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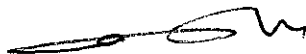3. This thesis is classified as

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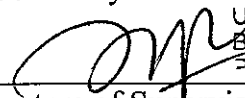|	Endorsed by	Dr. Shamsul Rahman Mohamed Kutty Associate Professor Civil Engineering Department Universiti Teknologi PETRONAS Bandar Seri Iskandar, 31750 Tronoh Perak Darul Ridzuan, MALAYSIA

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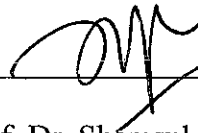
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TREATMENT OF PETROLEUM REFINERY WASTEWATER

USING MULTI-STAGE BIOLOGICAL REACTOR

by

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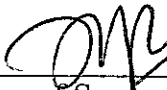I,   GASIM HAYDER AHMED SALIH

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ABSTRACT

Refining crude oil in petroleum refinery results in relatively large quantities of wastewater. Petroleum refinery wastewater (PRW) is highly polluted, hence proper and effective treatment is needed; currently requires multiple treatment processes. Therefore, the need for improved treatment processes never stops. Thinking green, biological treatment is always a cheaper and safer solution for wastewater treatment, as it involves the use of microorganisms to degrade organic matter. This study focused on development of integrated multi-stage biological treatment process for petroleum refinery wastewater. The study consisted of four phases, namely, biodegradability of PRW, PRW treatability in three configuration of sequencing batch reactors (SBR), degradation of volatile organic compounds in anaerobic-anoxic-aerobic SBR and testing of multi-stage biological reactor (MSBR) under different loads. PRW was found to be biodegradable in a 28-day batch study, with more than 95% COD removal in 24 hr under aerobic mode and 9 days under anaerobic mode. Three SBR configurations (aerobic, anaerobic-aerobic and aerobic with PRW and domestic wastewater mixed influent) were operated in parallel to determine the most effective configuration and reaction time. Anaerobic-aerobic SBR was found to be most effective with 90% COD removal and effluent COD 69 mg/L. Monitoring results indicated that 7 hr cycle duration for aerobic reactor and more than 24 hr for the anaerobic were needed. SBR train of anaerobic reactor followed by anoxic reactor and aerobic reactor was setup to treat PRW. Benzene, toluene, ethylbenzene and xylene (BTEX) are identified as volatile compounds which need to be treated in conditions that minimize volatilization. Therefore, BTEX were monitored throughout the train and were found to be almost completely degraded with 99% removal. An integrated multi-stage biological reactor (MSBR) was fabricated in duplicate and operated in parallel. Three volumetric organic loading rates (L_{org}) were applied to each reactor. COD removal percentage was found to be in the range between 95% and 97%, while the final effluent COD concentration was below 100 mg/L for the first four loads and relatively high for the other two loads (117 and 189 mg/L) and

also when PRW applied (181-228 mg/L). Results obtained from operating MSBR under different loads were used to model the reactor performance by artificial neural network. Tangent sigmoid transfer function at hidden layer and a linear transfer function at output layer with 6 neurons was the optimum transfer function. This selected model was utilized to simulate the MSBR behavior by using random data. Highest removal efficiency predicted was 98% at range of influent COD 255-3200 mg/L, and 5200-6300 mg/L, and for influent COD of 7300 mg/L. For influent COD range 900-3600 mg/L, the effluent COD predicted was below 100 mg/L. MSBR performed well under six different L_{org} and all the effluent COD were below 200 mg/L. It is recommended to investigate the performance of this reactor with other type of industrial and domestic wastewater.

