol and amine concentration. estimated budget capital cost Option (3) is approximately USD 27 million and this option consistently satisfy all the proposed discharge permit requirement. However, this method has an adverse impact on the public living near the facility because of heavy traffic to transport such large quantities of dewatered solids (waste) to landfill.

2.3 Biological Treatment of Produced Water

Biological treatment alone to treat produced water was not a favourable method for most of the researchers because the extremely high salinity concentration in the produced water would result in high osmotic pressure especially anaerobic treatment. The high osmotic pressure would adversely affect micro-organism development. In fact, several researchers have shown biological treatment to be able to treat PW. Combined biological treatment coupled with physical or membrane treatment has also been used to treat PW.

Rincon et al. [22] studied three categories of anaerobic biodegradation of water separated from extracted crude using up-flow anaerobic sludge blanket (UASB) with acclimatization to PW. The water separated from extracted light oil had good biodegradability, with 87% COD removal on average. For light oil, the remaining COD was made up of non-degradable and very slowly biodegradable fractions of the organic matter in the water. At HRT less than 10 hrs and the OLR greater than 3 g COD/L·d, the COD outlet rose as a consequence increased volatile fatty acid (VFA) concentration, indicating and overloading of methanogenic population; and also non VFA COD, indicating a decrease in the acidification efficiency. On the other hand, results with UASB reactors operated at a low loading rate and fed with water separated from extracted medium and heavy crude oil showed that purification efficiency was low (20% and 37% COD removal). Operating the UASB reactor with water separated from extracted medium oil for 6 months did not bring any improvement, indicating that no adaptation of the sludge to the treated wastewater occurred. They claimed treating these water separated from extracted medium and heavy oil by methanisation was not a practical and proposition.

Gallaghner [31] conducted a research by using a small fixed film anaerobic reactor with a low-density porous packing material to determine the ability of an anaerobic biological system to treat these organic acids in a simulated PW and to examine the potential for biodegradation of the naphthenic acids in the anaerobic environment. Microbial seed for the reactor were two pure cultures of brine-requiring acetoclastic methanogenic bacteria from Oregon Collection of Methanogens (OCM). The cultures were *Methanosarcina sicilae* C2J (OCM #653) and *Methanosarcina WH1* (OCM #750). The bioreactor showed bioactivity in terms of growth of biomass where gas production in simulated PW can occur when glucose is present (rapid gas production was noted), but did not occur when it was removed. He suggested that acetate-utilizing methanogens were either absent or inhibited by high salt concentrations and sulphide concentration or appropriate microorganisms were not present, despite seeding. Batch tests were also conducted to examine napthenic acid biodegradability under several conditions. The conditions used were seed from the anaerobic reactor, wetland sediments under aerobic and anaerobic conditions, and a sterile control. The naphthenic acid was dosed at 2 mg/mL. The incubations were for 30 d at 30 ℃. The results showed that no biodegradation of naphthenic acid was observed in anaerobic condition, but it was degraded under aerobic conditions. Loss of naphthenic acids was noted in aerobic experiment, although it appeared to be loss of straight-chain fatty acids rather than cyclics or aromatics.

Ji et al. [32] used anaerobic baffled reactor (ABR) to achieve high average h COD and oil removals of 65% and 88% for heavy oil produced water with poor nutrient (COD: TN: TP, 1200: 15: 1) and high salt concentration (1.15-1.46%), respectively.

The study was conducted for a total of 212 d; including the start-up of 164 d. Inoculum were mixtures of acclimated sediment taken from a heavy oil PW treatment plant and digested sludge from sewage wastewater treatment plant. The rod-shaped and spherical granules with colours of henna and black, in which Clostridia, *Methanosarcina* and *Methanothrx sp* were main population, were observed in each compartment (total of 6 equal compartments were used in this study) of ABR after the reactor's successful start-up (day 164). *Rhodopseudomonas* with the activity of lipase and halotelerant, as a kind of photosynthetic bacteria was also observed in the first five compartments. *Rhodopseudomonas* is beneficial to acidogenesis for hydrocarbons and recalcitrant organic under the condition of high strength of salt of heavy oil PW. Furthermore, ABR remained stable during 2.5 times the COD level shock load (0.50 kg COD/$m^3 \cdot$d) for four d.

A field demonstration in Wyoming, China, where a treatment train consisting of deoiling, followed by removal of water soluble organics using two-stage of Granular activated Carbon-Fluidized Bed reactor (GAC-FBR) [18] system consisting of a sequential anoxic and aerobic treatment to treat high concentration of organic acid present in PW from this site. Consistent removal of organics was observed when the upfront deoiling was not operating properly. Effluent O&G of less than 5 mg/L was consistently achieved with an O&G concentration of 53 mg/L after induced gas flotation. Most organic (i.e. BTEX, acetate) were removed to near or below detection limits. Effluent discharged from the GAC-FBR system was of high quality containing less than 1 μg/L benzene and low concentrations of all water soluble organics.

A novel suspended ceramic carrier was prepared by Dong et al. [28], which has high strength, optimum density (close to water) and high porosity. Two different carriers, unmodified and sepiolite-modified suspended ceramic were used to feed two Moving Bed Biofilm Reactors (MBBRs) with a filling fraction of 50% to treat oilfield PW. The hydraulic retention time (HRT) was varied from 36 to 10 hours. The results during a monitoring period of 190 d, showed that removal efficiency of COD was the highest in reactor 3 filled with sepiolite-modified carriers, followed by reactor

2 filled with the unmodified carrier, with the lowest in reactor 1 (activated sludge reactor), at an HRT of 10 hours. Similar trends were found in the removal efficiencies of ammonia nitrogen and polycyclic aromatic hydrocarbons. Reactor 3 was more shock resistant than reactor 2 and 1. The results indicate that the suspended ceramic carrier is an excellent MBBR carrier. This investigation also demonstrated that MBBR filled with the suspended ceramic biocarrier was an effective and feasible process for removal of COD, petroleum hydrocarbons, and ammonium nitrogen from the OPW in the tested organic loading range of 1.17-4.21 kg COD/m^{3}d, compared to the conventional activated sludge treatment. The modification of the ceramic biocarrier with sepiolite produced outcomes in the wastewater treatment efficiency. At HRT of 18 h, the concentrations of NH_3-N and COD of the effluent in the MBBRs meet the standard (NH_3-N < 15mg/L, COD_{cr} < 100mg/L) of petrochemical industry of China.

Activated sludge process has been the common method for treating oil-containing wastewater because it could maintain a total petroleum hydrocarbon (TPH) removal efficiency of 98-99% at a sludge retention time (SRT) of 20 d [17-33]. Tellez et al. (1992 to 2004) conducted several studies for a decade to study the feasibility of removing petroleum hydrocarbon from oilfield PW under laboratory and field conditions by activated sludge. In activated sludge, In 1992, Tellez et al. [34] evaluated the feasibility of bioreclamation of hydrocarbon contaminated brine water produced during oil and gas recovery from five typical oil field waste storage pits and separator tanks in south-eastern New Mexico. Studies focused on physical-chemical characterization and biodegradability of the samples. A commercially available culture, PETROBAC-S was selected for biodegradability evaluation. Batch biotreatability studies using a computer interfaced respirometer were conducted to evaluate the degradation of petroleum hydrocarbons under acclimated and non-acclimated biomass conditions. Results indicated that biological degradation using a non-acclimated culture was inhibited by produced water at dilution of 5:1 and 10:1, with inhibition being more predominant in the 5:1 dilution. However, with acclimated cultures, total petroleum hydrocarbon reductions of 65% to 98% were obtained under the same dilution ratios. Higher removal efficiencies are acquired when the acclimated culture was introduced to a higher TDS produced water than that of its acclimation water. In accordance with the research results provided, biological treatment of petroleum hydrocarbons present in produced waters is feasible. Biodegradation is substantial even at elevated TDS conditions of 5:1, or a combined sodium and chloride concentration of 36,000 mg/L. In 1996, [7] two different sources of PW were tested under continuous flow ranging from 375 L/d to 1800 L/d. One source of PW was an open storage pit; the other, a closed storage tank. The TDS concentrations of these sources exceeded 50,000 mg/L; total n-alkanes exceeded 100 mg/L; total petroleum hydrocarbons exceeded 125 mg/L; and total BTEX exceeded 3 mg/L. Removal of total n-alkanes, total petroleum hydrocarbon and BTEX remained consistently high over 99%. In 2002 [21], they evaluate the performance of a field (continuous-flow) activated sludge treatment system for removing petroleum hydrocarbons from South-western US oilfield generated PW. The activated sludge treatment unit maintained a TPH removal efficiency of 98-99% at solid retention time (SRT) of 20 d and a mixed liquor suspended solids concentration (MLSS) of 730 mg/L. In 2004 [35], they evaluated the impact of an activated sludge system in removing petroleum hydrocarbons from oilfield PW at a field-scale level. Five different MLSS concentrations of 700, 600, 500, 400, and 300 mg/L were used, along with a flow rate of 1890 L/d. TPH removal efficiency of 99% was observed while maintaining a mean effluent concentration of <1.0 mg/L. BTEX removals decreased below non-detectable levels (< 0.1 mg/L) at the outlet of the activated sludge unit.

Zhao et al. [23] investigated the use of B350M and B350 group of microorganisms immobilized on carriers in a pair of biological Aerated Filter (BAF) reactor to pre-treat oil field wastewater before desalination. By operating the biodegradation system for 142 d at HRT of 4 hours and volumetric load of 1.07 kg COD/m^{3}d eventually, the reactor immobilized with B350M achieved mean degradation efficiencies of 78% for total organic carbon (TOC) and 94% for oil, whereas that with B350 only reach 64% for TOC and 86% for oil. The degradation efficiencies of PAHs in the BAF immobilized with B350M and B350 microorganisms were 90% and 84%, respectively. It is found that certain PAHs such Phe, Chr, Baa, and Bbf are degraded effectively in the BAF system, maybe because they are easier to broken into small pieces. It is observed that the biological diversity of microorganisms in the reactor containing B350M is richer than that containing B350. A large quantity of filamentous microorganism developed in both reactors without causing foaming or bulking.

Sequencing batch reactor (SBR), aerated lagoon, waste stabilization pond, trickling filter, rotating biological contactor and filtration are also widely used to treat PW [36]. Freire et al. [37] reported the results of experiments carried out in a sequencing batch reactor (SBR) operated under 24 hour cycle, treating an effluent containing a mixture of oil field wastewater and sewage, in different percentages. The removal of phenols, ammonium and COD was monitored in several experimental runs, varying the dilution degree of oilfield wastewater (10 to 45% v/v). The removal of ammonium and phenols did not vary significantly in the experimental runs, attaining average values of 95% and 65%, respectively. COD removal efficiencies in the range of 30-50 % were attained in the experiments carried out with dilution percentages of 45% and 35% (v/v), respectively. An experiment carried out with a lower proportion of produced water (15%, v/v) keeping the salinity level corresponding to a higher proportion of industrial effluent (45%, v/v), led to an improvement in the COD removal; an indication that the recalcitrance of the organic compounds found in the effluent is the main source of the moderate COD removal efficiencies attained in the SBR system.

Another study was conducted to compare the TOC removal by three different biological systems including SBR, trickling filter and chemostat reactor with acclimated microorganisms in 180 mg/L of NaCl. A sample of acclimated bacteria in SBR reactor was analysed and the results showed that the more numerous of identified species are gram+ bacillus (60% of *Halobacillus*) and other halophilic species (25% of *Halomonas* and 15% of *Virgibacillus*). Total TOC removal in SBR was 80% which was higher than trickling filter and chemostat. However, the study showed that continuous operation of SBR could lead to a loss of biomass, since there was no sedimentation of the sludge in the reactor. These can be due to the dispersed growth of the microorganism or an inhibition of the bioflocculation process. To prevent biomass losses at every withdrawal step, a cross flow ultrafiltration (UF) unit was installed and the performance of the process is increased. The biomass is retained in the SBR and can allow a better biodegradation of the substrate. [24].

A recently developed biological method for wastewater, known as automated chemostat TreatmentTM (ACT) was introduced by Barash [13], and appears to provide a potent solution for existing challenges in the field of PW treatment. The tailor-made and pre-selected bacteria formulation known as “cocktail” were maintained in stable and low concentration while monitoring the system with a fully automated system. The “cocktail” is specifically designed to tolerant to extreme environment such as high temperatures (up to 45 ℃) or high salinity (up to 4%). During the process, the total organic carbon, COD and TPH removal efficiency was 88%, 89% and 99%, respectively. In addition, the ammonium was also reduced by 74%.

Aerated submerged fixed-film (ASFF) [38] process is a novel attached growth biological treatment system that uses totally submerged media to support biomass growing as a thin biofilm on their surfaces. *Bee-Cell 2000* was used as support media having porosity of 87% and specific surface area of 650 m^2/m^3. Also, diffusers provide bubbles of diffused air for both aeration and turbulence. The turbulence created by this way to prevent the excessive biofilm growth. The system achieved 71-93% COD removal efficiency at the organic loading rate of 1.310 to 15.797 g COD/m^3d. The system efficiency considerably increased with the increase in the organic loading rate because it can retain significant amount of attached biomass.

Li et al. [39] shown investigated using an anaerobic process coupled with micro-electrolysis (ME), focusing on changes in COD and biodegradability. Results showed that COD exhibited an abnormal change in the single anaerobic system which it increased within 168 hours before decreased to 222 mg/L after 360 hours of treatment (average removal was 15%). The BOD_5/ COD ratio of the water increase from 0.05 to 0.15. Comparatively, the effect of ME was also investigated. The COD underwent a slight decrease of the BOD_5/ COD ratio of the water improved from 0.05 to 0.17 after ME. Under idealize ME conditions (pH 6.0), using iron and active carbon (80 and 40 g/L, respectively), the COD removal efficiency was 38.3%. When coupled with micro-electrolysis the total COD removal improved to 53.3%.

Performance of a submerged hollow fiber membrane bioreactor (MBR) [29] has been studied for the treatment of brackish oil and natural gas field PW. The bacteria which grow in conventional activated sludge and MBR cannot survive in these conditions; therefore acclimatization of bacteria is vital. The performance of the biological system, membrane permeability, the rate and extent of TPH biodegradability have been investigated under different sludge age and F/M ratios. One year of operation of MBR was able to remove COD up to 80-85% efficiency. The COD removal rate slightly increased with SRT due to the higher concentration of biomass which is the main agent that decomposes organic compounds. Hydrocarbon removal efficiency of 99% was achieved. The increase of sludge age increased the removal efficiency of oil and grease dramatically from 60% to 85%. The MBR removed almost all the light hydrocarbons from nC9 to nC13 and important reduction of hydrocarbons ranged between C13 and C40 was also observed. The results obtained by gas chromatography analyses showed that the MBR system could be very effective in the removal of TPH from produced water and a significant improvement in the effluent quality was achieved. The corresponding permeability after physical cleaning was restored to 60% and to 95% after subsequent chemical cleaning.

Fakhru'l-Razi et al. [27] compared biological treatment of effluent between coupling membrane to SBR (MSBR) and MSBR/reverse osmosis (RO) with isolated tropical halophilic microorganisms. The MSBR was operated at different HRT of 20 and 44 hours. The results showed that at HRT 20 hours, the combined process effluent COD, TOC and O&G removal efficiencies were 90%, 92% and 91%, respectively. Whereas at the highest HRT of 44 hours, the average COD, TOC and O&G removal efficiencies were 92.4%, 94.3%, and 94.2% respectively. They also studied the possible adverse effect of NaCl salt concentration on microbial activity over different ranges of TDS. The average TOC removal efficiencies at TDS of 35,000, 100,000, 150,000, 200,000 and 250,000 were 90.8%, 86.9%, 73.3%, 60.7% and 41%, respectively. When MSBR attached with RO treatment (HRT 20 hours), MSBR/RO was able to removed

TOC and COD to 8 and 23 mg/L (99% and 95% removal efficiency), respectively. O&G concentration was below detection limit. It was found that the isolated microorganisms played an important role in the degradation of the pollutants and membrane separation was required for ensuring a stable permeate quality.

Shpiner et al. [40] observed that waste stabilization pond (WSP) operating with an anaerobic section, oil skimming and 300% recycling were all found to remove COD. WSP with a deep separating baffle between the aerobic and anaerobic zones and three shallow baffles serving as oil stoppers were employed using different process configurations (HRT, aerobic and anaerobic conditions, oil skimming, effluent recycle). Seven different species cultures collection bacteria were used to seed the reactor: *Rhodococcus rhodochrous, Rhodococcus ruber, Ralstonia sp, Acinetobacter venetianus and Paenibaccilus naphtalenovorans*. The reactor was operated for 6 months and at HRT of 6 d, the COD and O&G removals were 85% and 82%, respectively and improved over time.

Lu et al. [26] conducted an anoxic hydrolysis-aerobic treatment on a hydrolysis acidification/bio-contact oxidation system (HA/BCO) using immobilized microorganisms on combine plastic carriers to purify oilfield water with high salinity 46,530 mg/L and low organic load of 302.mg/L. This field test was operated for 3 months with HRT of 32 hours and a volumetric load of 0.28 kg COD/m ^{3}d. It was able to remove COD by 63.5%, ammonia nitrogen (NH_3-N) by 45%, TSS by 79.5% and TPH by 68%. The use of maize powder can enhance environmental adaptability of microorganisms and biodegradation ability and is recommended as a nutrient supplement to maintain good treatment performance. Table 2.3 shows comparison of different biological processes for treatment of PW for the past 20 years.

Gilbert et al. [34], Zhao et al. [23], Lu et al. [26], Gallaghner [31], Shpiner et al. [40] and other researchers believe microbial treatment is necessary to enhance the treatment of PW since biological treatments are often very sensitive to fluctuating condition. A PW acclimated culture is recommended for all biological treatment activities. A suitable species are carefully chosen according to the characteristic of PW. Sublette et.al [41] recommended for sour produced water, a sulphide-tolerant strain of the chemautotroph and facultative anaerobe *Thiobacillus denitrificans* can be used to remove inorganic sulphide. *T.denitrificans* was successfully removed sulphide for 99% for routine discharges of 5000 bbl/d containing 100 mg/L sulfide. Baskaran and Nemati [42] observed that utilization of and sulfate reducing bacteria (SRB) consortium originated from an oil reservoir led to sulphate reduction rates which are higher than those previously reported for system operated in similar influent pH values (pH 7). SRB is dominated by *Desulfovibrio sp*. and *Desulfovibrio sp.* Piubeli et al. [19] recommended *Halomonas sp* to enchance degradation of COD and PAHs with addition of nutrients. COD reduction increased from 20% without additions to as much as 65-80% with addition of phosphate combined with alanine or gluronic acid, or tryptone in combination with glucuronic acid. Kapdan and Erten [43] suggested *Halanaerobium lacusrosei*, anaerobic salt tolerant bacteria as dominant microbial to enhance COD removal from the saline wastewater under anaerobic conditions. The culture us able to remove up to 3445 mg COD/L with over 70% efficiency at 3% salt concentration and 19 h of hydraulic retention time. COD removal efficiency can be increased to 84% by extending the hydraulic retention time to 30 h for the same wastewater composition. Okoro and Ahmud [44-45] have studied two different type of pure culture using same sample from Wemco treatment plat at Chevron's Escarvos tank to degrade hydrocarbon in produced water; *Alcaligene sp*. and *Aspergillus fumigatus*. *Alcaligene sp*. after 40 d of exposure to treat PW reduced oil and grease (1407mg/L), n-alkane (608 mg/L), aromatics (13.88 mg/L), NSO compounds (12.68 mg/L) and PAHs (0.0655 mg/L) to 19.58 mg/L, 16.87 mg/L, 1.25 mg/L, 0.98 mg/L and 0.0096 mg/L, respectively. While, *Aspergillus fumigatus* after 120 d of exposure, n-alkane, aromatics, NSO compounds and PAHs reduced to 78.5 mg/L, 1.58 mg/L, 1.22 mg/L and 0.0168 mg/L, respectively. Both cultures are effective in degrading the PAHs and NSO compounds.