ABSTRAK

Penapisan minyak mentah di loji penapisan petroleum menyebabkan kuantiti besar relatif air sisa. Penapisan petroleum air buangan (PRW) adalah sangat tercemar, justeru itu rawatan yang betul dan efektif adalah perlu kini iaitu proses rawatan berganda. Oleh itu, perlunya proses rawatan yang lebih baik. Berfikir hijau, rawatan biologi adalah penyelesaian selamat dan murah untuk rawatan air sisa kerana ia melibatkan penggunaan mikroorganisma untuk mendegradasi bahan organik. Kajian ini fokus kepada pembangunan bersepadu rawatan berperingkat proses biologi untuk air sisa penapisan petroleum. Kajian mengandungi empat fasa iaitu biodegredasi PRW, kebolehrawatan PRW dalam tiga konfigurasi reaktor kelompok penjujukan (SBR), degradasi sebatian organik meruap dalam anaerobik-anoxik- aerobik SBR dan ujian reaktor biologi berperingkat (MSBR) di bawah beban beza. PRW didapati terbiodegradasi selama 28-hari dalam kelompok kajian dengan lebih daripada 95% penyingkiran COD dalam 24 jam di bawah mod aerobik dan 9 hari di bawah mod anaerobik. Tiga konfigurasi SBR (aerobik, anaerobik-aerobik and aerobik dengan PRW dan campuran influen air sisa domestik) telah dikendalikan secara selari untuk menentukan masa tindakbalas dan konfigurasi yang lebih efektif. Anaerobik-aerobik SBR didapati lebih efektif dengan 90% penyingkiran COD dan 69 mg/L efluen COD. Hasil pemantauan mencadangkan perlunya 7 jam tempoh kitaran untuk reaktor aerobik dan lebih daripada 24 jam untuk anaerobik. Jujukan reaktor anaerobik SBR diikuti oleh reaktor anoxik dan reaktor aerobik disediakan untuk merawat PRW. Benzene, toluene, ethylbenzene dan xylene (BTEX) dikenalpasti sebagai sebatian meruap yang perlu dirawat dalam keadaan pengewapan minimum. Oleh itu, BTEX dipantau sepanjang jujukan dan didapati hampir sepenuhnya didegredasi dengan penyingkiran 99%. Reaktor biologi integrasi berperingkat (MSBR) telah direka dalam dua salinan dan dikendalikan secara selari. Tiga isipadu muatan kadar organik (L_{org}) telah diaplikasi untuk setiap reaktor. Peratusan penyingkiran COD telah didapati berada dalam julat di antara 95% dan 97%, manakala kepekatan efluen COD akhir adalah di bawah 100 mg/L untuk empat beban pertama dan tinggi relatif bagi kedua-dua beban

yang lain (117 mg/L dan 189 mg/L) dan juga apabila PRW diaplikasikan (181-228 mg/L). Keputusan yang diperolehi dari operasi MSBR di bawah beban yang berbeza telah digunakan untuk membina prestasi reaktor dengan Buatan rangkaian neural. Fungsi peralihan tangent sigmoid pada lapisan tersembunyi dan fungsi pindah linear pada lapisan output dengan 6 neuron adalah fungsi pindah optimum. Model terpilih ini digunakan untuk mensimulasikan kelakuan MSBR dengan menggunakan data rawak. Kecekapan penyingkiran tertinggi dianggarkan adalah 98% pada kadar influen COD 255-3200 mg/L, dan 5200 - 6300 mg/L, dan untuk influen COD pada 7300 mg/L. Bagi influen COD antara 900 - 3600 mg/L, efluen COD dianggarkan di bawah 100 mg/L. MSBR beroperasi dengan baik dibawah perbezaan enam L_{org} dan kesemua efluen COD adalah dibawah 200 mg/L. Adalah dicadangkan untuk mengkaji prestasi reaktor ini dengan air sisa industri dan domestik jenis yang lain.