Table 2. 3: Comparison of different biological processes for treatment of produced water

Year	**Substract**	**Sample Characteristic (mg/L)**	**Inocolum**	**Salt Content (mg/L)**	**Operational Condition**	**Process Treatment**	**Final Removal**	**Ref.**
1992	OPW	TOC: 155 - 722 TPH: 385 - 886	Acclimated activated sludge	TDS: >50000	TOC: 83 % - 96 % TPH: 65 % - 92 %	Activated Sludge System	COD: > 99 % TPH: > 99 % O&G: > 99 %	[34]
1994	SPW	Phenol: 70	Hypersaline soil	15 % salt solution	12 hrs cycling	SBR	Phenol: 99.5 %	[46]
1996	OPW	TNA: 126 BTEX: 3.1 TPH:135	Acclimated activated sludge	TDS: >50000	Flowrate: 378 L/d MLSS: 373 mg/L	Activated Sludge System	COD: > 99 % TPH: > 99 % O&G: > 99 %	[7]
1996	OPW	COD: 1009 O&G: 72	Acclimated sludge	-	OLR: 1.5-8.7 kg COD/m^3d	Anoxic-aerobic-GAC-FBR	COD: 95.8 % O&G: 92.4 %	[18]

*OPW= Oilfield Produced Water; SPW= Synthetic PW; SBR= Sequencing Batch Reactor; GAC-FBR= Granular Activated Carbon- Fluidized Bed Reactor

Table 2. 3: Comparison of different biological processes for treatment of produced water (continued)

Year	**Substract**	**Sample Characteristic (mg/L)**	**Inocolum**	**Salt Content (mg/L)**	**Operational Condition**	**Process Treatment**	**Final Removal**	**Ref.**
2000	SPW	Naphthenic Acid: 104 ± 10.6 mg	Mixed 2 pure cultures into anaerobic digester & municipal sludge.	-	HRT: 1 dy	Fixed film anaerobic reactor	Naphthenic Acid: 112.5 ± 16.3 mg	[31]
2002	OPW	COD: 431 ± 25 TPH: 126 ± 30 O&G: 147 ±35	Acclimated activated sludge	TDS: 35023	SRT: 20 dys	Activated Sludge System	COD: 92 % TPH: 98 % O&G: 98 %	[21]
2003	Light OPW	COD: 1150 Phenols: 21.5	Brewery UASB sludge	-	OLR: <1.80 kg COD/m ³d HRT: > 18 hr	UASB	COD : 83 % Phenols: 14.6 -28.40	[22]
2003	Medium OPW	COD: 890	Brewery UASB sludge	-	OLR: 0.53-1.09 kg COD/m ³d HRT: > 18 hr	UASB	COD : 20 %	[22]

*OPW= Oilfield Produced Water; SPW= Synthetic PW; UASB= Up-flow Anaerobic Sludge Blanket Reactor

Table 2. 3: Comparison of different biological processes for treatment of produced water (continued)

Year	**Substract**	**Sample Characteristic (mg/L)**	**Inocolum**	**Salt Content (mg/L)**	**Operational Condition**	**Process Treatment**	**Final Removal**	**Ref.**
2003	Heavy OPW	COD: 275	Brewery UASB sludge	-	OLR: 1.07 kg COD/m^3·d HRT: > 18 hr	UASB	COD : 33 %	[22]
2006	OPW	TOC: 38 Oil: 20 PAHs: 920 ng/mL	Activated sludge + Immobilized microorganisms (B350M)	-	OLR: 0.18-0.33 kg COD/m^3·d HRT: 4 hr	Aerobic, upflow, submerged BAF	B350M:- TOC: 78 % Oil: 94 % PAHs: 90 %	[23]
2006	OPW	TOC: 38 Oil: 20 PAHs: 920 ng/mL	Activated sludge + Immobilized microorganisms (B350)	-	OLR: 0.18-0.33 kg COD/m^3·d HRT: 4 hr	Aerobic, upflow, submerged BAF	B350:- TOC: 64 % Oil: 86 % PAHs: 84 %	[23]
2006	OPW	COD: 399 TOC: 130	Acclimated microorganisms	180000	24 hrs cycling	(SBR/UF)	TOC: 80 %	[24]

*OPW= Oilfield Produced Water; BAF= Biological Aerated Filter; SBR/UF= Sequencing Batch Reactor/Ultrafiltration

Table 2. 3: Comparison of different biological processes for treatment of produced water (continued)

Year	Substract	Sample Characteristic (mg/L)	Inocolum	Salt Content (mg/L)	Operational Condition	Process Treatment	Final Removal	Ref.
2006	OPW	COD: 399 TOC: 130	Acclimated microorganisms	180000	-	Chemostat	TOC: 19 %	[24]
2007	PW	COD: 975 - 1023	Acclimated activated sludge	-	OLR: 1.31-15.797 kg COD/m ³·d	ASFF	COD: 70.8-93.1 %	[38]
2007	OPW	TOC: 580 BTEX: 600	-	TDS: 10000	HRT: 9.6 hr	SMZ adsorption/ MBR	TOC: 92 % BTEX: 95 %	[47]
2008	OPW	-	-	-	OLR: 7.1 kg COD/m ³·d	Bio-film reactor (Kaldnes MBBR)	BOD_5: 99 %	[48]
2009	OPW	COD: 345 NH_3-N: 82 TSS: 155 TPH: 23	Mixed culture microorganism contaminated soil + anaerobic sludge	-	OLR: 0.28 kg COD/m ³·d HRT: 32 hr	HA/BCO	COD: 83.5 % NH_3-N: 45 % TSS: 79.5 % TPH: 68 %	[26]

*OPW= Oilfield Produced Water; APW= Artificial Produced Water; ASFF= Aerated Sub-merged Fixed Reactor; HA/BCO= Hydrolysis acidification/ bio-contact oxidation system

Table 2. 3: Comparison of different biological processes for treatment of produced water (continued)

Year	**Substract**	**Sample Characteristic (mg/L)**	**Inocolum**	**Salt Content (mg/L)**	**Operational Condition**	**Process Treatment**	**Final Removal**	**Ref.**
2009	Heavy OPW	COD: 450-600 Oil Conc.: 50-200	Acclimated oil sediment + sewage sludge	11442 - 14603	OLR: 0.20-0.50 kg COD/m ^{3}d HRT: 60 hr	ABR	COD : 65 % oil Conc.: 88 %	[32]
2009	APW	COD: 1200 O&G: 500 L/L	Cultured bacteria added into ponds	6000	HRT: 6 d	WSP	COD: >85 % O&G: 82 %	[40]
2010	OPW	COD: 1240 TOC: 540	Hypersaline soil	-	OLR: 0.62 kg COD/m ^{3}d	MSBR	COD: 113 TOC: 43	[27]
2010	OPW	COD: 1542 TOC: 340 TPH: 117.4 NH_3-N: 18	Mixed culture microorganism from pre-treated water	-	-	ACT	COD: 89 % TOC: 88 % TPH: 99 % NH3-N: 74 %	[13]

*OPW= Oilfield Produced Water; APW= Artificial Produced Water; ABR= Anaerobic Baffled Reactor ; WSP= Waste Stabilization Pond ; MSBR= Membrane SBR; ACT= Automated Chemostat Treatment

Table 2. 3: Comparison of different biological processes for treatment of produced water (continued)

Year	Substract	Sample Characteristic (mg/L)	Inocolum	Salt Content (mg/L)	Operational Condition	Process Treatment	Final Removal	Ref.
2010	OPW	COD: 390 ± 37	Municipal sludge	-	-	EO/ MBR	COD: 92 %	[49]
2011	OPW	COD: 343-365	Activated sludge	-	OLR: 1.17 - 4.21 kg COD/m ³d HRT: 36, 18, 10 hr	MBBR	COD: 47 - 62 %	[28]
2011	OPW	COD: 343-365	Activated sludge + suspended ceramic granule	-	OLR: 1.17 - 4.21 kg COD/m ³d HRT: 36, 18, 10 hr	MBBR	COD: 63-77 %	[28]
2011	OPW	COD: 343-365	Activated sludge + Ceramic granule modified with sepiolite	-	OLR: 1.17 - 4.21 kg COD/m ³d HRT: 36, 18, 10 hr	MBBR	COD: 74-79 %	[28]
2012	OPW	COD: 2371 TPH: 2301	MBR treating leachate sludge	Salinity: 8.7 ‰	SRT: 30 d	Submerged MBBR	COD: 80-85 % TPH: 97-99 %	[29]

*OPW= Oilfield Produced Water; MBBR= Moving Bed Biofilm Reactor ; EO/MBR: Electrolytic Oxidation/Membrance Bioreactor

2.4 Anaerobic Processes

Anaerobic treatment is technologically simple with low energy consumption. The final product is biogas which is a mixture of methane (55-75 vol %) and carbon dioxide (25-45 vol %) that can be used for heating and upgrading natural gas quality or co-generation [50]. Anaerobic microbial decomposition is a process in which microorganisms derive energy and grow by metabolising organic material in an oxygen-free environment resulting in the production of methane (CH_4), ammonia (NH_3), hydrogen sulphide (H_2S) and carbon dioxide (CO_2).

2.4.1 Principle of the Anaerobic Digestion Process

Anaerobic microbiological decomposition is a process in which micro-organisms derives energy and grow by metabolising organic material in an oxygen free environment resulting in the production of methane (CH_4). A digestion process may be subdivided into the following four phases, each requiring its own characteristic group of microorganisms as given in Figure 2.1 [51].

1) Hydrolysis: where enzymes excreted by fermentative bacteria (exo-enzymes) convert non-soluble biopolymers to soluble organic compounds which can pass through the cell walls and membranes of the fermentative bacteria.
2) Acidogenesis: acidogenic bacteria excrete enzymes for hydrolysis and convert soluble organic compounds to volatile fatty acids (VFA) and CO_2, H_2, NH_3 and H_2S, as well as new cell material.
3) Acetogenesis: acetogenic bacteria convert intermediary acid into acetate, H_2, CO_2 as well as new cell material.
4) Methanogenesis: methanogenic bacteria then convert acetate, H_2, carbonate, formate or methanol into methane, CO_2 and new cell material.

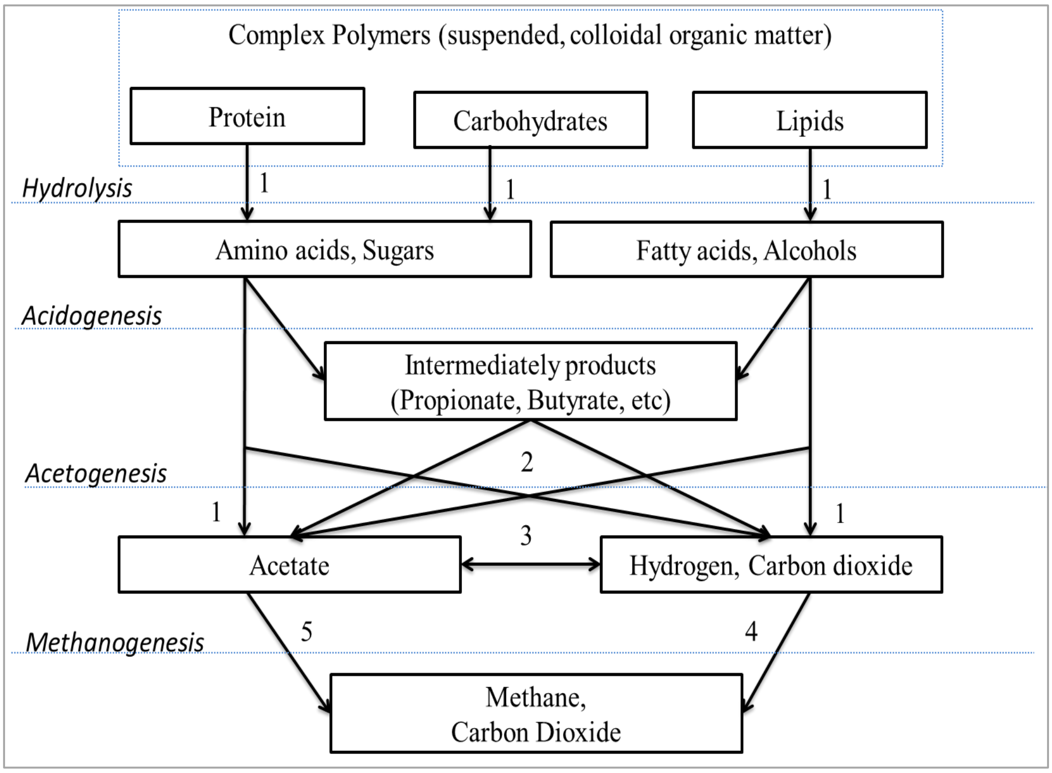


Figure 2.1: Simplified schematic representation of anaerobic degradation process.

Numbers indicate the bacterial groups involved: 1. Hydrolytic and fermentative bacteria, 2. Acetogenic bacteria, 3. Homo-acetogenic bacteria, 4. Hydrogenotrophic methanogens, 5. Aceticlastic methanogens.

2.4.2 Advantages and Disadvantages of Anaerobic Treatment

Advantages of anaerobic treatment are numerous over conventional aerobic treatment systems and can be summarised as follows [50].

1) Reduction of solids to be handled; excess sludge production on the basis of biodegradable COD in anaerobic treatment is significantly lower compared to aerobic processes. Reduction of excess sludge production up to 90%.
2) Modern anaerobic treatment processes can handle very high loads, exceeding values of 30 g COD/L/d at ca. 30 ℃ and up to 50 g COD/L/d at ca. 40 ℃ for medium strength mainly soluble wastewater. High applicable COD loading rates reaching 20-35 kg COD per m^3 of reactor per day, requiring smaller reactor volume. Up to 90% reduction in space requirement when using

expended sludge bed systems. The space requirements of anaerobic treatment are lower than conventional systems and thus, the construction costs are relatively low.

3) Anaerobic treatment processes generally consume little energy or no use of fossil fuel for treatment, saving about 1 kWh/ kgCOD removed, depending on aeration efficiency. At ambient temperature the energy requirements are in the range 0.05-0.1 kWh/m3 (0.18-0.36 MJ/m^3), depending on the need for pumping and recycling effluent.
4) Provision of energy source through methane recovery. Production of about 13.5 MJ CH_4 energy/kg COD removed, giving 1.5 kWh electricity (assuming 40% electric conversion efficiency)
5) rapid start up (< 1 week), using granular anaerobic sludge as seed material
6) no or very little use of chemicals
7) plain technology with high treatment efficiencies
8) anaerobic sludge can be stored unfed, reactors can be operated during agricultural campaigns only (4 months per year in the sugar industry)
9) excess sludge has a market value
10) high rate systems facilitate water recycling in factories (towards closed loops)
11) Facilitation of sludge dewatering.
12) Relatively odour free end product.
13) Almost complete retention of the fertiliser nutrients nitrogen (N), phosphate (P) and potassium (K). During anaerobic treatment biodegradable compounds are effectively removed, leaving a number of reduced compounds in the effluent, as well as ammonium, organic N-compounds, sulphide, organic P-compounds and pathogens. Depending on the further use a complementary treatment step is needed.

The disadvantages of anaerobic treatment are summarised below [52].

1) The high sensitivity of methanogenic bacteria to a large number of chemical compounds. In many cases anaerobic organisms are capable of adapting to these compounds

2) The first start-up of an installation without the presence of proper seed sludge can be time consuming due to the low growth yield of anaerobic bacteria
3) When treating waste (water) containing sulphurous compounds, the anaerobic treatment can be accompanied by odour due to the formation of sulphide. An effective solution to this problem is to employ a micro-aerophilic post-treatment step, to convert sulphide to elemental sulphur.
4) The capital costs are high. Large, covered tanks along with pumps for feeding and circulating sludge, head exchangers and compressor for gas mixing are required.
5) The quality characteristics of the supernatant from anaerobic sludge digestion are poor. The supernatant contain suspended solids, dissolved and particulate organic materials (oxygen-consuming compounds), nitrogen and phosphorus. This return flow adds to the solids, oxygen demand and nutrient loads to the treatment system.

2.4.3 Up-flow Anaerobic Sludge Blanket (UASB) Reactor

UASB reactor was developed in 1980 by Prof. Gatze Lettinga (Wageningen University) and since then has been successfully treating a wide range of industrial effluents including those with inhibitory compounds. UASB reactor is essentially a suspended growth system in which proper hydraulic and organic loading rate is maintained in order to facilitate the dense biomass aggregation know as granulation. The success of UASB reactor relies on the establishment of a dense sludge bed in the lower part and a three phase gas-liquid-solids separator (g-l-s separator) in the upper part of the reactor [53]. The sludge bed is formed by accumulation of incoming suspended solids and bacterial growth. The size of granules is about 1.3 mm diameter. The dense aggregates are not susceptible to washout from the system under practical reactor condition and efficiently retains complex microbial consortium without the need for immobilization on a carrier material by forming biological granules with good settling characteristics [54]. The concentration of biomass in the reactor may become as high as 50 g/L. This granulation process allows loading rates in UASB reactors far beyond the common loading rates applied in conventional activated sludge processes. This result in reduction in the reactor size required for treatment and leads to lower investment costs in addition to the reduced operating costs due to the absence of aeration [55].

2.4.4 Hybrid Up-flow Anaerobic Sludge Blanket (HUASB) Reactor

HUASB (a combination of UASB and packing media) reactor allows treatment of low strength wastes by maintaining long solid retention time (SRT) independent of the hydraulic retention time (HRT) [56]. This system reduces the need for elevated temperatures [57], channelling problem and loss of biomass due to flotation associated with poorly performing UASB [58]. The packing material separates biogas bubbles from the biomass, acts as a support material for biomass growth and even has a notable efficiency as a suspended solids (SS) separator [59]. The packing material causes the flocculated biomass to precipitate over the sludge blanket to serve as suitable and natural hydrophobic core for the development of granular sludge [60]. Many studies have found out that hybrid UASB is efficient in treating dilute to medium strength wastewater [53].

2.4.5 Factors Affecting Anaerobic Processes

The common rate-limiting reaction in anaerobic digestion is the conversion of volatile acids to methane gas by methane-forming bacteria, which are strict anaerobes and extremely sensitive to changes in temperature and pH. The success of anaerobic reactor depends on maintaining the environmental factors close to the comfort zone of the microorganisms involved in the process. Therefore, it is essential that the environment in the anaerobic digestion tank be maintained at condition optimum for methane-forming bacteria. Several environmental conditions must be maintained for proper operation of anaerobic digestion of sludge [52].

The range of extreme conditions and the optimum conditions for maximum methane production are listed in Table 2.4

Table 2. 4: Environmental and Operating Conditions for Maximum Methane Production during Anaerobic Digestion of Wastewater Sludge

Variable	**Optimum**	**Extreme**
pH	6.8-7.4	6.4-7.8
Oxidation Reduction Potential (ORP) (mv)	-520 to -530	-490 to -550
Volatile Acids (mg/L as acetic acid)	50-500	>2,000
Alkalinity (mg/L as $CaCO_3$)	1500-3,000	1000-5000
Temperature		
Mesophilic	30-35 ℃	20-40 ℃
Thermophilic	50-56 ℃	45-60 ℃
Hydraulic Detention Time (days)	10-15	7-30
Gas Composition		
Methane (CH_4) (%v)	65-70	60-75
Carbon Dioxide (CO_2) (%v)	30-35	25-40

2.4.5.1 pH and Alkalinity

Two groups of bacteria namely acidogens and methanogens exist in terms of pH optima i.e. acidogens 5.5-6.5 and methanogens 7.5-8.2. The operating pH for combined cultures is 6.8-7.4 with neutral pH being the optimum. For pH outside the range of 6.5-7.5, the rate of methane production is low, as shows in Figure 2.2 [61].

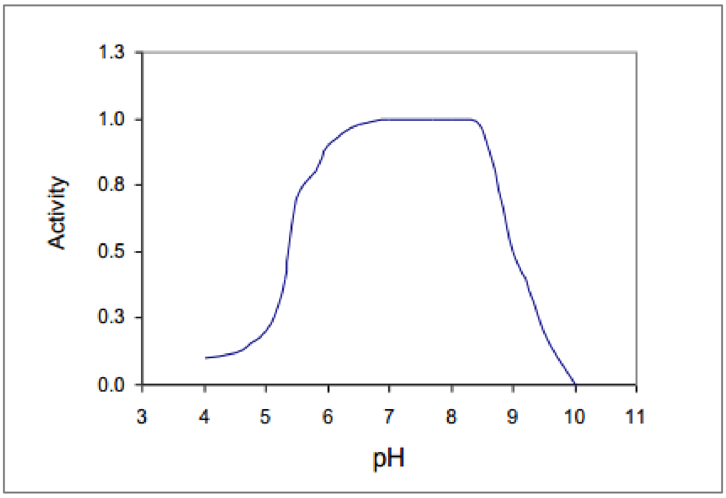


Figure 2. 2: Relative activity of methanogens to pH

Alkalinity is essential for proper pH control. Alkalinity is derived from the breakdown of organics and is present primarily in the form of bicarbonates, which are in equilibrium with the carbon dioxide in the gas at a given pH. This relationship between alkalinity, the carbon dioxide in the digester gas, and pH is illustrated in Figure 2.3 [52]. A sufficient amount of hydrogen carbonate (denoted as bicarbonate alkalinity) in the solution is important to maintain the optimal pH range required for methanogenesis. Low pH reduces the activity of methanogens and causes accumulation of VFA and hydrogen [50]. If VFA accumulate, pH starts to drop and the alkalinity present within the system neutralizes the acid and prevents further drop in pH [61]

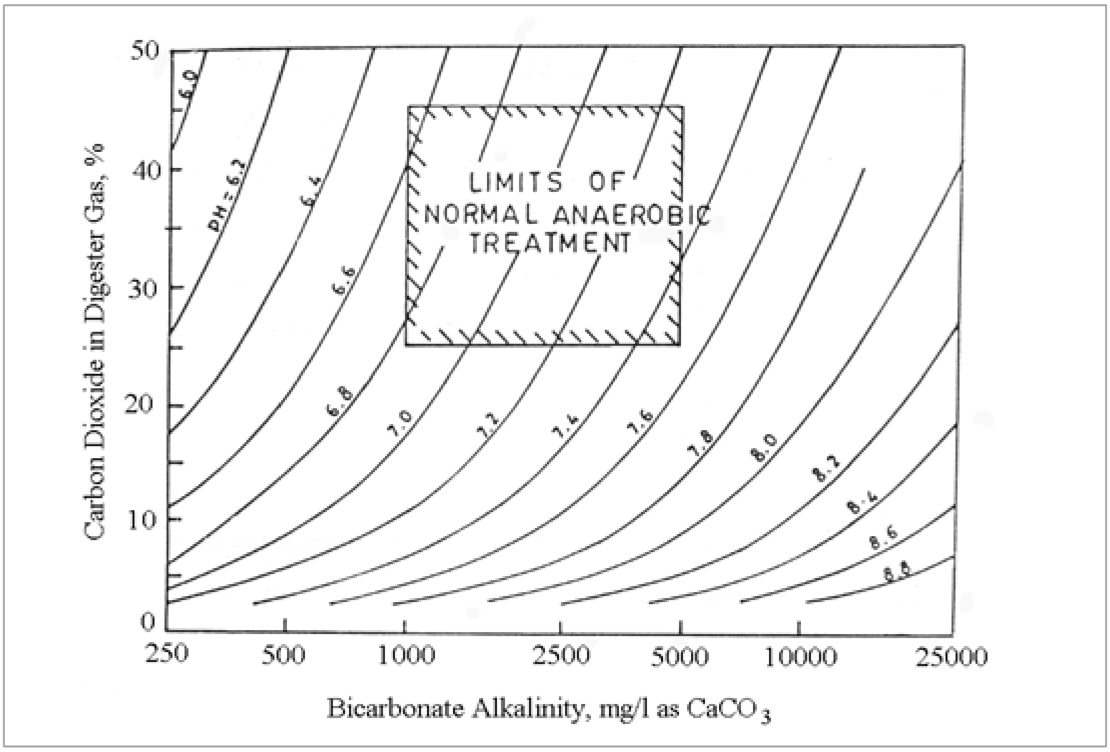


Figure 2. 3: Relationship between pH, CO_2 and bicarbonate alkalinity

2.4.5.2 Temperature

Anaerobic digestion systems can operate at different temperature ranges; Psychrophilic (< 20 ℃), mesophilic (20-40 ℃) and thermophilic (50-60 ℃) as shows in Table 2.3. As bacterial growth and conversion process are slow under low temperature, phychrophilic digestion requires a long retention time, resulting in large reactor volume. Rate of methane production increases with increase in temperature and good methane generation is obtained with mesophilic organisms. Mesophilic digestion requires smaller reactor volume. Operation under thermophilic condition offers improved biodegradability of organic compounds, however, due to sensitivity of thermophilic organisms to variation of OLR, influent composition, pH and other factors, the start-up and operation is cumbersome [54]. The choice of temperature is determined by the relationship between energy requirement and biogas yield [50].

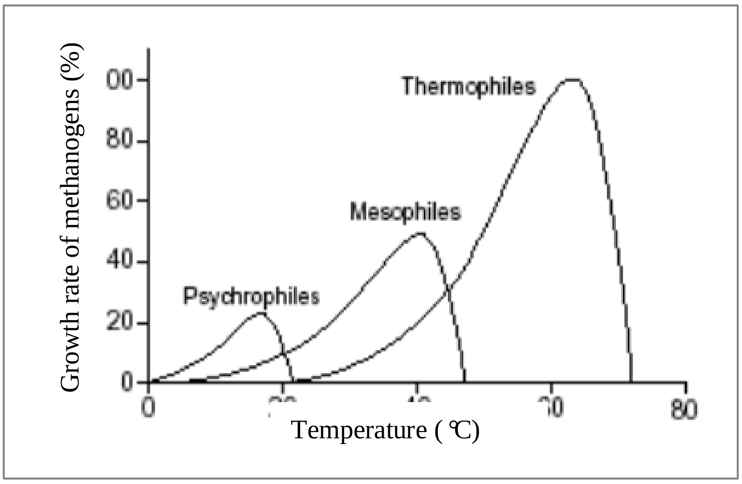


Figure 2. 4: Effect of temperature on anaerobic activity

Classic UASB shows good removal of COD which is greater than 72% at lower temperatures (10-14 ℃). When bacterial activity is lower, solid accumulation in the reactor is more pronounced with better solids retention. Based on the result from a study [62], HUASB containing filter rings showed no advantage and at lower temperature performed slightly worse than classic UASB. However, several researchers investigated the efficiencies of HUASB and existing UASB in mesophilic conditions e.g. Gupta et al. [63] found that COD removal in HUASB was approximately 5% more than UASB reactor. HUASB is capable of resisting shock load (2 times) as compared to UASB (1.5 times). With HUASB, the problem of plugging and choking of effluent and vent pipes, the usual occurring problems of UASB reactor can be avoided. Hutnan et al. [53] compared the performance of the selected anaerobic high rate reactors operated simultaneously at 37 ℃. They observed intensive biomass washout from UASB occurred at organic loading, B_v = 6 kg/m^{3}d while significant biomass losses from HUASB were noticed only at B_v = 12 kg/m^{3}d. Another study [64] investigated the performance of HUASB in mesophilic (maintained in room temperature) and thermophilic (46 ± 2 ℃) condition. HUASB in mesophilic temperature was able to reduce COD to 84% while in thermophilic condition, 91% of COD was removed at optimum temperature of 46 ℃. This study shows HUASB is an efficient system in both mesophilic and thermophilic temperatures.

2.4.5.3 Toxicity

Several compounds exhibits a toxic effect at excessive concentration such as VFA, ammonia, cations (e.g Na^+, K^+, Ca^+), heavy metals, sulphide and xenobiotics which adversely affect methonegenesis:-

1. *Volatile Fatty Acid (VFA)*: Failure to control temperature increase can result in biomass washout with accumulation of VFA due to inhibition of methanogenesis [50]. It will also result in decrease of pH under which condition methanogenesis cannot occur anymore. At high temperature, production of VFA is higher compared to the mesophilic temperature range [54]. Low pH can accumulate VFA. At higher partial pressure of H_2, propionic acid degrading bacteria will be severely inhibited thereby causing excessive accumulation of higher molecular weight VFAs such as propionic and butyric acids. If the situation is left uncorrected, the process may eventually fail and end up in the condition known as “SOUR” or “STUCK” [61].

2. *Light metal ion (especially Na)*: PW which usually contains high suspended solids (SS) and is heavily polluted and difficult to degrade [43] and can cause anaerobic digester upset or failure. Besides, biological treatment may be hindered by the presence of sodium salt, which can cause inhibition and toxicity problems in the methanization process and affects the metabolism of microorganisms due to plasmolysis in the presence of salt [26]. Sodium concentration in the reactor may increase because of the use of NaOH or Na_2CO_3 for pH control [65]. The level of inhibition depends on the concentration of sodium ion. McCarty [66] reported that sodium is essential for methanogens in the range of 100-200 mg/L and will begin to inhibit moderately

in the range of 3500-5500 mg/L and above 8000 mg/L to be strongly inhibitory to methanogens at mesophilic temperatures. Therefore, before biological treatment, adaptation of microorganisms by serial dilution to inhibitory substances and incorporation methods to remove or counteract toxicants can significantly improve treatment efficiency [67].

Feijoo et al. [68] reported that sodium concentration on mesophilic reactor may inhibit methanization by 50% from 4-10 g/L Na^+/L. While Vallero et al. [69] reported that when 10 g Na^+/L was abruptly added to a thermophilic UASB reactor, methane production was inhibited completely. Panswad et al. [70] studied high salt acclimatization and showed that the biomass was able to adapt to high salt environment when there was no significant drop of mixed liquor suspended solids (MLSS). COD removal efficiency decreased as salt concentration went up. The salt effect was more severe on the non-acclimated system and anaerobic performance would still be satisfactory as long as the salinity concentration is less than 10 g/L [71]. However, Kimata-Kino et al. [72] examined the salt-tolerance of granule in mesophilic UASB reactors either increased gradually (stepwise) or abruptly, and identified the threshold limit in both approaches. The concentration of NaCl was added abruptly (increased from 0 g/L to 20, 30, 40, 45, or 50 g/L) and gradually (increased from 0 to 64 g/L or 0 to 40 g/L). They suggested that 32 g NaCl/L is a practical level for mesophilic UASB operation where only 13% decrease of methane production was observed. They learned that combining abrupt and gradual salinity increases could shorten the adaptation period. They were able to shorten the adaptation period to only 30 d by increasing the salinity abruptly to 20 g/L, followed by gradual adaptation to 30 NaCl/L

3. *Ammonia*: Free ammonia (FA) inhibitory concentration for mesophilic treatment ranged from 25-140 mg N-FA/L, whereas free ammonia inhibitory concentration for thermophilic treatment ranged from 390-700 mg N-FA/L (after a long acclimation period) [73]. Several authors have found that anaerobic fermentation of wastes with high concentration of ammonia was easily inhibited

and less stable at thermophilic temperatures than at mesophilic temperatures [67]. Gallart and Winter [74] reported that methane production was inhibited 50% by 0.22 g/L FA at 37℃ and 0.69 g/L FA at 55℃ indicating that thermophilic flora tolerated at least twice as much FA as compared to mesophilic flora.

4. *Sulphide*: Sulphate reducing bacteria (SRB) in the presence of sulphate, resulting in hydrogen-sulphide production and this process competes with methanogenesis. Sulphide, mainly the un-dissociated form, H_2S, can cause inhibition of methongenic. Range of 150-1100 mg S-DS/L (total dissolved sulphide) and 50-250 mg S-FS/L (free hydrogen sulphide) can produce inhibitory effects. It is recommended to operate anaerobic treatment in the ratio COD: sulphate higher than 10, and lower ratios were thought to be inhibitory for methanogenesis because of the high sulphide concentration. [73]

2.5 Aerobic Processes

As both anaerobic and aerobic treatment of saline effluent have given only moderate performance on COD removal, the combination of the two modes of treatment with an aim to improve the performance of the overall treatment process has been considered [75].

2.5.1 Sequencing Batch Reactor (SBR)

SBR is a promising biological process for treating industrial wastewaters and it is a variant of activated sludge process. Hypersaline wastes are generated during industrial activities that include chemical manufacturing, oil and gas production and waste minimization practices. Biological treatment to remove organics without dilution will require the use of halophilic organisms which have special adaptations for survival at high salinities. Woolard and Irvine [46] conducted a study with a moderate halophile isolated from the Great Salt Lake, Utah, U.S.A. The organism was able to degrade phenol in simulated oil field produced water containing 15% salt if iron, nitrogen and phosphorus were added to the medium. This organism was used to develop a halophilic sludge in a Sequencing Batch Reactor (SBR) operated at 15% salt during a 7 month study period. An average phenol removal of over 99.5% was achieved with this reactor and specific substrate removal rates were similar to those reported for more conventional treatment cultures.

Table 2.5 shows treatment of high salinity wastewater by aerobic treatment using SBR [75]. Besides salinity, PW has high concentration of ammonia, sulphide, heavy metals and many other toxic substances and it is highly recommended for biomass to acclimatize to those toxic substances [76]. Dilution of PW is also recommended to adjust the characteristics of the final mixture according to a predefined strategy to evolve the applied organic loading rate and toxic substances in the digester to achieve biomass acclimatization [73]. However, dilution will increase both digester and thus the capital cost of the treatment plant, and the energy demand for heating the sludge to process temperature [77].

Table 2. 5: Treatment of high salinity wastewater by aerobic treatment using Sequencing Batch Reactor (SBR)

Year	**Substract**	**Halophilic Inocolum**	**Salt Content (g/L)**	**V (L)**	**HRT (hr)**	**MLVSS (g/L)**	**OLR (kg COD/m ^{3}d)**	**F/M (kg COD/kg of MLVSS/d)**	**COD Influent (g/L)**	**COD Removal (%)**	**Ref.**
1995	Synthetic (phenol)	yes	150	1	24	1	0.25	0.25	0.25	99.5	[46]
2003	Synthetic (≈SFPW)	yes	10	10	20	4.1	0.7	0.17	0.55	87.9	[78]
2004	Synthetic (glucose. acetate)	no	60	5	6	-	4.8	-	1.2	32	[79]
2004	Tartaric Industry eff.	yes	120	5	240	3.5	0.4	0.12	4.3	83	[80]
2005	Tannery wastewater	yes	35	10	120	2	0.6	0.30	3	95	[81]
2005	Tannery wastewater	yes	40	10	79	7.2	1.1	0.15	3.6	91	[81]

*SFPW: Seafood processing wastewater.

2.6 Originality and Significance of the Study

Current treatment method at TCOT is not able to comply with the DOE standard B limits i.e. COD, boron, phenol and, oil and grease. Hence, the effectiveness of biological treatment to treat produced water, particularly by anaerobic treatment is the highlight of the study. Therefore, the study is significant for TCOT to deal with the produced water efficiently and cost effectively to ensure compliance with the standards before the effluent is discharged to inland or the nearest stream which is the Kertih River.

CHAPTER 3

METHODOLOGY

3.0 Chapter Overview

Chapter 3 presents the methodology of the study which involved two phases. The first phase was to evaluate the performance of anaerobic treatment to treat raw PW by UASB and HUASB reactors under mesophilic condition at HRT of 5, 4, 3, 2 and 1. A pre-treatment (ferric chloride as coagulant) by coagulation and flocculation techniques was studied to compare its effect on PW treatment using UASB and HUASB reactors. Phase two was to observe the performance of aerobic treatment by SBR as post-treatment of effluent from UASB and HUASB reactors. Overview of experiments carried out to evaluate the performance of biological treatment in produced water is summarized in a flowchart in Figure 3.1.

3.1 Glassware, Chemical and Reagent

Glassware was cleaned with 5% Decon detergent (Prolabo) using steam heating glassware washer (Lancer 1400UP) and dried in an oven at 60 ℃. BOD bottle and reused COD vials were soaked overnight with 5% Decon detergent then rinsed with distilled water before sterilisation (SHINOVA Vertical Pressure Steam Sterilized) and dried in an oven at 60 ℃.

All chemicals and reagents for sample processing and analyses in the study are listed in Table 3.1. The chemicals were of analytical grade and no further purification was required.

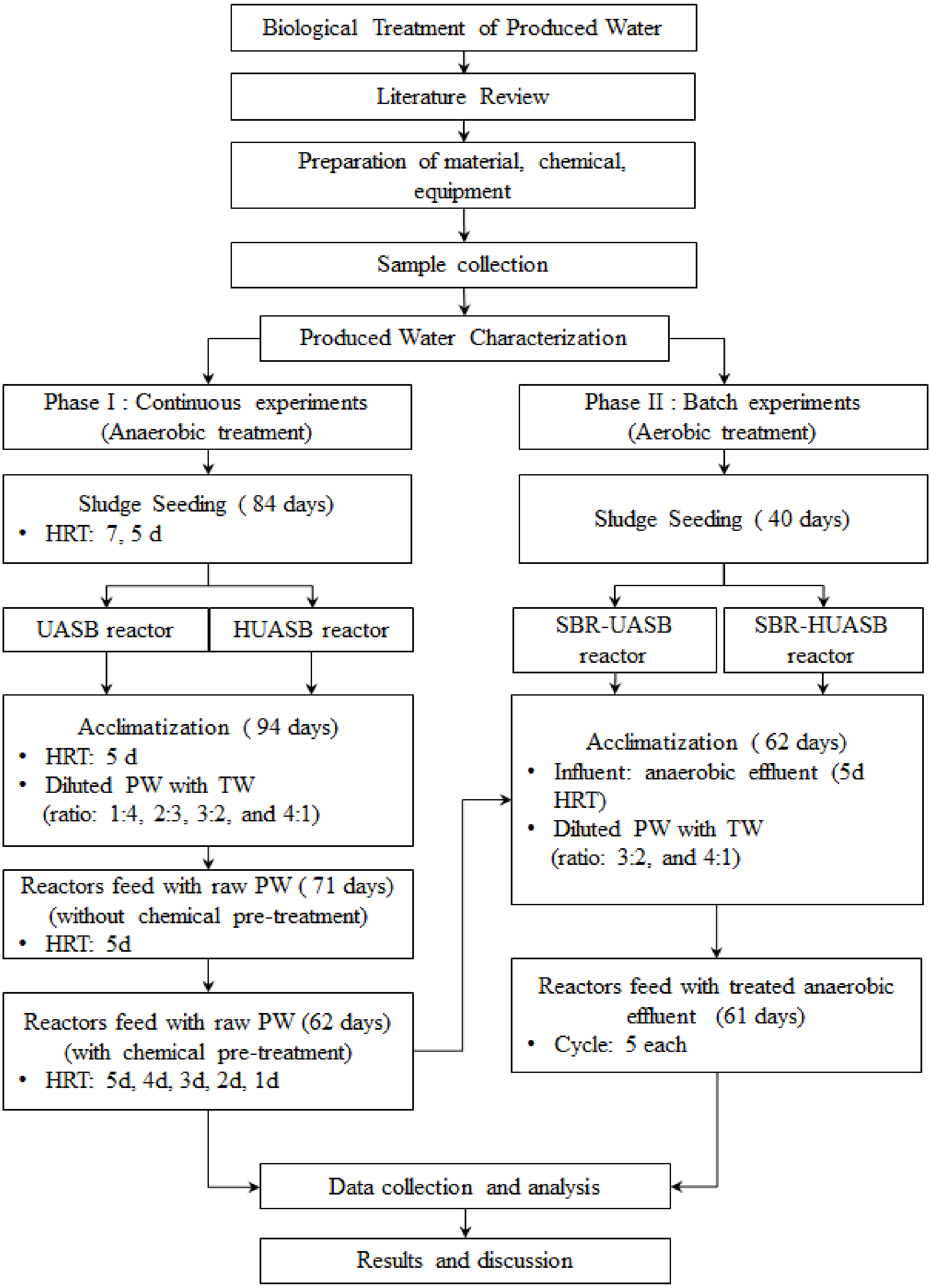


Figure 3. 1: Flowchart of overall experimental activities involved in this research

Table 3. 1: List of chemicals and reagents

Name of chemical	**Assay**	**Supplier**	**Purpose of use**
Acetate	99.99 % ≤	Merck	Anaerobic growth medium
Propionate	99.99 % ≤	Merck	
Butyrate	99.99 % ≤	Merck	
$MgCl_4.6H_2O$	99.99 % ≤	Merck	
$CaCl_2$	99.99 % ≤	Merck	
$FeCl_2.4H_2O$	99.99 % ≤	Merck	
NH_4Cl	99.99 % ≤	Merck	
K_2HPO_4	99.99 % ≤	Merck	
Na_2SO_4	99.99 % ≤	Merck	
Yeast	99.99 % ≤	Merck	
Sucrose	99.99 % ≤	Merck	
$ZnCl_2$	99.99 % ≤	Merck	
$CuCl_2$	99.99 % ≤	Merck	
$NiCl_2.6H_2O$	99.99 % ≤	Merck	
$MnSO_4.6H_2O$	99.99 % ≤	Merck	
$(NH_4)_3MO_7.4H_2O$	99.99 % ≤	Merck	
H_3BO_3	99.99 % ≤	Merck	
$CoCl_2.6H_2O$	99.99 % ≤	Merck	
EDTA	99.99 % ≤	Merck	
$NaHCO_3$	99.99 % ≤	Merck	Supply bicarbonate, alkalinity
BOD nutrient buffer pillow	-	Hach	BOD_5 test
$K_2Cr_2O_7$	99.99 % ≤	Merck	COD test
Ag_2SO_4	99.99 % ≤	Merck	
$HgSO_4$	99.99 % ≤	Merck	
Potassium hydrogen phthalate	99.99 % ≤	Merck	
H_2SO_4	99.99 % ≤	Merck	COD and Boron test
n-hexane	99.99 % ≤	Merck	Oil and Grease test
$FeCl_3$ (30%)			Chemical treatment
Sodium	100%	Merck	AAS standard
Magnesium	100%	Merck	
Calcium	100%	Merck	
Ferum	100%	Merck	
NaOH	99.99 % ≤	Merck	pH adjustment
Chloride	100%	Merck	IC standard
Sulphate	100%	Merck	IC standard
Method 10252 reagent set	-	Hach	Boron test
Method 8014 pillow	-	Hach	Barium test
Method 8038 reagent set	-	Hach	Nitrogen-Ammonia test
Method 8019 reagent set	-	Hach	Total Phosphorus test
Method 8218 reagent set	-	Hach	Volatile Fatty Acid test
Method 8047 reagent set	-	Hach	Phenol test
Filter Whatman (934AH)	-	Fisher Co	TSS and VSS test

3.2 Produced Water

Produced water samples were taken from TCOT in Kertih, Terengganu, Malaysia. Samples of produced water were stored at 4℃ until use. COD reading was taken fortnightly to ensure the sample preservation step had no noticeable effect the waste water composition. Produced water samples were taken twice on 10th November, 2010 and 8th March, 2011. The sample characteristics are shown in Table 3.2.

3.3 Sludge Sampling and Seeding

The inoculum for seeding of the UASB and HUASB reactor were taken from a mesophilic anaerobic digester of a local petrochemical company. It contained 18.0 g TSS with volatile fraction of 84.72%. 2.75 litres of the sludge was decanted to remove debris and solid particles before fed with a growth medium composed of 1.8 g/L acetate, 0.2 g/L propionate, 1.0 g/L butyrate, 0.2 g/L $CaCl_2$, 0.2 g/L $MgCl_4.6H_2O$, 50 mg/L $FeCl_2.4H_2O$, 1.0 g/L NH_4Cl, 0.5 g/L K_2HPO_4, 0.25 g/L Na_2SO_4 and 1.0 g/L yeast. Sucrose was used as the carbon source. Trace elements added were 0.5 mg/L $ZnCl_2$, 0.5 mg/L $CuCl_2$, 1.0 mg/L $NiCl_2.6H_2O$, 1.0 mg/L $MnSO_4.6H_2O$, 0.5 mg/L H_3BO_3, 0.5 mg/L $(NH_4)_3Mo_7.4H_2O$, 0.5 mg/L $CoCl_2.6H_2O$, 0.5 mg/L $AlCl_3$ and 4.0 mg/L EDTA. The growth medium has been recommended by the Oregon Collection of Methanogens for MSH medium [31] and Nutrient Requirement for UASB process [82-83]. The pH of PW was adjusted to 6.5-7.5 using 2N Sodium hydroxide (NaOH) solution. Sodium bicarbonate ($NaHCO_3$) was provided to improve the buffering capacity (2.5-3.5 g $CaCO_3$/L). The reactors was fed with 7.0-8.0 g/L of high strength growth medium for 40 d, and decreased gradually to 4.0 g/L for 10 d at HRT of seven d and 1.0 g/L for 34 d at HRT of five d. Seed biomass for SBR reactor was taken from a treatment plant of a refinery in Melaka. The sludge was fed with the same growth medium as for anaerobic sludge.

Table 3. 2: Produced Water Characteristics

Sampling Date: 10th November 2010				Sampling Date: 8th March 2011			
Parameter	**mg/L**	**Parameter**	**mg/L**	**Parameter**	**mg/L**	**Parameter**	**mg/L**
*Sodium	6240	COD/N/P ratio	350/3.2/0.4	Sodium	10637	COD/N/P ratio	350/4.8/0.5
*Potassium	125	COD/BOD$_5$ ratio	1.9	Calcium	199	COD/BOD$_5$ ratio	2.25
*Calcium	325	TSS	57.33	Magnesium	164	BOD$_5$	599
*Magnesium	230	BOD$_5$	862	Barium	7.0	COD	1345
*Barium	<0.50	COD	1597	Chloride	10687	pH	8.72
*Strontium	10	TOC	0.501	Sulphate	676	NH$_3$-N	18.6
*Iron	0.30	pH	7.93	Boron	13.8	Oil & Grease	15
*Chloride	9530	NH$_3$-N	14.7			Phenol	30.2
*Sulphate	6250	* TDS	19070			Total Phosphorus	1.8
*Bikarbonate	1810	Oil & Grease	30			Color (PtCo)	1518
*Carbonate	n.d.	Phenol	13.8				
*Boron	17	Total Phosphorus	2.0				
*Aluminium	<1.0	Color (PtCo)	678.7				
*Silicon	27						
*Phosphorus	<0.30						
*Lithium	1.6						

* Sample was sent to Core Laboratories (M) for sample characteristic. Ref. [84]; n.d.: not detected;

3.4 Experiment Procedure (Phase I: Anaerobic Treatment)

3.4.1 Up-flow Anaerobic Sludge Blanket (UASB) reactor

A plexiglass reactor, Armfield Anaerobic Digester W8 [85] with internal diameter of 14.0 cm and a liquid height of 32.5 cm was used as the UASB reactor. Total volume of the reactor was 5310 mL and total working volume was 5000 mL in mesophilic condition (35 ± 2 ℃). A temperature controller was connected to a heating blanket to maintain the temperature which was measured by a temperature probe. A multi-channel peristaltic pump (Masterflex, Cole Palmer) was used to continuously feed the reactor with PW at 5 d HRT for 288 d and with varying HRT from 4 d to 1 d for 25 d (3 cycle for each HRT). A sampling port at the bottom of the reactor was used for sludge sampling. There was no mechanical mixing or effluent recirculation to the reactor. A stirrer was used in the feed tank to ensure homogeneous influent quality. Samples were collected from effluent tank by daily basis for analysis. A schematic diagram of the experimental setup is shown in Figure 3.2.

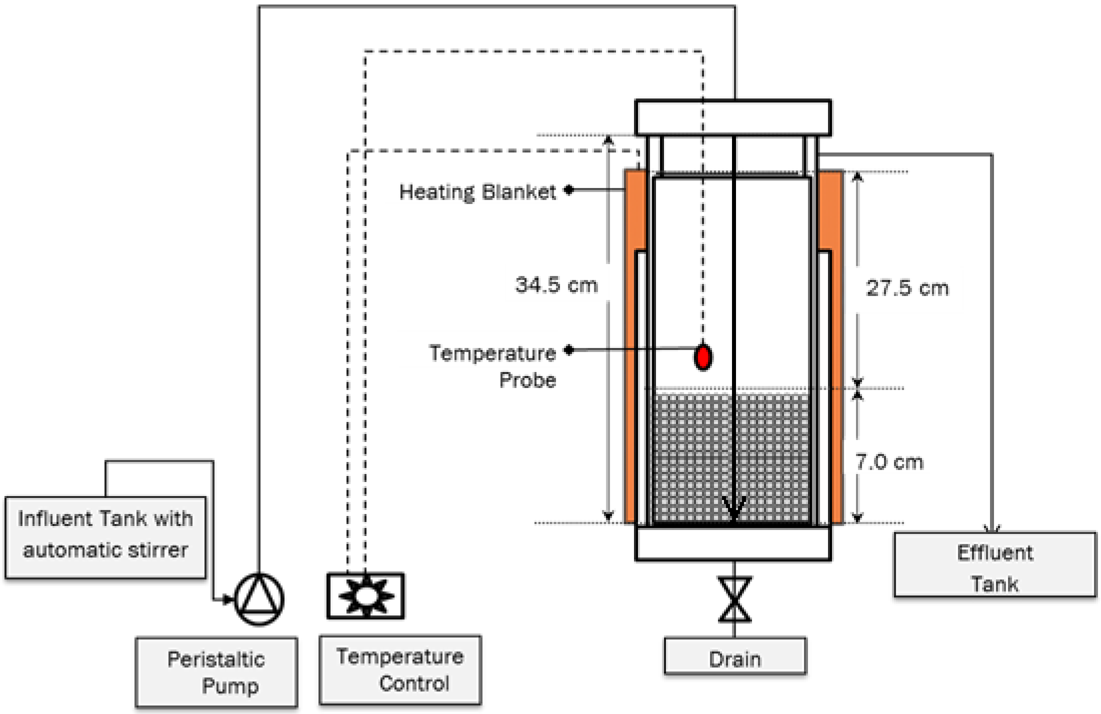


Figure 3. 2: Schematic diagram of UASB reactor

3.4.2 Hybrid Up-flow Anaerobic Sludge Blanket (HUASB) reactor

The HUASB reactor set-up was same as the UASB reactor described above but with an additional section of plastic media as fixed film. Total of 70 plastic media with 3 cm diameter were packed in this section. A schematic diagram of the experimental setup for HUASB reactor is shown in Figure 3.3.

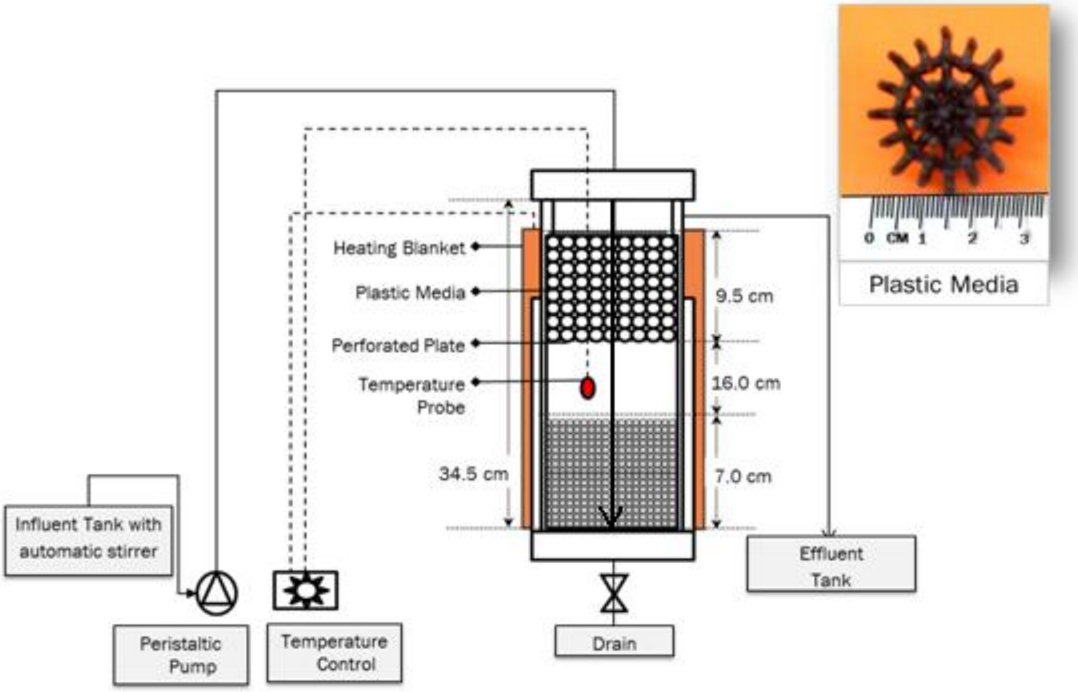


Figure 3. 3: Schematic diagram of HUASB reactor with plastic media

3.4.3 Acclimatization with Produced Water

Sample characteristic (Table 3.2) show that sodium of PW was 6240 mg/L which can be categorized as moderately inhibitory to methanogens and therefore, acclimatization of methanogens over prolonged periods of time could increase the tolerance and shorten the lag phase before methane production begins [76], minimize the toxicity built up and allow microorganism sufficient time to adapt. Hence, the reactors were seeded with five different dilutions of PW and tap water (TW) without any micro or macro nutrients added. The dilution ratios were 1PW:4TW, 2PW:3TW, 3PW:2TW, 4PW:1TW and 5PW:0TW (100% PW) with the HRT of five d.

3.4.4 Acclimatization with Produced Water (Chemical treatment using Ferric Chloride)

PW sampled on 8th March 2011 was high in turbidity and color as shown in Table 3.2. Coagulation and flocculation was performed in a standard jar-test apparatus that comprised of six paddle rotors and equipped with 6 beakers of 1 L volume to estimate the optimum pH and coagulant dosage. PW samples stored in a refrigerator at 4 ℃ were removed and conditioned for about 4 to 5 hr under ambient temperature. Samples were agitated for re-suspension of settled solids before any test was conducted [86]. Each beaker used for testing was filled with 500 mL of sample. The experimental process consisted of two subsequent stages: rapid mix for 2 min at 150 rpm and followed by slow mix for 20 min at 30 rpm. According to Maleki et al. [87] removal efficacies of heavy metal and COD was 28% and 86%, respectively, at pH 10 (optimum for ferric chloride with 2000 mg/L dosage). Therefore, pH of initial samples was fixed at pH 10 and the ferric chloride dosage was varied between 600 and 3000mg/L. The same dosage (600 mg/L to 3000 mg/L) without adjusting the pH value was also carried out to study the comparison. After settling, about 200 mL of supernatant was withdrawn for the determination of pH, turbidity and color. Ferric chloride at pH 10 with dosage of 2200 mg/L was chosen to pre-treat PW.

3.4.5 UASB and HUASB Operation

The reactors were seeded immediately with pre-treated produced water (no dilution of PW and tap water) with HRT of 5 d for 64 d, HRT of 4 d for 10 d, HRT of 3 d for 4 d, HRT of 1 d for 3 d and HRT of 1 d for 2 d; nutrients were added to achieve a COD:N:P:S ratio of 350:7:1:1.

No information or literature review of boron and barium removal by coagulation and flocculation using ferric chloride is available. Furthermore, TCOT is concerned about boron and barium exceeding standard B (Standard B for boron and barium is 4 mg/L and 2 mg/L). Therefore, boron and barium parameters were added to investigate the suitability to use ferric chloride as coagulant by coagulation and flocculation.

3.5 Experiment Procedure (Phase II: Aerobic Treatment)

3.5.1 Sequencing Batch Reactor (SBR) reactor

Two 1 L measuring cylinders were used as SBR to treat effluent of UASB and HUASB. The working volume was 700 mL. Diffused aerators were used to supply oxygen to biomass. Reactor feeding and decanting was carried out manually. The reactors were operated at ambient temperature (27±2 °C). A schematic diagram of experimental setup for SBR is shown in Figure 3.4

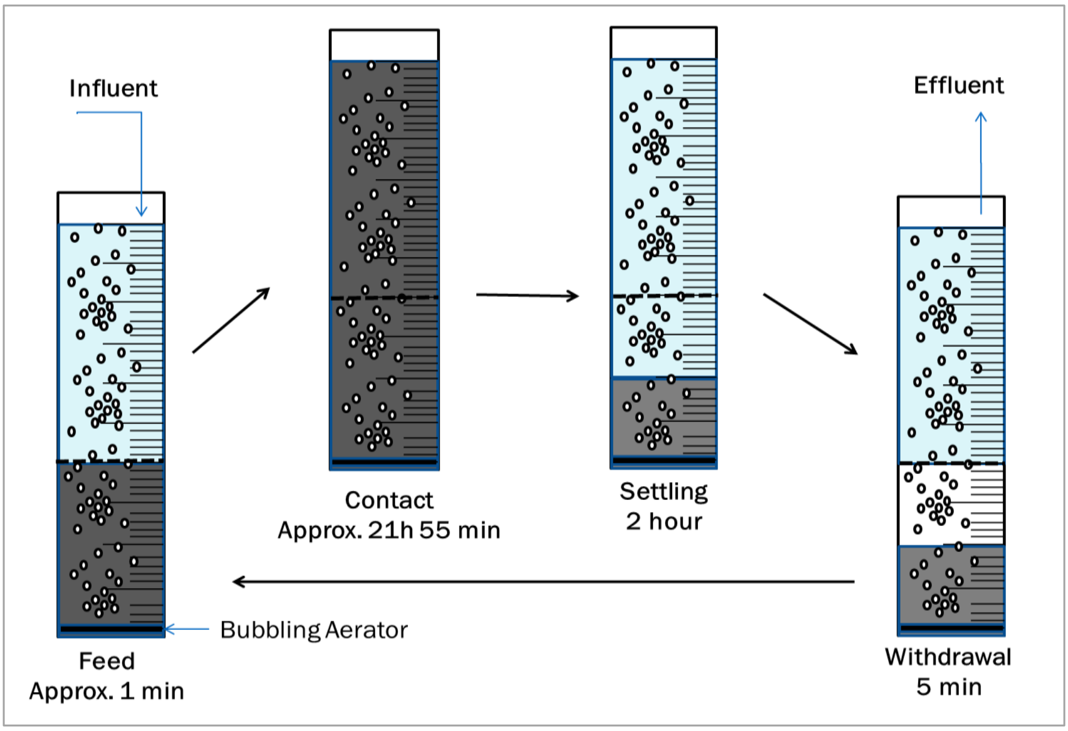


Figure 3. 4: Schematic diagram of SBR reactor

The SBR was acclimated with diluted pre-treated UASB and HUASB effluent of 5 d of HRT (TPW) in tap water (TW): 3TPW:2TW, 4TPW:1TW. Supplementary nutrient, i.e. nitrogen (NH_4Cl) and phosphorous (K_2HPO_4) were added to achieve ratio of COD: N: P of 100: 5: 1 [24]. The pH of influent was adjusted between 6.5-7.0 using 0.2 N sulphuric acid (H_2SO_4) solution.

3.5.2 SBR Operation

The SBR was fed with pre-treated UASB and HUASB effluent at various HRT for a minimum of 5 cycles for each HRT. Each cycle consisted of the following four phases:

1. Stage 1: Feed, approx. 1 min (instantaneous)
   Addition of influent into reactor in a time which represents the entire load (volume, V) corresponding to a given period (cycle duration)
2. Stage 2: Contact, approx. 21 hr and 55 min
   Biodegradation takes place when the microorganisms remove the organic substrate in the presence of oxygen supplied by aerator.
3. Stage 3: Settling , 2 hr
   The aerator was stopped in order to induce the settling of biomass.
4. Stage 4: Withdrawal, 5 min
   Withdrawal of treated water (equal to the volume, V)

3.6 Analytical Methods

3.6.1 Basic Water Quality Parameters

The UASB and HUASB reactors effluent were analysed for basic water quality parameters viz. biochemical oxygen demand (BOD), pH, alkalinity, total suspended solids (TSS), volatile suspended solids (VSS), turbidity, phenol, oil and grease. Laboratory analyses were conducted according to the *Standard Methods* [88]. For COD, a modified closed reflux colorimetric method was developed as recommended by Sato et al. [89] for high salinity sample. The pH meter model Sension 4 with Platinum Series pH electrode (Model 51910) was used for pH measurement. Turbidity was measured using turbidity meter (Model PN 100, Eutech). Analyses of barium (method 8014 pillow), boron (method 10252 reagent set), volatile fatty acid (method 8218 reagent set), ammonia-nitrogen (method 8038 reagent set), total phosphorus (method 8019 reagent set) and phenol (method 8047 reagent set) tests were conducted according to *Hach Method* [90]

3.6.2 Polycyclic Aromatic Hydrocarbon (PAH) Analysis

The effluent UASB and HUASB reactors was extracted with 300 mL of a mixture of hexane: dichloromethane (85:15 v/v), and concentrated to 5 mL for PAH quantitation [91]. GC-MS analysis were performed with a Carlo Erba GC8000 Series system coupled to a mass spectrometer (fisons MD800). A 30 m HP-5 column (5% phenylmethysilicone; 0.25 mm ID., 0.25 µm film thickness) was used. The oven temperature was increased from 60 to 175 ℃ at 6 ℃/ min, further increased at a rate of 3 ℃/ min until 240 ℃ and finally held at 300 ℃ for 7 min. Injector and transfer line temperatures were 280 ℃ and 300 ℃, respectively. Data acquisition was carried out in selected ion monitoring (SIM). Each PAH was separately quantified using a five-point calibration of mixed standard solutions in the range from 500 to 1000 µg/L. Recoveries of PAHs were obtained by this method using the four surrogate standards for the real samples: [$^2H_8$] naphthalene, [$^2H_{10}$] anthracene, [$^2H_{12}$] benzo[*a*]anthracene, and [$^2H_{12}$] benzo[*ghi*]perylene. The two deuterated PAHs [$^2H_{10}$] pyrene and [$^2H_{12}$] perylene served as internal standards [92].

3.6.3 Ion Analyses

Nitrite (NO_2^-), nitrate (NO_3^-), chloride (Cl^-), bromide (Br^-) and fluoride (F^-) were measured using Ion chromatography following *Standard Methods* 4110 B [88].

CHAPTER 4

RESULTS AND DISCUSSION

4.0 Chapter Overview

Chapter 4 presents the results of the study which involved anaerobic treatment by UASB, HUASB (COD, VFA, PAH) and aerobic treatment by SBR (COD). The result of boron, barium, turbidity and color after pre-treatment (ferric chloride as coagulant) by coagulation and flocculation techniques are also discussed.

4.1 Sludge Seeding of Methanogenic Bacteria

Sample characteristics of PW shows that the COD of PW was 1597 mg/L and therefore, the reactor was fed with 1.0 g/L of medium growth at 5 d HRT before acclimatization with diluted PW. The COD removal ranged from 80 to 96%. The sludge contain 19.67 g MLVSS with 89.94% of volatile fraction. The influent COD, effluent COD and COD removal efficiency in the UASB reactor during sludge seeding is shown in Figure 4.1 and summarized in Table 4.1.

Table 4. 1: COD removal in different feed and HRT during sludge seeding

Day	**HRT(d)**	**OLR (g/L day)**	**Influent COD (mg/L)**	**Effluent COD (mg/L)**	**COD Removal Efficiency (%)**	**TSS (g/L)**	**MLSS (g/L)**
1-39	7	1.07	5950-10100	240-1330	83.3-96.5	21.2	18.0
40-49	5	0.57	3250-5000	140-1000	80.4-96.8	-	-
40-49	5	0.22	1000-1500	65-210	79.2-96.1	21.9	19.7

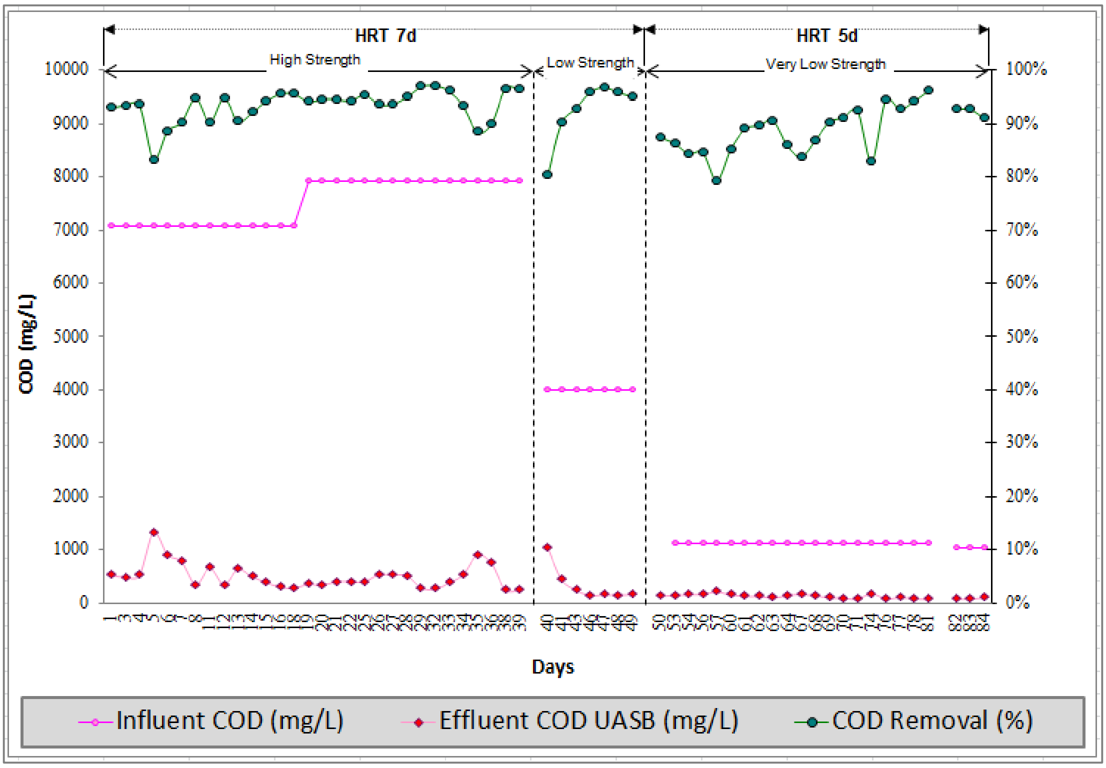


Figure 4. 1: The influent and effluent COD and COD removal efficiency in UASB reactor during sludge seeding

4.2 pH and Alkalinity of UASB and HUASB Reactors

Alkalinity of the reactor was maintained between 2.5-3.5 g $CaCO_3$/L. The pH of influent was adjusted to 6.5-7.5. The pH of effluent ranged from 8.1 to 8.9, presumably as a result of alkalinity supplementation, but did not appear to have any adverse effect on reactor performance. These values are within the range for optimal functioning of anaerobic reactors.

4.3 Anaerobic Treatment of Produced Water Without Pre-Treatment

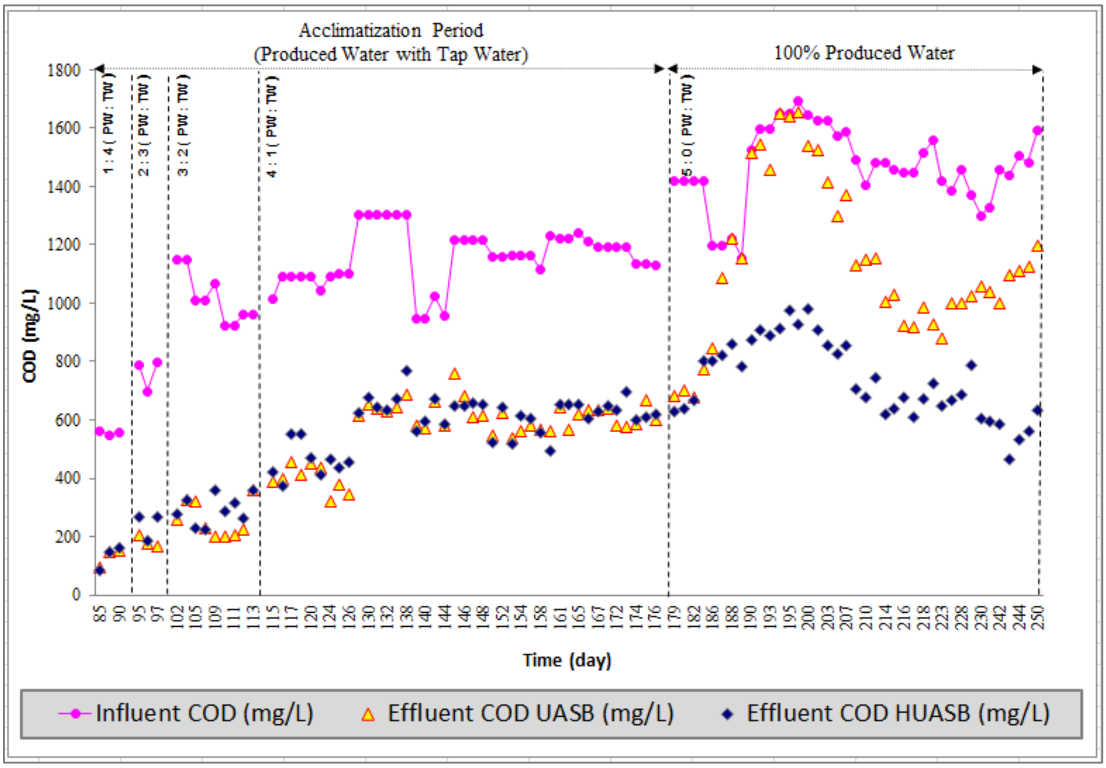
Both the UASB and HUASB reactors were fed with different volumetric mixtures of PW and TW. The dilution ratio were 1PW:4TW, 2PW:3TW, 3PW:2TW, 4PW:1TW and 5PW:0TW (100% PW). Table 4.2 presents the feeding protocol and Figure. 4.2 shows performance of the reactors.

The increase in organic loading rate (OLR) resulted in higher effluent COD concentration and hence lower treatment or COD removal efficiency. Both reactor yielded comparable COD efficiencies when diluted PW was used as feed. The efficiency dropped from 78% to about 50% when PW:TW ratio was 1:4 and 4:1 respectively. The result agreed with Feijoo et al. [68] and McCarty [66] Feijoo et al. reported that sodium concentration on mesophilic reactor may inhibit methanization by 50% from 4-10 g/L Na^+/L. McCarty reported that inhibition of methanogen at mesophilic temperature is severe by sodium if above 8000 mg/L.

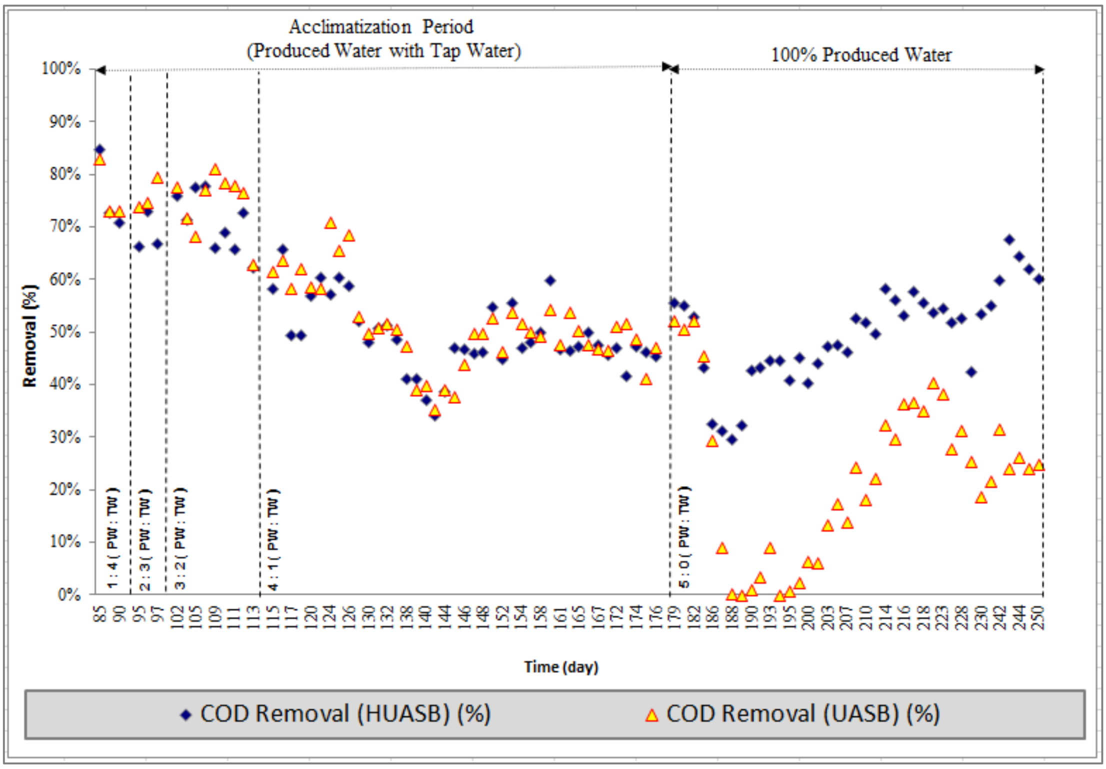
The HUASB reactor was observed to treat undiluted PW better than the UASB reactor. COD removal efficiency of the HUASB and UASB reactors when fed with undiluted PW was 48.5% and 26.1% respectively. The HUASB reactor was more stable than the UASB reactor, as also reflected by the narrower range of COD removal efficiencies i.e. 29.5% to 67.5% compared to 0 to 52.2%. The result agreed on Gupta et al. [63] finding that HUASB is capable of resisting shock load as compared to UASB.

Table 4. 2: COD removal in UASB and HUASB reactors with different feed dilution and 5 d HRT

Day	**Dilution**	**OLR (g/L·day)**	**Influent COD (mg/L)**	**Effluent COD (mg/L)**		**COD Removal (%)**	
				UASB	**HUASB**	**UASB**	**HUASB**
85-90	1PW:4TW	0.11	550-570	96-150	86-160	72.9-82.9	70.9-84.6
91-97	2PW:3TW	0.15	700-800	165-210	188-266	73.8-73.4	66.3-73.1
98-113	3PW:2TW	0.20	925-1150	200-360	220-360	62.8-76.4	66.1-76.0
114-176	4PW:1TW	0.23	1010-1300	350-760	375-770	37.6-70.1	34.2-65.6
177-250	5PW:0TW	0.29	1400-1650	680-1650	470-860	0.0-52.0	29.5-67.5



(a) COD concentrations



(b) COD Removal

Figure 4. 2: COD removal in UASB and HUASB reactors fed with PW without pre-treatment.

4.4 Pre-Treatment of Produced Water

Coagulation and flocculation was applied as pre-treatment to see the effect on anaerobic treatment of PW. The technique is simple but generates sludge and increases concentration of metal in the effluent [17]. Since most colloids have negative charge, they are mutually stabilized by electrostatic repulsion. Metal salts form positively charged species when dissolved in water, which destabilize negatively charged contaminant colloids, encouraging interaction, aggregation and floc formation. These floc aggregates are more easily separated from the water through flotation or settling [12]. The sampled PW contained high suspended solids and turbidity as shown in Table 3.2. Therefore, pre-treatment by using coagulation and flocculation studies were performed and ferric chloride was chosen to pre-treat PW before feeding into anaerobic biological reactors.

The suitability of ferric chloride on the color and turbidity removal was studied (Figure 4.3 and Figure 4.4). The suitability of ferric chloride on the efficiency of boron and barium removal was also studied (Figure 4.5 and Figure 4.6). Coagulant dosage varied between 600mg/L to 3000mg/L for ferric chloride ($FeCl_3$), with and without pH adjusted to 10. The best yields of color, turbidity, boron and barium removal using ferric chloride without pH adjustment was obtained at dosage 2197.8 mg/L (Table 4.3).

According to Maleki et al. [87], at higher pH value hydroxide ions compete with organic compounds for metal adsorption sites and the precipitation of metal-hydroxide occurs mainly by co-precipitation. With pH value at 10, the best color, turbidity, and boron and barium removal for ferric chloride was obtained at dosage of 2197.8 mg/L (Table 4.4).

According to McMullen et al. [93], conventional method of removing boron such as treatment with aluminum sulfate, ferric salts and lime is proven ineffective to lower down boron content to a level of about 0.6 mg/L from treated water containing less than 2 mg/L compared to magnesium salt solution in $Ca(OH)_2$ slurry.

Golder et al. [94] also stated that with chemical precipitation, boron removal efficiency was in the ranged of 29.3-41.9 % only with ferric chloride at pH 8.7. With electrotreatment, boron removal can be higher; up to 59%. However, in this study, boron was reduced to 5.5 mg/L from 13.8 mg/L with 60.14% removal efficiency when pH was fixed at 10 using ferric chloride as coagulant.

Barium was reduced to 0.8 mg/L from 7 mg/L, total 88.6% removal when pH was fixed at 10 using ferric chloride as coagulant. Coagulant and flocculation is a chemical process which highly depended on pH value.

Ferric chloride with dosage of 2197.8 mg/L also yielded a final pH of 7.75 that was close to the preferable pH (6.5-7.5) to operate anaerobic treatment [50] as post-treatment.

Table 4. 3: Effect of ferric chloride dosage on parameter reduction

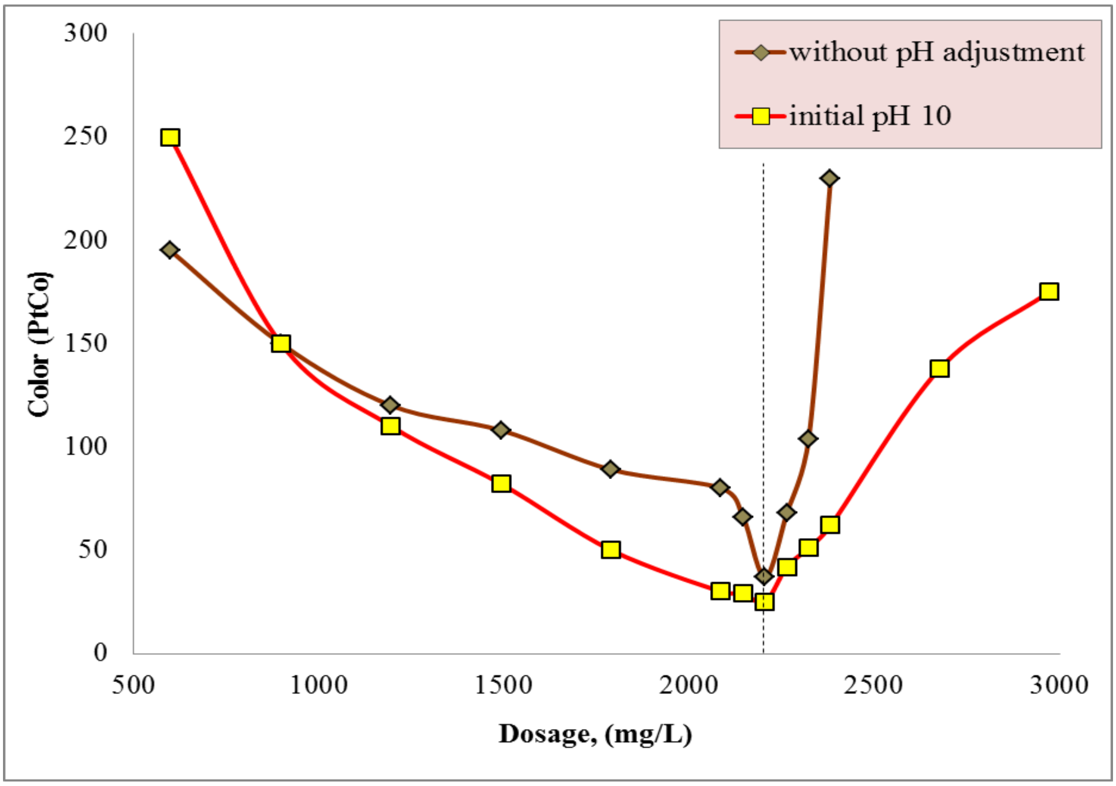
Jar #	**Volume**			**Dosage (mg/L)**	**pH**		**Turbidity**		**Color**		**Boron**		**Barium**	
	Sample A (mL)	**Coagulant B (mL)**	**A + B (L)**		**Initial**	**Final**	**Concentration (NTU)**	**Removal (%)**	**Concentration (PtCo)**	**Removal (%)**	**Concentration (mg/L)**	**Removal (%)**	**Concentration (mg/L)**	**Removal (%)**
Control	500	0	500	0	8.92	8.92	225.0	-	1518	-	13.8	-	7.0	-
1	500	1.0	0.5010	598.8	8.92	8.14	19.0	91.6	195	87.2	12.2	11.6	1.0	85.7
2	500	1.5	0.5015	897.3	8.92	7.92	13.6	94.0	150	90.1	11.4	17.4	0.3	95.7
3	500	2.0	0.5020	1195.2	8.92	7.76	10.4	95.4	120	92.1	10.2	26.1	1.0	85.7
4	500	2.5	0.5025	1492.5	8.92	7.28	9.6	95.7	108	92.9	9.2	33.3	1.6	77.1
5	500	3.0	0.5030	1789.3	8.92	5.46	9.1	96.0	89	94.1	7.5	45.7	2.0	71.4
6	500	3.5	0.5035	2085.4	8.92	4.84	8.6	96.2	80	94.7	6.6	52.2	2.3	67.1
6.a*	500	3.6	0.5037	2144.6	8.92	4.73	7.5	96.7	66	95.7	6.4	53.6	2.3	67.1
6.b*	500	3.7	0.5037	2203.7	8.92	4.55	3.9	98.3	37	97.6	6	56.5	2	71.4
6.c*	500	3.8	0.5038	2262.8	8.92	4.32	5.2	97.7	68	95.5	6.2	55.1	2.1	70.0
6.d*	500	3.9	0.5039	2321.9	8.92	4.25	8.9	96.0	104	93.1	6.8	50.7	2.3	67.1
7	500	4.0	0.5040	2381.0	8.92	4.17	11.7	94.8	230	84.8	7.4	46.4	2.5	64.3
8	500	4.5	0.5045	2675.9	8.92	3.56	-	-	-	-	8.7	37.0	2.8	60.0
9	500	5.0	0.5050	2970.3	8.92	2.91	-	-	-	-	10.3	25.4	2.8	60.0

*Optimization

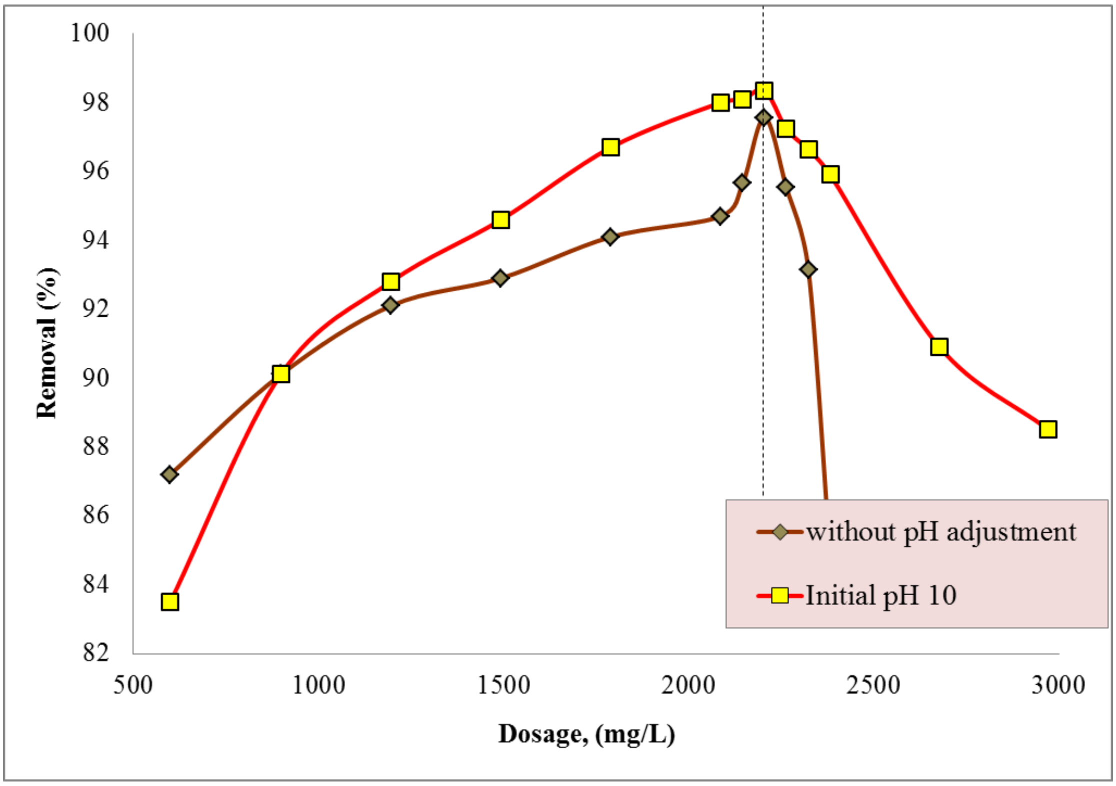
Table 4. 4: Effect of ferric chloride dosage on parameter reduction at pH 10

Jar #	**Volume**			**Dosage (mg/L)**	**pH**		**Turbidity**		**Color**		**Boron**		**Barium**	
	Sample A (mL)	**Coagulant B (mL)**	**A + B (L)**		**Initial**	**Final**	**Concentration (NTU)**	**Removal (%)**	**Concentration (PtCo)**	**Removal (%)**	**Concentration (mg/L)**	**Removal (%)**	**Concentration (mg/L)**	**Removal (%)**
Control	500	0	500	0	8.92	8.92	225.0	-	1518	-	13.8	-	7.0	-
1	500	1.0	0.5010	598.8	10.00	8.93	7.35	96.7	250	83.5	10.8	21.7	5.6	20.0
2	500	1.5	0.5015	897.3	10.00	8.58	5.49	97.6	150	90.1	6.8	50.7	4.2	40.0
3	500	2.0	0.5020	1195.2	10.00	8.21	3.66	98.4	110	92.8	5.3	61.6	3.1	55.7
4	500	2.5	0.5025	1492.5	10.00	8.24	2.29	99.0	82	94.6	4.6	66.7	2.0	71.4
5	500	3.0	0.5030	1789.3	10.00	8.15	1.52	99.3	50	96.7	5.2	62.3	1.0	85.7
6	500	3.5	0.5035	2085.4	10.00	7.87	1.31	99.4	30	98.0	5.8	58.0	1.0	85.7
6.a*	500	3.6	0.5037	2144.6	10	7.80	1.28	99.4	29	98.1	5.7	58.7	1	85.7
6.b*	500	3.7	0.5037	2203.7	10	7.75	1.08	99.5	25	98.4	5.5	60.1	0.8	88.6
6.c*	500	3.8	0.5038	2262.8	10	7.73	1.57	99.3	42	97.2	5.7	58.7	1.1	84.3
6.d*	500	3.9	0.5039	2321.9	10	7.71	1.66	99.3	51	96.6	6	56.5	1.2	82.9
7	500	4.0	0.5040	2381.0	10.00	7.71	1.76	99.2	62	95.9	6.2	55.1	1.4	80.0
8	500	4.5	0.5045	2675.9	10.00	6.26	2.51	98.9	138	90.9	6.6	52.2	2.4	65.7
9	500	5.0	0.5050	2970.3	10.00	5.17	3.91	98.3	175	88.5	7.1	48.6	3.4	51.4

*Optimization

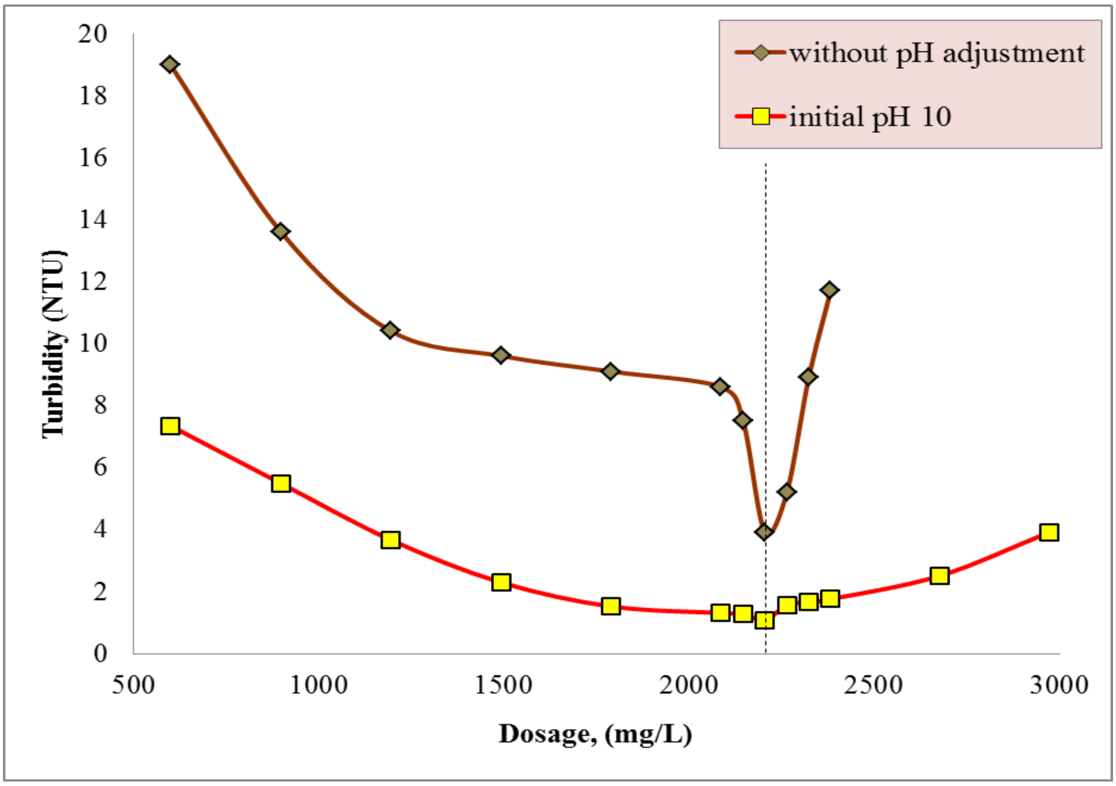


(a) Residual color

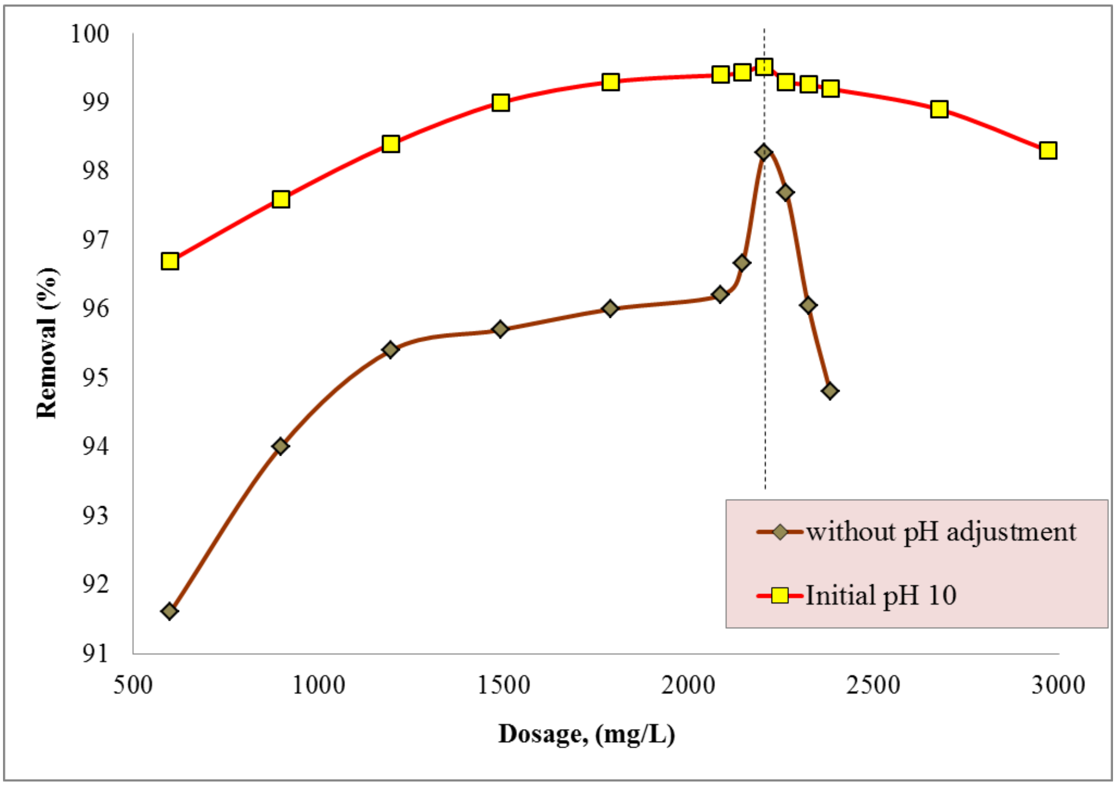


(a) Color removal efficiency

Figure 4. 3: Effect of ferric chloride on the removal of color

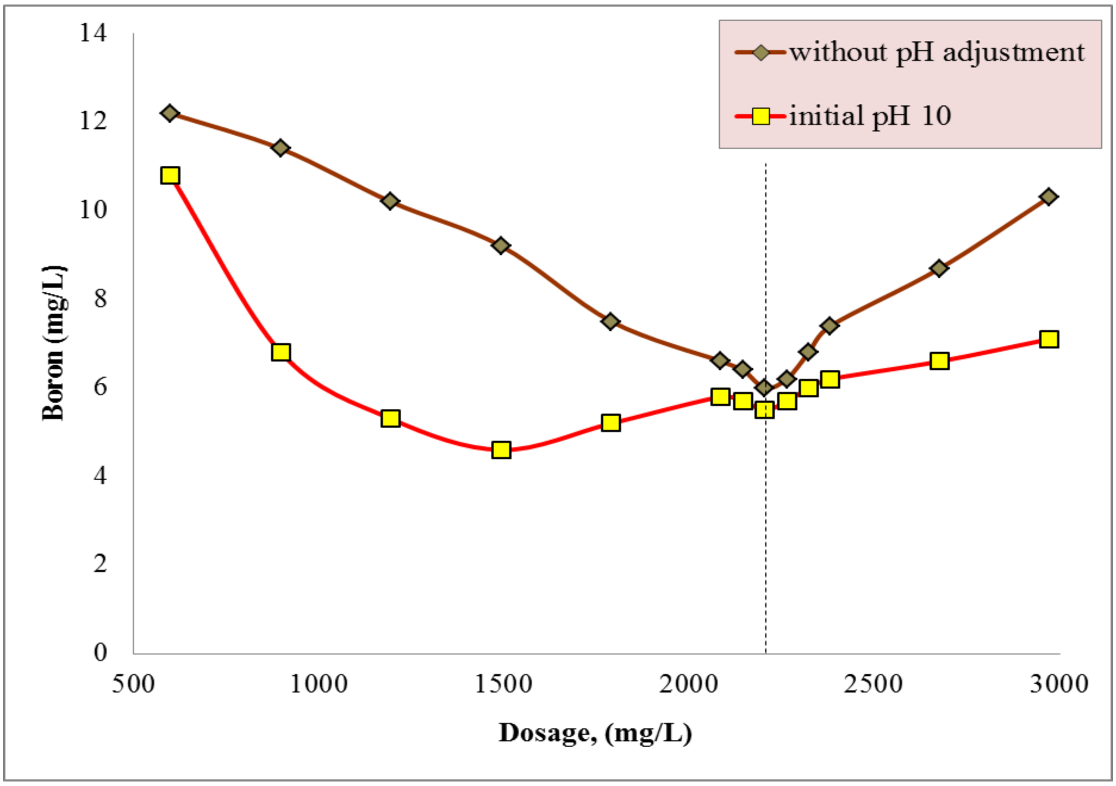


(a) Residual turbidity

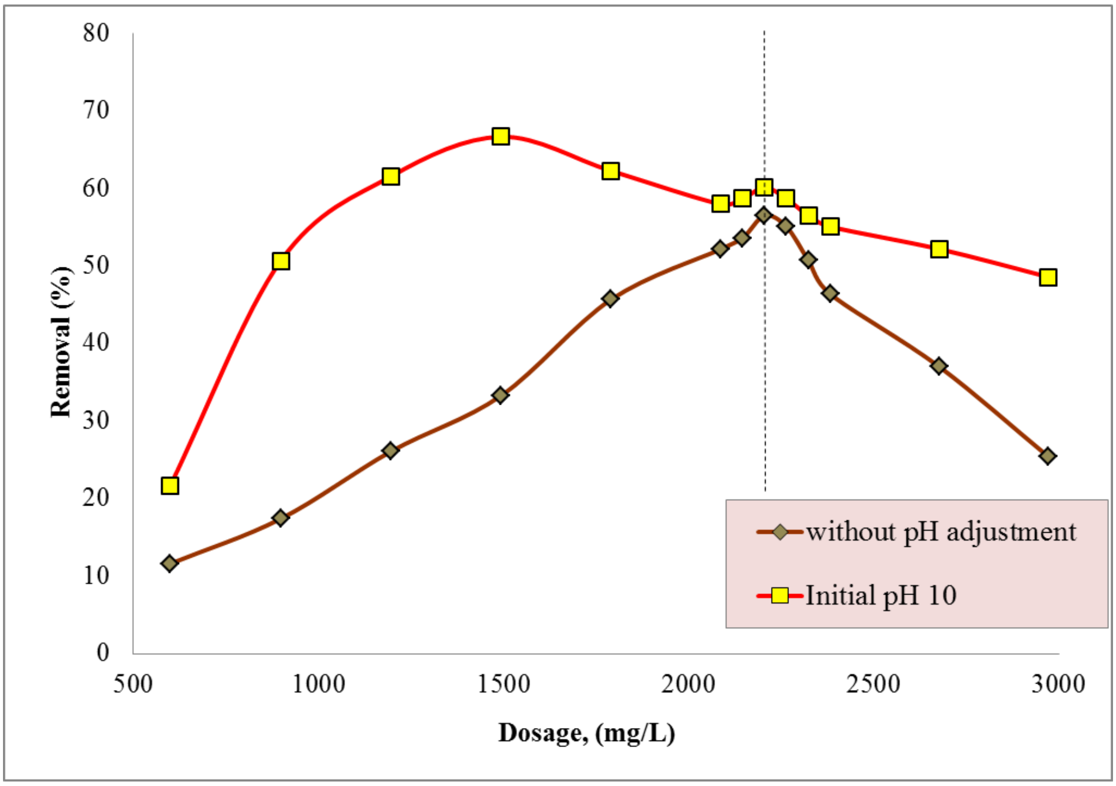


(b) Turbidity removal efficiency

Figure 4. 4: Effect of ferric chloride on the removal of turbidity.

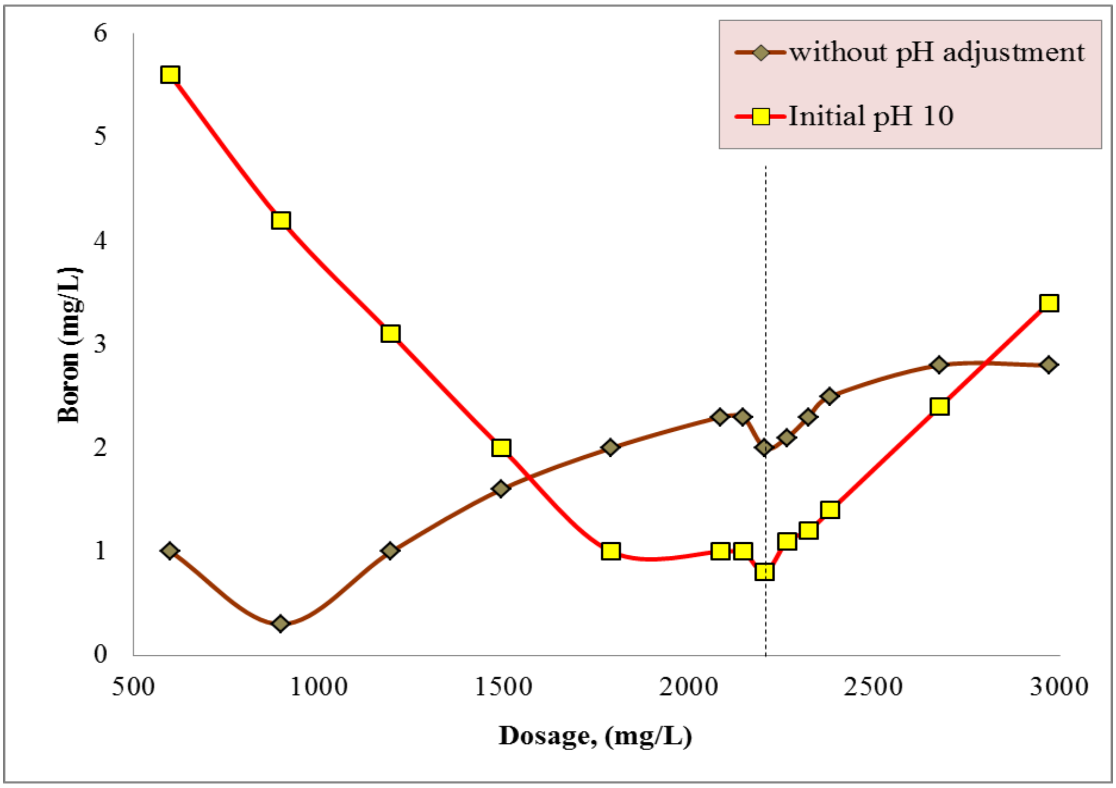


(a) Residual Boron

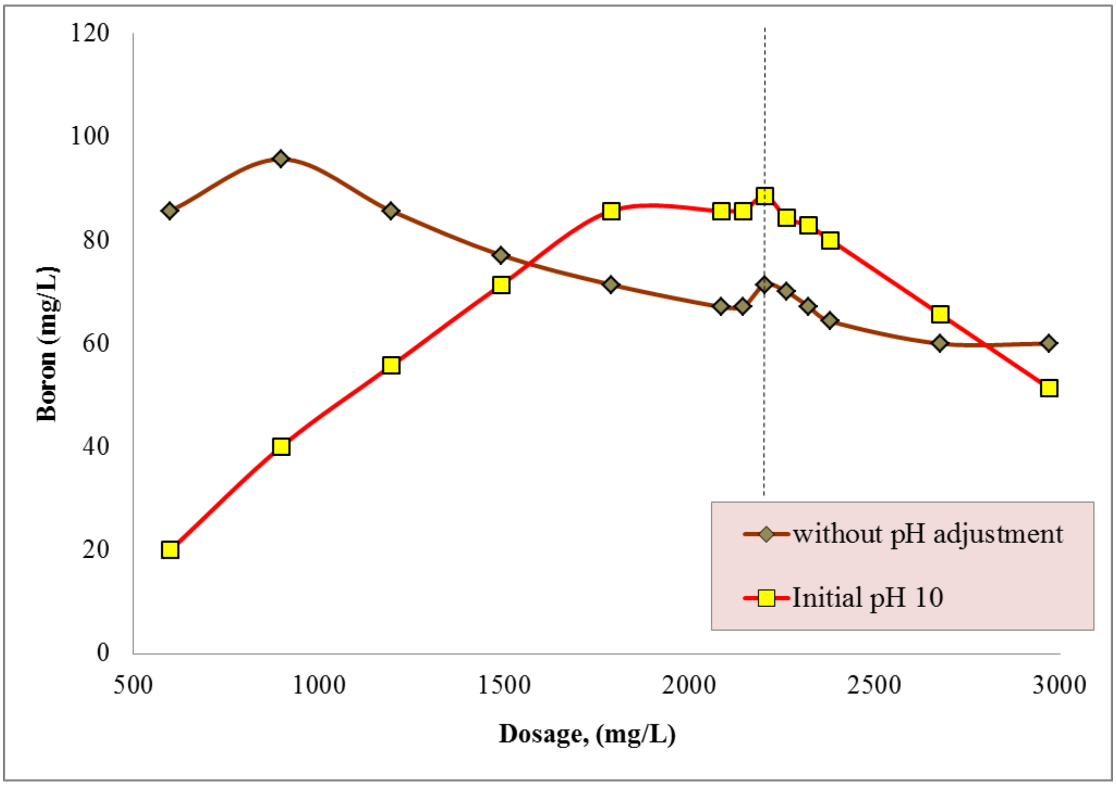


(b) Boron removal efficiency

Figure 4. 5: Effect of ferric chloride on the removal of boron.



(a) Residual Barium



(b) Barium removal efficiency

Figure 4. 6: Effect of ferric chloride on the removal of barium.

4.5 Anaerobic Treatment of Pre-treated Produced Water

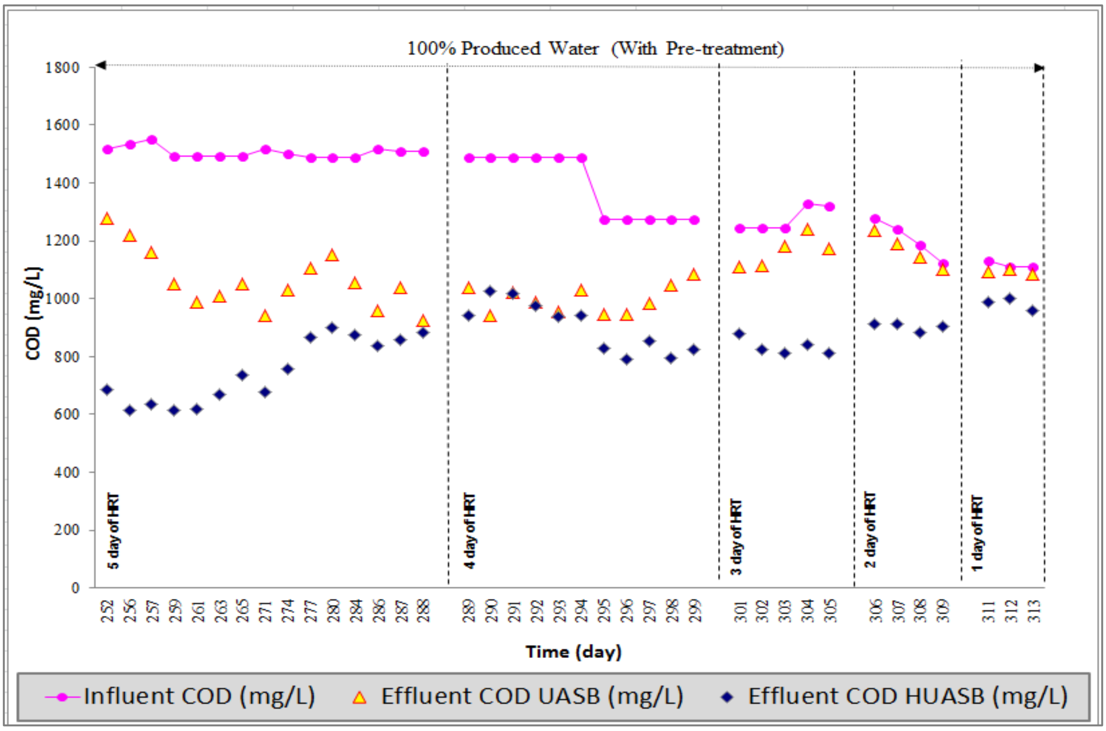
4.5.1 COD and TSS Results

The influent and effluent COD of UASB and HUASB reactors during treatment of pre-treated PW is presented in Table 4.5. Comparison of COD removal by anaerobic treatment of pre-treated PW using UASB and HUASB is shown in Figures 4.8. COD removal in both reactors reduced with lowering of HRT as a consequent of the increased organic load. The COD removal efficiency was 15.9-38.8% and 39.5-59.9% for the UASB and HUASB reactors respectively, at 5 d HRT. The corresponding values at 1d HRT were only 0.5-3.8% and 9.8-13.4%. The VSS content also drastically dropped from 9.5 to 1.8 g/L in the UASB reactor and 20.2 to 9.0 g/L in the HUASB reactor when the HRT was reduced from 5 to 1 d. The observation also confirms the superior biomass retention characteristics of HUASB reactor over UASB reactor.

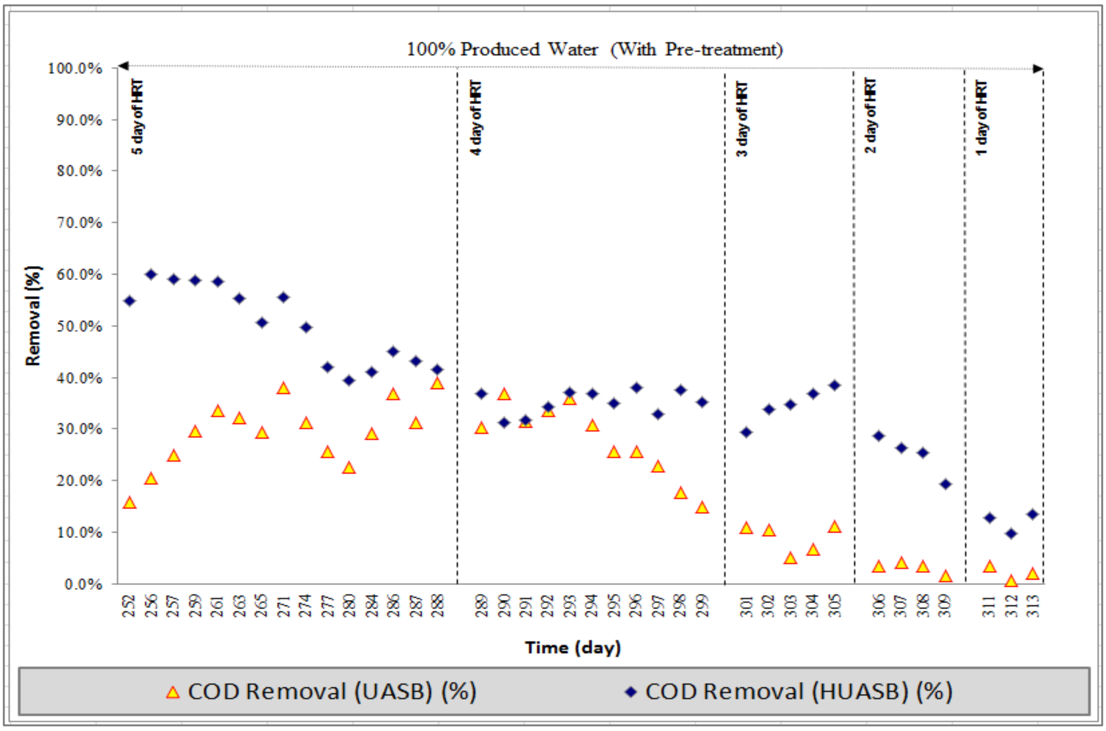
Over the study period, the HUASB reactor shown the capabilities in resisting shock load compared to the UASB reactor. Gupta et al. [63] found that COD removal in HUASB was approximately 5% more than UASB reactor. However, COD removal in HUASB was approximately 20% more than UASB reactor in this study. A comparison with Table 4.5 shows that COD reduction at 5d HRT was higher for raw PW than pre-treated OW. This may be due to long period of acclimatization, 71 d for PW treatment compared to after pre-treatment of ferric chloride, 38 d only (maximum COD removal was 59.9% removal efficiency)

Table 4. 5: COD removal at different HRT during treatment of pre-treated PW

Day	**HRT (d)**	**OLR (g/L·d)**	**Influent COD (mg/L)**	**TSS (g/L)**		**VSS (g/L)**		**Effluent COD (mg/L)**		**COD Removal (%)**	
				UASB	**HUASB**	**UASB**	**HUASB**	**UASB**	**HUASB**	**UASB**	**HUASB**
251-288	5	0.28	1490-1560	11.9	9.5	26.4	20.2	950-1280	615-900	15.9-38.9	39.6-59.9
289-299	4	0.35	1280-1490	11.6	8.8	25.5	20.1	950-1100	790-1020	14.8-36.8	31.2-38.0
300-305	3	0.43	1250-1330	9.9	6.7	25.1	18.9	1100-1250	810-880	5.1-10.9	29.3-38.4
306-309	2	0.60	1120-1280	9.3	6.2	18.7	14.0	1100-1250	880-910	1.7-4.0	19.2-28.8
311-313	1	1.12	1100-1130	2.7	1.8	12.6	9.0	1050-1100	960-995	0.5-3.4	9.8-13.4



(a) COD Concentrations



(b) COD removal

Figure 4. 7: COD removal in UASB and HUASB reactors at different HRT during treatment of pre-treated PW

According to Rincon et al. [22], biodegradability of water separated from extracted crude oil varies considerably with the type of petroleum involved (light, medium or heavy crude); light oil tends to have good biodegradability. Light oil, in their paper, was referred to water extracted from condensate oil with COD of 1150 mg/L. The sample collected from TCOT had COD of 1530 mg/L which indicated the produced water was extracted from light oil. However, the design of TCOT as such gathers all produced water (light, medium and heavy) into a single settling tank before discharging to coastal sea. As petroleum compounds can be grouped into four fractions (saturates, aromatic, resin and asphaltenes), the differences in biodegradability of PW could be linked to the relative proportions of these four fractions in PW. According to Stephenson [95], water produced with paraffinic oil often has high concentrations of simple fatty acids, while water produced with asphaltenic oils contains notable amounts of naphthenic acids. Gallagher [31] observed in fixed film anaerobic reactor, naphthenic acid were not degraded under anaerobic condition but were degraded under aerobic condition. This is probably the reason of SBR able to degrade COD up to 75% of removal since asphaltenic oil is not degradable in anaerobic condition with maximum removal of average 50% for both UASB and HUASB in HRT of 5 d as shown in Section 4.6.1 during aerobic treatment by SBR.

4.5.2 Volatile Fatty Acids (VFA) Results

The volatile fatty acid results of the UASB and HUASB reactors are presented in Table 4.7 and Figure 4.10. Both reactors were operating well at 5 d HRT, maintaining low levels of VFAs (about 10 mg/L with maximum COD removal was 59.9% removal efficiency). This showed that the methanisation of the PW occurred without any problem. Rincon et al. [22] observed that at HRT less than 10 hrs and the COD outlet rose as a consequence increased volatile fatty acid (VFA) concentration, indicating and overloading of methanogenic population; and also non VFA COD, indicating a decrease in the acidification efficiency. However, this research found that the VFA concentration increased rapidly as the HRT was decreased. At 1 d HRT, the VFA concentration was 480-590 and 474-581 mg/L for the UASB and HUASB reactors, respectively. About 50% of the COD was acidified, but was not metabolized by the methanogenic bacteria. The accumulation of VFA observed with the decreasing of HRT showed that the methanogenic bacteria were not able to eliminate all the VFA that were produced from the acidification of the organic matter indicating an over-loading of the methanogenesis. Thus, both reactors became imbalance and the methanogenic bacteria were out-competed by the acidogenic bacteria.

Table 4. 6: VFA removal of UASB and HUASB at different HRT during treatment of pre-treated PW

Day	HRT	Influent VFA (mg/L)	Effluent UASB	Effluent HUASB
			VFA (mg/L)	VFA(mg/L)
251-288	5 days	590-598	12-40	38-45
289-299	4 days	590-598	40-224	67-256
300-305	3 days	590-598	308-521	226-303
306-309	2 days	590-598	345-561	371-496
311-313	1 days	590-598	480-590	474-581

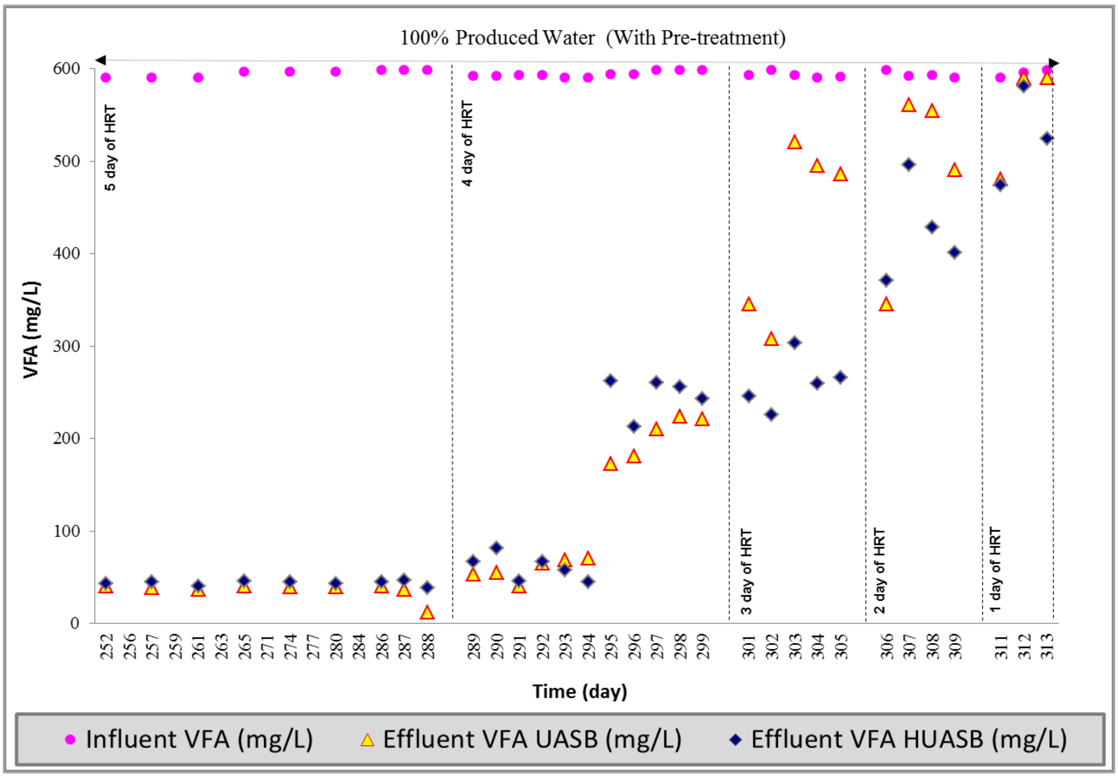


Figure 4. 8: VFA removal in UASB and HUASB reactors at different HRT during treatment of pre-treated PW

4.5.3 Polycyclic Aromatic Hydrocarbons (PAHs) Results

PAH refer to hydrocarbons containing two or more fused benzene rings. Table 4.8 shows the 16 PAHs classified as priority compounds by the USEPA [96]. Aromatic hydrocarbons span the whole range from readily to poorly biodegradable, depending on the nature of the actual compound. Biodegradation half-lives ranging from less than a day up to several months, with lower molecular weight (and more abundant) compounds being more degradable. PAHs are relatively insoluble and will be present mainly in, or associate with, the dispersed oil. [97]. They are expected to be associated with particulates and oil droplets in the PW. As the discharge plume for the most fields will rise towards the surface after discharge, these compounds will follow the plume, or be retained at certain depths of the water column depending upon the buoyancy of the supporting particulate [98].

Table 4. 7: 16 priority polycyclic aromatic hydrocarbon (PAH) compounds

Compound	**Abbreviation**	**Formula / MW**	**Number of Rings**
Naphthalene	Nap	$C_{10}H_8$ / 128	2
Acenaphtylene	Acy	$C_{10}H_8$ / 152	3
Acenaphthene	Ace	$C_{10}H_{10}$ / 154	
Fluorene	Flu	$C_{13}H_{10}$ / 166	
Phenanthrene	Phe	$C_{13}H_{10}$ / 178	
Anthracene	Ant	$C_{13}H_{10}$ / 178	
Fluoranthene	Fla	$C_{16}H_{10}$ / 202	4
Pyrene	Pyr	$C_{16}H_{10}$ / 202	
Benzo[a]Anthracene[a]	BaA	$C_{18}H_{12}$ / 228	
Chrysene[a]	Chr	$C_{18}H_{12}$ / 228	
Benzo[b]Fluoranthene[a]	BbF	$C_{20}H_{12}$ / 252	5
Benzo[k]Fluoranthrene[a]	BkF	$C_{20}H_{12}$ / 252	
Benzo[a]Pyrene[a]	BaP	$C_{20}H_{12}$ / 252	
Indeno[1,2,3-cd]Pyrene[a]	Ind	$C_{22}H_{12}$ / 276	6
Dibenzo[a,h]Anthracene[a]	DbA	$C_{22}H_{14}$ / 278	
Benzo[g,h,i]Perylene	BPer	$C_{22}H_{12}$ / 276	

Naphthalene (two ring compound) is characterized by moderate solubility and lower bioaccumulation potential than PAHs with 3 or more rings, are rapidly degraded in the water column. Naphthalene in PW therefore represents a low risk effect in the environment. Accumulation of PAHs increases with increasing molecular weight, however, as the size of the molecules increases, they become less able to pass through cell membrane. Concentration of higher molecular weight PAHs with four rings or more in crude oil are low and given their very low aqueous solubility, are usually present at very low dissolved concentration in PW. They tend to remain associated with oil droplets and bind tightly to particulate phases and have low availability to aquatic organisms [99]. Tables 4.9 and 4.10 show PAHs removal in the UASB and HUASB reactors, respectively. The total PAHs concentration in the influent was 238.8 µg/L, mainly comprising of naphthalene (95%). Both reactors were able to remove total PAH with 98-99% efficiency at all HRT studied. The residual individual PAH concentration was very low; at sub-ppb levels. When microorganisms absorb and intake the alkane in wastewater, the PAHs maybe degraded by microorganism concurrently [23]. Chang et al. [100] conducted a research to compare the degradation of PAHs using different type of sludge, municipal and petrochemical active sludge. They reported the order of degradation rate for PAHs in petrochemical sludge under anaerobic conditions was: acenaphthene > fluorene > phenantherene > anthracene > pyrene; and order od degradation rate for municipal was phenantherene > pyrene > acenaphthene > fluorene > acenaphthene. PAH degradation rate were generally faster in petrochemical sludge sample probably due to assemblage of bacterial species with enzymatic capabilities have grater capacities for degrading complex PAH mixture. Petrochemical sludge sample probably contained a greater amount of PAH-degrading autochthonous microorganisms where the primary agent in PAH degradation in petrochemical sludge sample with or without the anaerobic consortium. Since the anaerobic sludge used on this study was collected from a local petrochemical company, the order of degradation rate for PAHs in matched exactly with their order of degradation rate in petrochemical sludge; acenaphthene > fluorene > phenantherene > anthracene > pyrene with degradation of efficiency of 100.0%, 100.0%, 89.9%, 76.0% and 36.1% for HUASB. For UASB, the degradation efficiency as per order is 100%, 78.6%, 78.0% 34.1% and 16.7%.

Table 4. 8: Summary of polyaromatic hydrocarbons (PAHs) removal in different HRT after pre-treatment for UASB

Day	**HRT**	**Low Molecular Weight PAH**						**High Molecular Weight PAH**				**ΣPAH**	
		2 Ring Nap		**3 Ring Acy, Ace, Flu, Phe**		**4 Ring Ant, Fla, Pyr, BaA, Chr**		**5 Ring BbF, BkF, BaP**		**6 Ring Ind, DbA, BPer**			
		Conc. (ppb)	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**
Influent		227.48		2.94		7.17		0.58		0.67		238.84	-
251-288	5	0.81	99.6	0.48	83.6	0.63	91.2	0.58	86.1	0.67	0.0	2.5	99.0
289-299	4	0.41	99.8	0.52	82.4	0.61	91.5	0.44	87.5	0.67	0.0	1.97	99.2
300-305	3	0.12	99.9	0.60	79.5	1.21	83.2	0.58	0.0	0.67	0.0	1.93	99.2
306-309	2	0.26	99.9	0.50	82.9	1.76	75.5	0.58	0.0	0.67	0.0	2.52	98.9
311-313	1	0.04	100.0	1.09	62.9	0.53	92.7	0.38	88.5	0.67	0.0	2.04	99.1

Nap= Naphthalene; Acy= Acenaphtylene; Ace= Acenaphthene; Flu= Fluorene; Phe = Phenanthrene; Ant= Anthracene; Fla=Fluoranthene; Pyr= Pyrene; BaA= Benzo[a]Anthracenea; Chr= Chrysenea; BbF= Benzo[b]Fluoranthenea; BkF=Benzo[k]Fluoranthrenea; BaP= Benzo[a]Pyrenea; Ind= Indeno[1,2,3-cd]Pyrenea; DbA= Dibenzo[a,h]Anthracenea; BPer= Benzo[g,h,i]Perylen

Table 4. 9: Summary of polyaromatic hydrocarbons (PAHs) removal in different HRT after pre-treatment for HUASB

Day	**HRT**	**Low Molecular Weight PAH**						**High Molecular Weight PAH**				**ΣPAH**	
		2 Ring Nap		**3 Ring Acy, Ace, Flu, Phe**		**4 Ring Ant, Fla, Pyr, BaA, Chr**		**5 Ring BbF, BkF, BaP**		**6 Ring Ind, DbA, BPer**			
		Conc. (ppb)	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**	**Conc. (ppb)**	**Removal (%)**
Influent		227.48		2.94		7.17		0.58		0.67		238.84	-
251-288	5	0.50	99.6	0.10	96.6	0.54	92.4	0.44	24.1	0.67	0.0	2.5	99.1
289-299	4	0.21	99.8	0.64	78.1	0.57	92.0	0.28	51.1	0.67	0.0	1.97	99.0
300-305	3	0.16	99.9	1.95	33.6	0.53	92.6	0.44	24.1	0.67	0.0	1.93	98.4
306-309	2	0.06	99.9	0.83	71.7	0.66	90.7	0.54	7.5	0.67	0.0	2.52	98.8
311-313	1	0.12	100.0	0.89	69.8	0.84	88.2	0.58	0.0	0.67	0.0	2.04	98.7

Nap= Naphthalene; Acy= Acenaphtylene; Ace= Acenaphthene; Flu= Fluorene; Phe = Phenanthrene; Ant= Anthracene; Fla=Fluoranthene; Pyr= Pyrene; BaA= Benzo[a]Anthracenea; Chr= Chrysenea; BbF= Benzo[b]Fluoranthenea; BkF=Benzo[k]Fluoranthrenea; BaP= Benzo[a]Pyrenea; Ind= Indeno[1,2,3-cd]Pyrenea; DbA= Dibenzo[a,h]Anthracenea; BPer= Benzo[g,h,i]Perylen

4.6 Aerobic Treatment of Pre-treated Produced Water

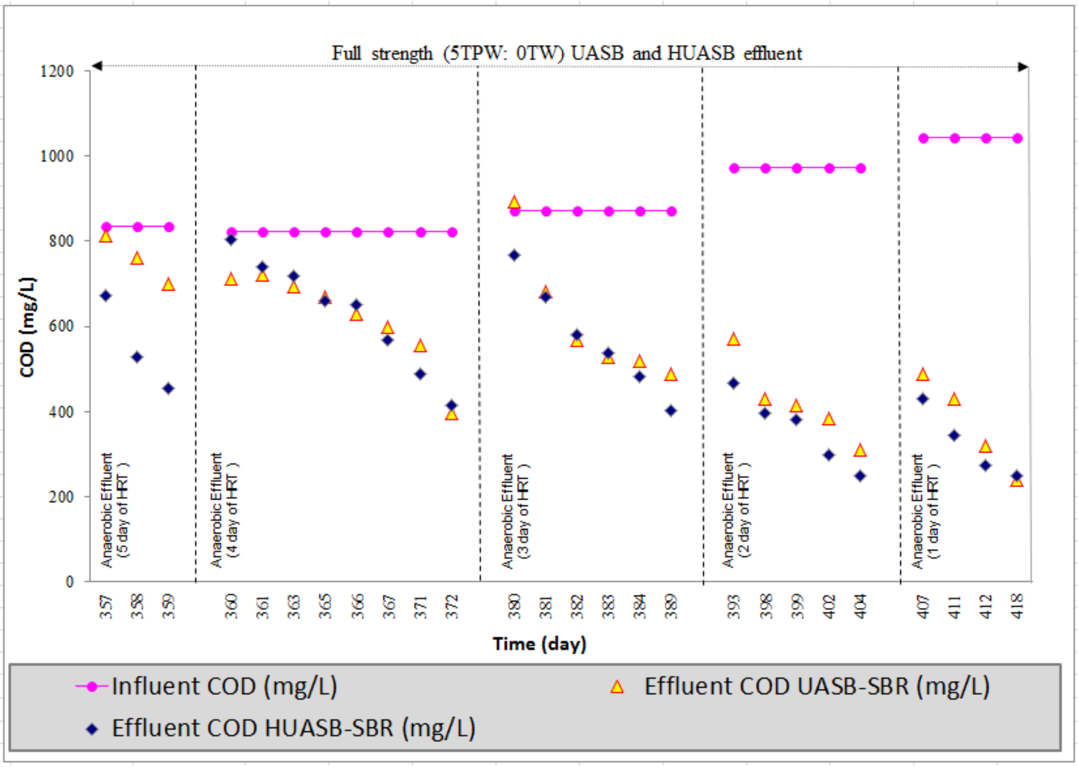
4.6.1 COD and TSS Results

Anaerobic biodegradation system provides advantages over aerobic biodegradation e.g. high treatment efficiency, low sludge generation, no oxygen requirement and low nutrient requirement. The developed microorganisms later can thrive in a salty environment under low COD load without requiring additional nitrogen (N) and phosphorus (P) to decompose refractory compounds [23]. However, in Phase I, even though it demonstrated huge decrease of organic pollutants (COD) but reduction of N and P was low. Nutrient removal in anaerobic reactors is primarily due to their assimilation into microbial cells during growth rather than biological degradation [101]. The nutrients can be used later in aerobic treatment but it was insufficient with ratio of C: N: P of 100: 0.914: 0.144 and 100: 1.371: 0.143, therefore, supplementary nutrient, i.e. nitrogen (NH_4Cl) and phosphorous (K_2HPO_4) were added to give ratio of COD: N: P of 100: 5: 1 [24].

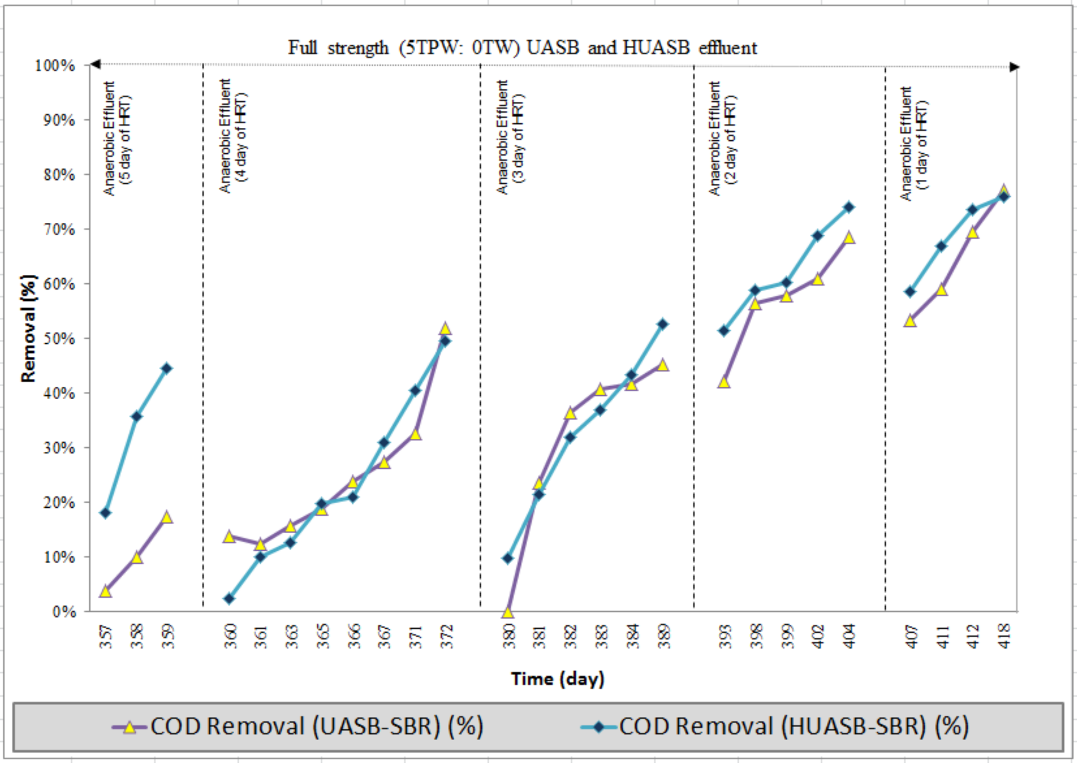
Pre-treated PW having gone through anaerobic treatment (Section 4.5) was used as feed for anaerobic sequencing batch reactors (SBRs). Thus, there were two SBRs, one each, treating the effluent from UASB and HUASB. For the first 60 d, the sludge was acclimated with diluted treated produced water (TPW) of 5 d HRT in tap water (TW): 3TPW: 2TW, 4TPW: 1TW. Table 4.11 (Figure 4.11) shows the effluent COD from the SBR receiving full strength (5TPW: 0TW) UASB and HUASB effluents. The HUASB-SBR performed marginally better than UASB-SBR. Its average COD removal efficiency when treating 5d HRT anaerobic effluent was 31% compared to 10% for the UASB-SBR.

Table 4. 10: The effluent COD from the SBRs receiving full strength (5TPW: 0TW) UASB and HUASB effluents

Day	**UASB/ HUASB HRT (d)**	**Influent COD (mg/L)**	**TSS (g/L)**		**VSS (g/L)**		**Effluent COD (mg/L)**		**COD Removal (%)**	
			UASB	**HUASB**	**UASB**	**HUASB**	**UASB**	**HUASB**	**UASB**	**HUASB**
335-359	5	822-845	7.7-10.3	6.6 - 9.8	6.0-6.6	4.6-6.0	699-813	455-674	3.8-17.3	18.0-44.6
360-379	4	820-823	8.4-10.3	8.5-9.5	5.0-6.5	4.9-5.8	396-599	415-568	27.4-52.0	30.9-49.5
380-389	3	852-894	9.5-11.2	9.0-11.1	4.4-7.0	5.0-6.9	490-529	404-537	40.8-45.2	37.0-52.6
390-404	2	958-987	8.9-11.2	9.1-12.1	6.1-7.3	5.8-7.5	310-415	250-380	57.9-68.6	60.3-73.9
405-418	1	1038-1048	8.1-8.6	8.1-8.4	5.8-6.5	5.9-6.2	240-430	249-344	59.0-77.1	66.9-76.0



(a) COD Concentrations



(b) COD removal

Figure 4. 9: COD removal in SBRs receiving full strength (5TPW: 0TW) UASB and HUASB effluents

Co-substrate caused noticeable variation of bacterial community structure. Normally co-substrate is added in order to improve the treatability and bioavailability of the more refractory matter for microbial degradation. Its effect has been widely studied in bioremediation of contaminated soil and wastewater containing inhibitory organic compounds or highly chlorinated environmental pollutants. Co-substrate may be produced after anaerobic treatment or PW itself may contain natural co-substrate that enhance aerobic degradation [102]. As the influent was changed to shorter day HRT anaerobic effluents, the COD removal efficiency in both SBRs increased. For the 1 day HRT anaerobic effluent, the average COD removal efficiency for HUASB-SBR and UASB-SBR was 72% and 68% respectively. Thus the HUASB effluent was more amenable to aerobic post-treatment than the UASB effluent.

Total COD removal efficiency after anaerobic-aerobic treatment is listed in Table 4.12 (Figure 4.12). The results indicate that in overall, anaerobic-aerobic treatment of HUASB-SBR performed marginally better than UASB-SBR as the influent was changed to shorter day HRT from HRT of 5 d to HRT of 1 day.

Table 4. 11: Summary of total COD removal efficiency of produced water after anaerobic-aerobic treatment

HRT	**UASB-SBR**				**Total COD Removal Efficiency (%)**	**HUASB-SBR**				**Total COD Removal Efficiency (%)**
	Anaerobic		**Aerobic**			**Anaerobic**		**Aerobic**		
	COD after treatment (mg/L)	**COD removal efficiency (%)**	**COD after treatment (mg/L)**	**COD removal efficiency (%)**		**COD after treatment (mg/L)**	**COD removal efficiency (%)**	**COD after treatment (mg/L)**	**COD removal efficiency (%)**	
5*	1132.3	24.7	-	-	24.7	549.4	63.6	-	-	63.6
5**	974.7	35.6	729.6	13.7	52.2	859.5	43.2	491.9	40.1	67.7
4**	1038.3	18.4	516.7	37.4	62.7	823.5	35.3	490.5	23.3	64.6
3**	1198	7.7	513.2	42.6	60.2	822	34.6	474.3	44.3	63.2
2**	1145.7	3.1	370	62.5	69.2	901	23.7	358.4	67.7	70.1
1**	1094.3	2.0	330	68.5	70.4	982.3	12.0	289.4	72.1	74.0

*without pre-treatment;

** with pre-treatment

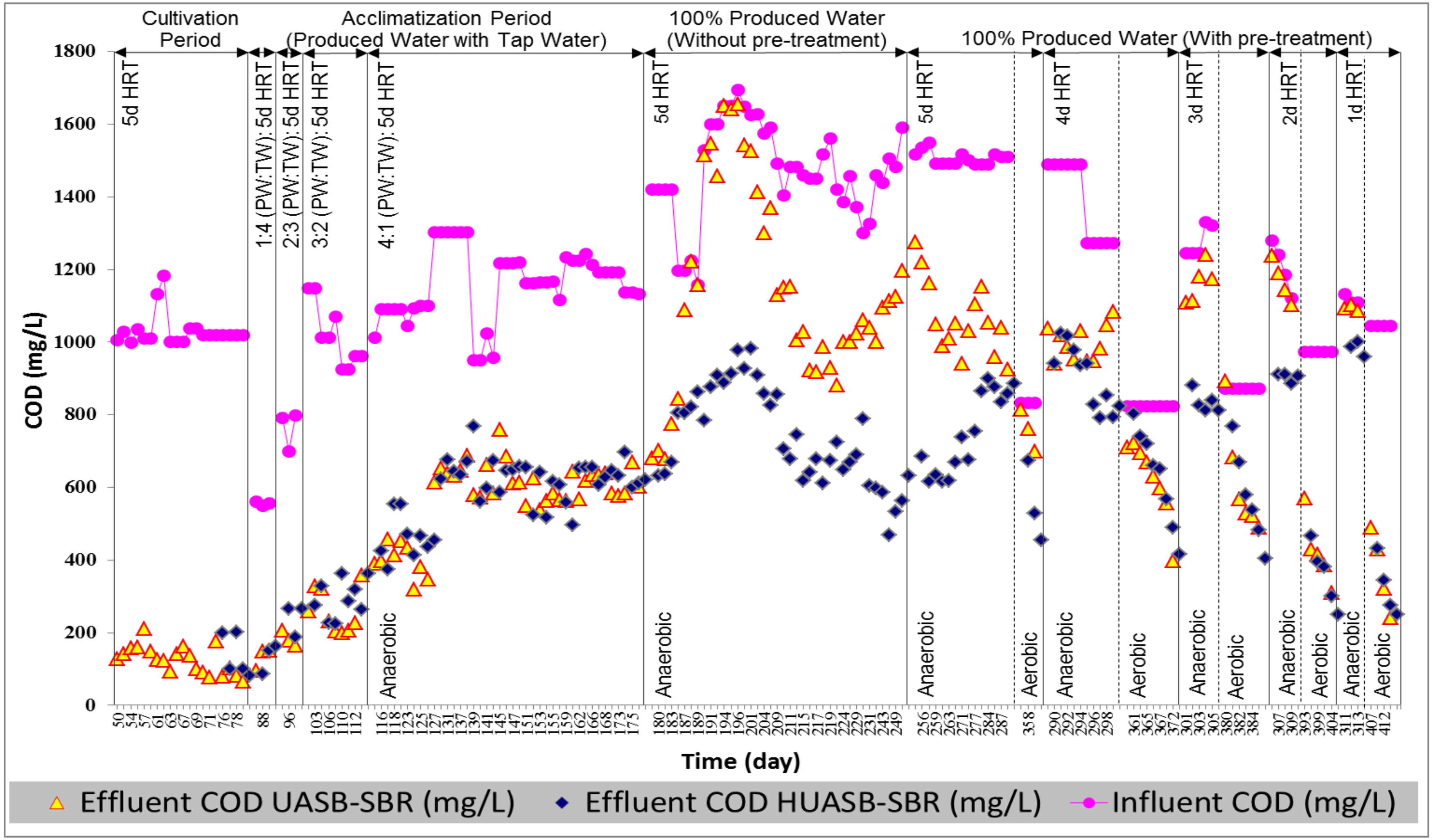


Figure 4. 10. Overall anaerobic-aerobic treatment of produced water.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.0 Chapter Overview

Chapter 5 discuss the conclusion and recommendation.

5.1 Conclusions and Recommendations

The treatment of produced water using UASB and HUASB reactors to remove COD at five different dilutions of produced water (PW) and tap water (TW) were studied. The dilution ratios were 1PW:4TW, 2PW:3TW, 3PW:2TW, 4PW:1TW and 5PW:0TW. COD reduction is better in HRT of 5 d before pre-treatment with ferric chloride. This may be due to long period of acclimatization, 71 d of treatment with the maximum COD removal was 67.49%, compared to after pre-treatment of ferric chloride, 38 d only treatment with the maximum COD removal was 59.92%. Longer acclimatization in HUASB reactor showed that overall VFA removal was in the range of 1-10 mg/L. Naphthalene is the major constituent representing 93.0 % of total 16 priority PAHs found in the influent. Both reactors were able to degrade PAHs almost completely with degradation efficiency greater than 99.6%, in all HRTs tested.

The effect of chemical pre-treatment (coagulation and flocculation using ferric chloride) on anaerobic treatment of PW was studied. Color and turbidity were reduced by almost 98.0%. Boron was reduced to 5.5 mg/L from 13.8 mg/L and barium was reduced to 0.8 mg/L from 7 mg/L, with total of 60.1% and 88.6%, respectively, of removal efficiency when pH was fixed a 10 using ferric chloride as coagulant. Ferric chloride with dosage of 2197.8 mg/L at optimal pH value of 10 was chosen to pre-treat produced water sample since it gave the best yield and the final pH of 7.8 was close to the pH to operate anaerobic treatment as post-treatment. Longer period or duration of acclimatization/biodegradation is suggested based on the results shown longer period is required after pre-treatment with chemical coagulant to enable microorganism to acclimatize well. Besides, determination for each fraction the individual compounds (saturates, aromatic, resin and asphaltenes) present in the PW is recommended since biodegradability of PW could be linked to difference in composition of each type of oil processes.

The performance of SBR treating anaerobically pre-treated PW seems to be marginally better as the influent was change to shorter day HRT of anaerobically pre-treated PW effluent; the average COD removal efficiency of HUASB-SBR was performed marginally better than UASB-SBR effluent. The results indicate that in overall, anaerobic-aerobic treatment of HUASB-SBR performed better than UASB-SBR as the influent was changed to shorter day HRT from HRT of 5 d to HRT of 1 d. Even though, SBR system is easy to use compared to other system but SBR is difficult to implement because of losses of biomass due to the dispersed growth of the microorganism and because poor clarification causes turbid effluent. In addition, large volumes are required for the SBR in the order to obtain high biodegradation. Ferric chloride coagulation-HUASB-SBR treatment barely met the discharge standard. Therefore, membrane is recommended to be coupled to a SBR to prevent organic shocks and retain slow growth of microorganism such as microfiltration (MF) or ultra-filtration (UF) and reverse osmosis (RO) because of its efficiency, ease and economical operation. In these processes, the suspended solids and colloidal material are removed by MF or UF while RO removes dissolved solids, organic and ionic matters. Combined treatment such as physical-biological-membrane (e.g.ultrafiltration-reverse osmosis) process is recommended for onshore facilities where enough space is available.

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APPENDIX A

PRODUCED WATER OVERBOARD DISCHARGE LIMITS

Country	Legal Basis	Licensing/ Monitoring Authorities	Discharge Limits for Produced Water	Comments
Albania	Barcelona Convention1	-	40 mg/L; 100 mg/L max	United Nations Environmental Program (UNEP): Convention on Protection of the Mediterranean Sea Against Pollution.
Algeria	Barcelona Convention1	-	40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
Angola		Ministry of Petroleum	No Standard set	Environmental Legislation being drafted.
Argentina	Resolution No. 105/92	SRNAH	Case-by-case	No regulations for offshore legislation; onshore regulations applied in principle.
Australia (Western)	-	Dept. of Minerals & Energy (DOME)	30 mg/L; 50 mg/L max	Operators must submit mud plan for review; testing and monitoring may vary; site specific. Only Olefins and Ester based SBM are allowed. Local species toxicity testing required for base oils and some additives. Assessed by DOME.
Azerbaijan	-	State Committee of Ecology	48 mg/L	Environmental testing of products. Certificate awarded for approved products
Bahrain	KUWAIT Convention 2	-	40 mg/L; 100 mg/L max	Covers Red Sea and Persian Gulf Regions
Belgium	OSPAR Convention3	-	40 mg/L PARCOM Decision 86/1	
Brazil	-	Instituta Brazil Medio Ambiente (IBAMA)	20 mg/L max.	Looking at using four test species for testing of drilling fluids
Bulgaria	BLACK SEA Convention4	-	-	UNEP: Convention on the Protection of the Black Sea against pollution
Cameroon	WCARC5	Ministry of Industrial & Commercial Development	-	UNEP: West & Central African Region Convention (WCARC) on Protection of Marine and Coastal Environment
Canada Chile	Act RSC 1987 SEPC6	Newfoundland offshore Canada Offshore Petroleum Board -	40 mg/L avg.; 80 mg/L max -	Encourage operators to reduce bulk disposal. Injection must be reviewed as option. End of well testing of drilling muds. EIA required prior to production drilling operations. Protocol for Protection of the South-East Pacific Against

				Pollution from Land-Based Sources.

Country	**Legal Basis**	**Licensing/ Monitoring Authorities**	**Discharge Limits for Produced Water**	**Comments**
China	GB 4914-85	National Offshore Oil Corp./EPB State Oceanic Administration	30-50 mg/L avg.; 75 mg/L max.	Standard dependent on location of operation/ pollution fees. Regulations differ from each region with China. Samples collected and testing for toxicity under a Toxicity Assessment Report (TAR). State Oceanic Administration issues final approval certificates. Regulations under review and will become more restrictive in future. EIA required to support development plan.
Colombia	SEPC6	-	Removal of 80% of oil	Protocol for Protection of the South-East Pacific Against Pollution from Land-Based Sources.
Congo	WCARC5	Department of Energy	-	UNEP: West & Central African Region Convention on protection of Marine and Coastal Environment
Cote D'ivoire	WCARC5	-	-	UNEP: West & Central African Region Convention on Protection of Marine and Coastal Environment
Denmark (North Sea)	OSPAR Convention3	-	40 mg/L PARCOM Decision 86/1	Tests other than PARCOM used: Algae — 72-hr EC50 —1400 mg/L; Gammaride — 10-day LC50— 13 mg/L; Shrimp — 96-hr EC50 — 18,000 mg/L; Testing for both drilling fluids & produced water treating chemicals /worst case mud system & pre- approval of chemicals.
Denmark(Baltic Sea)	HELCOM Convention7	-	15 mg/L max.; 40 mg/L (Alternative)	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea-Bed & its Subsoil.
	SEPC6	-	-	Protocol for Protection of the South-East Pacific Against Pollution from Land-Based Sources.
Egypt	Decree No. 338/95	EGPC/ EEAA	15 mg/L max.; 40 mg/L max. (Alternative)	Special dispensation may be awarded by EBPC. Also Egypt is a member of the Barcelona Convention. EIA at drilling stage.

Country	**Legal Basis**	**Licensing/ Monitoring Authorities**	**Discharge Limits for Produced Water**	**Comments**
Equatorial Guinea	-	-	-	-
Estonia	HELCOM Convention7	-	15 mg/L max.; 40 mg/L (Alternative)	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea-Bed & its Subsoil.
Finland (North Sea)	OSPAR Convention3	-	40 mg/L PARCOM Decision 86/1	-
Finland (Baltic Sea) France (North Sea)	HELCOM Convention7 OSPAR Convention3	Agency for Environment Energy Mgt.	15 mg/L max.; 40 mg/L (Alternative) 40 mg/L PARCOM Decision 86/1	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea-Bed & its Subsoil.
Finland (Baltic Sea) France (North Sea) France (Mediterranean Sea)	HELCOM Convention7 OSPAR Convention3 Barcelona Convention1	Agency for Environment Energy Mgt. Agency for Environment & Energy Mgt.	15 mg/L max.; 40 mg/L (Alternative) 40 mg/L PARCOM Decision 86/1 40 mg/L; 100 mg/L max	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea-Bed & its Subsoil. UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
Finland (Baltic Sea) France (North Sea) France (Mediterranean Sea) Gabon	HELCOM Convention7 OSPAR Convention3 Barcelona Convention1 WCARC5	Agency for Environment Energy Mgt. Agency for Environment & Energy Mgt.	15 mg/L max.; 40 mg/L (Alternative) 40 mg/L PARCOM Decision 86/1 40 mg/L; 100 mg/L max	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea-Bed & its Subsoil. UNEP: Convention on Protection of the Mediterranean Sea Against Pollution. UNEP: West & Central African Region Convention on Protection of Marine and Coastal Environment

Country	Legal Basis	Licensing/ Monitoring Authorities	Discharge Limits for Produced Water	Comments
Finland (Baltic Sea) France (North Sea) France (Mediterranean Sea) Gabon Gambia	HELCOM Convention7 OSPAR Convention3 Barcelona Convention1 WCARC5 WCARC5	Agency for Environment Energy Mgt. Agency for Environment & Energy Mgt.	15 mg/L max.; 40 mg/L (Alternative) 40 mg/L PARCOM Decision 86/1 40 mg/L; 100 mg/L max	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea- Bed & its Subsoil. UNEP: Convention on Protection of the Mediterranean Sea Against Pollution. UNEP: West & Central African Region Convention on Protection of Marine and Coastal Environment UNEP: West & Central African Region Convention on Protection of Marine and Coastal Environment
Georgia	BLACK SEA Convention4	-	-	UNEP: Convention on the Protection of the Black Sea Against Pollution.
Germany (Baltic Sea)	HELCOM Convention7	-	15 mg/L max.; 40 mg/L (Alternative)	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea- Bed & its Subsoil.
Germany (North Sea)	OSPAR Convention3	-	40 mg/L PARCOM Decision 86/1	
Ghana	WCARC5	Ministry of Energy	-	UNEP: West & Central African Region Convention on Protection of Marine and Coastal Environment
Greece	Barcelona Convention1	-	40 mg/L avg.; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
	MD KEP 3/91; 42/97	Ministry of Mining and Energy	75 mg/L avg.; 100 mg/L max.	More stringent standards applied on case-by-case basis. EIA for production operations.
Iran	KUWAIT Convention 2	Ministry of Energy	-	UNEP: Covers Red Sea and Persian Gulf Regions
Iraq	KUWAIT Convention 2	-	40 mg/L avg.; 100 mg/L max	UNEP: Covers Red Sea and Persian Gulf Regions

Country	Legal Basis	Licensing/ Monitoring Authorities	Discharge Limits for Produced Water	Comments
Ireland (North Sea)	Rules and Procedures for Offshore Petroleum Exploration Operations. OSPAR3	Department of the Marine and Natural Resources	40 mg/L avg.	Ireland is a member of OSPARCOM. Regulator is pushing for zero discharge regimes.
Israel	Barcelona Convention1	-	40 mg/L avg.; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
Italy	Dm of 28.7 1994	Ministry of Environment	40 mg/L avg.	More stringent standards may be applied on Produced Water. EIA at drilling stage.
Kuwait	KUWAIT Convention2	-	40 mg/L avg.; 100 mg/L max	UNEP: Covers Red Sea and Persian Gulf Regions
Lebanon	Barcelona Convention$_1$	-	40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
Libya	Barcelona Convention$_1$	-	40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
Lithuania	HELCOM Convention7		15 mg/L max.; 40 mg/L (Alternative)	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea- Bed & its Subsoil.
Malaysia	-	Dept. of Energy	.-	Companies go through Patrons Environ. Dept. for approval. Toxicity test certificates are required
Mexico		Ministry of Energy (SEMARNAP)	40 mg/L avg.; 100 mg/L max.	Environmental testing required.
Monaco	Barcelona Convention1		40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
Morocco	Barcelona Convention$_1$		40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.

Country	Legal Basis	Licensing/ Monitoring Authorities	Discharge Limits for Produced Water	Comments
Netherlands	Mining reg. 1996. Reg. 687/ 1224, 1987; OSPAR Convention3	Ministry of Economic Affairs/State Supervision of Mines	40 mg/L avg.; 100 mg/L max.	Gas platforms are exempt from 40 ppm limit where best available technology already installed. Testing for both drilling fluids & produced water treating chemicals pre- approval of chemicals. EIA required
New Zealand	-	Regional Council	-	-
Nigeria	Act No. 34/68: Regs 1992	Ministry of Petroleum Resources/EPA Director of Petroleum Resources (DPR) with permit application.	40 mg/L avg.; 72 mg/L max.	Results compared to diesel oil toxicity Test whole drilling fluid and base oil if synthetic oil base mud used Monitoring of site required. EIA required.
Norway	PARCOM 10/10/1 1988; OSPAR Convention3	Norwegian Pollution Control Authority (SFT)	40 mg/L avg.; 100 mg/L max	Monitoring of discharge may be required. Tests other than PARCOM used: Barnacle — Balanus improvisus — EC50 < 1,000 m/kg high toxic; Bivalve — Mytilus edulis — EC50 >1 mg/kg — moderate toxicity; Testing for both drilling fluids & produced water treating chemicals, pre-approval of chemicals. EIA required prior to drilling and development.
Oman	Decree No. 10/1/1982 KUWAIT Convention2	Ministry of Petroleum Resources/ Ministry of Environment	40 mg/L avg.; 100 mg/L max.	UNEP: Covers Red Sea and Persian Gulf Qatar lf Regions. EIA required prior to drilling.
Panama	SEPC6	-	-	Protocol for Protection of the South-East Pacific Against Pollution from Land-Based Sources.
Peru	SEPC6	-	-	Protocol for Protection of the South-East Pacific Against Pollution from Land-Based Sources.

Country	**Legal Basis**	**Licensing/ Monitoring Authorities**	**Discharge Limits for Produced Water**	**Comments**
Poland	HELCOM Convention7	-	15 mg/L max.; 40 mg/L (Alternative)	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea- Bed & its Subsoil.
	OSPAR Convention3	-	40 mg/L PARCOM Decision 86/1	-
Qatar	KUWAIT Convention2	-	40 mg/L avg.; 100 mg/L max.	UNEP: Covers Red Sea and Persian Gulf Regions
Country	Legal Basis	Licensing/ Monitoring Authorities	Discharge Limits for Produced Water	Comments
Romania	BLACK SEA Convention4	-	-	UNEP: Convention on the Protection of the Black Sea Against Pollution.
Russia	Water Code 1995/ GOST 1977	Committee of Ecology/ Fisheries	0.05 mg/L MPC	MPC-Maximum Permissible Concentration. Limitations based on concentrations at the edge of a mixing zone
Russia (Baltic Sea)	HELCOM Convention7	-	15 mg/L max.; 40 mg/L (Alternative)	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea- Bed & its Subsoil.
Russia (Black Sea)	BLACK SEA Convention4	-	-	UNEP: Convention on the Protection of the Black Sea Against Pollution.
Russia—Sakhalin Island	-	-	0.05 mg/L MPC	MPC-Maximum Permissible Concentration. Limitations based on concentrations at the edge of a mixing zone
Saudi Arabia	KUWAIT Convention2	-	40 mg/L; 100 mg/L max	UNEP: Covers Red Sea and Persian Gulf Regions
	WCARC5	-	-	UNEP: West & Central African Region Convention on Protection of Marine and Coastal Environment
Spain (North Sea)	OSPAR Convention3	-	40 mg/L PARCOM Decision 86/1	-
Spain (Mediterrane an Sea)	Barcelona Convention1	-	40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.

Country	Legal Basis	Licensing/ Monitoring Authorities	Discharge Limits for Produced Water	Comments
Sweden (Baltic Sea)	HELCOM Convention7	-	15 mg/L max.; 40 mg/L (Alternative)	Helcom Recommendation 9/5: Concerning Exploration & Exploitation of the Sea- Bed & its Subsoil.
Sweden (North Sea)	OSPAR Convention3	-	40 mg/L PARCOM Decision 86/1	-
Syria	Barcelona Convention1	-	40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
Thailand	NEQA 1992: Gov. Reg. 20/90	Department of Mineral Resources	40 mg/L avg.; 100 mg/L max.	Discharge limit has no legislative basis and is defined on a case-by-case basis
Trinidad	-	-	40 mg/L max.	-
Tunisia	Order of 1989	ANPE	10 mg/L max.	Zero discharge conditions have been applied in some cases. EIA required at each stage of development.
Turkey (Black Sea)	BLACK SEA Convention4	-	-	UNEP: Convention on the Protection of the Black Sea Against Pollution.
Turkey (Mediterranean Convention)	Barcelona Convention1	-	40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.
Ukraine	BLACK SEA Convention4	-	-	UNEP: Convention on the Protection of the Black Sea Against Pollution.
United Arab Emirates	KUWAIT Convention2	-	40 mg/L; avg. 100 mg/L max.	UNEP: Covers Red Sea and Persian Gulf Regions
United Kingdom	PARCOM 10/10/1988 OSPAR Convention3	Department of Trade & Industry/ Marine Pollution Control Unit	40 mg/L; avg. 100 mg/L max.	Chemicals tested & placed in categories (0-5) with 0 being no notification required, 1 being all discharges to be notified, & 5 being excess of 1,000 tons per installation per year to be notified. Testing for both drilling fluids & produced water treating chemicals pre-approval of chemicals EIA required prior to production drilling.

Country	Legal Basis	Licensing/ Monitoring Authorities	Discharge Limits for Produced Water	Comments
United States	40 CFR 435	EPA/MMS	29 mg/L; 42 mg/L max	No visual sheen; discharge prohibited in near-shore areas. Drilling fluids monthly and end of well testing. EIA required prior to production drilling operations.
Venezuela	Decree No. 833/1995	MARNR	20 mg/L	Special exemptions granted if environmental impact is not significant. EIA required at drilling stage.
Vietnam	Decision No. 333/QB 1990	Petrovietnam/ Ministry of Science, Technology & Environment (MOSTE)	40 mg/L	Toxicity testing of base fluid and additives by Petrovietnam Research & Development Center for Petroleum Safety and Environment (RDCPSE). EIA required prior to drilling.
Vietnam (EEPVL)	-	-	-	-
Yugoslavia	Barcelona Convention[1]	-	40 mg/L; 100 mg/L max	UNEP: Convention on Protection of the Mediterranean Sea Against Pollution.