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LIST OF ABBREVIATIONS

Abbreviation		Unit
ACD	Accidental Contaminated Drain	
ANN	Artificial Neural Network	
BNR	Biological Nitrogen Removal	
BOD_5	5-days Biochemical Oxygen Demand	mg/L
BPR	Biological Phosphorus Removal	
BTEX	Benzene, Toluene, Ethylbenzene and Xylene	
COD	Chemical Oxygen Demand	mg/L
DAF	Dissolved Air Flotation	
DO	Dissolved Oxygen	mg/L
DOE	Department of Environment	
DW	Domestic Wastewater	
ETS	Effluent Treatment System	
FEQ	Final Equalization Tank	
FFBP	Feed-forward backpropagation	
GC-FID	Gas Chromatograph-Flame Ionization Detector	
GC-MS	Gas Chromatography-Mass Spectroscopy	
HPLC	High Performance Liquid Chromatography	
HRT	Hydraulic Retention Time	
HSEQ	High Strength Equalization Tank	
IGF	Induced Gas Flotation	
LEARNGDM	Gradient Descent Momentum algorithms	
LOGSIG	Log Sigmoid transfer function	
L_{org}	Organic Volumetric Loading Rates	$kg/m^3 \cdot d$
MAPE	Mean Absolute Percentage Error	
MLSS	Mixed Liquor Suspended Solid	mg/L
MLVSS	Mixed Liquor Volatile Suspended Solids	mg/L
MSBR	Multi-Stage Biological Reactor	
MUCT	Modified UCT	

NN	Neural Network	
OCD	Oily Contaminated Drain	
OLR	Organic Loading Rate	$kg/m^3 \cdot d$
P&T	Purge and Trap	
PRW	Petroleum refinery wastewater	
PURELIN	Linear transfer function	
R^2	Correlation Coefficient	
RAS	Return Activated-Sludge	
RMSE	Root Mean Square Error	
SBR	Sequencing Batch Reactor	
sCOD	Soluble COD concentration	mg/L
SIM	Selected Ion Method	
STP	Sewage Treatment Plant	
TANSIG	Tangent Sigmoid transfer function	
TKN	Total Kjeldahl Nitrogen	mg/L
TOC	Total Organic Carbon	mg/L
TRAINLM	Levenberg–Marquardt algorithms	
TSS	Suspended Solid	mg/L
UASB	Up-flow Anaerobic Sludge Blanket	
UCT	University of Cape Town	
VAF	Variance Accounted For	
VFA	Volatile Fatty Acids	mg/L
VIP	Virginia Initiative Plant	
VSS	Volatile Suspended Solids	mg/L

CHAPTER 1

INTRODUCTION

Each petroleum refinery is uniquely designed and configured depending on the refining technology used, crude oil processed and source of raw water, in addition to end products produced (IPIECA, 2010). Petroleum refineries use relatively large volumes of water and the generated wastewater characteristics generally vary from one refinery to another. Wastewater generated from the refineries is normally a combination of process water, run-off water and sanitary wastewater, mainly cooling system water, desalting water, stripping steam water and water used for flushing during maintenance and shut down (Al Zarooni and Elshorbagy, 2006). Wastewaters released by petroleum refineries and petrochemical industries contain high level of pollutants and characterized by the presence of large quantities of oil products and chemicals (Suleimanov, 1995).

Discharging petroleum refinery effluent without proper treatment would be hazardous to the environment. Wastewater treatment process is involved processes to remove organic compounds and other hazardous substances which make it complex and costly. Initially, on-site treatment was limited to the primary stage of gravity separation treatment for oil and grease removal by means of separators and dissolved air flotation units for removal of free, dispersed and emulsified oil; and because of the increased emphasis on treatment and the increased sophistication of treatment process, later configurations lead to incorporating secondary treatment (Dold, 1989).

The treatment of wastewater from petroleum refineries includes in-plant source control, pretreatment and end-of-pipe treatment (Wang et al., 2006). Although pollution source reduction and control involved many advantages such as reduces the overall pollutant load that must be treated in an end-of-pipe wastewater treatment system (Fahim et al., 2009), and reduces pollutant before it is diluted in the main wastewater stream and provides an opportunity for recovery. Despite these

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advantages, end-of-pipe wastewater treatment –which this study addresses- is the final stage for meeting regulatory discharge requirements and protection of receiving water bodies.

Alternative wastewater treatment methods are important to petroleum refineries to ensure that they meet the regulatory limit of effluent set by the authorities. Despite the existence of several methods for petroleum wastewater treatment, studies are being carried out to develop treatment processes that are simple, reliable, time effective and cost saving. Therefore, many researchers are interested in providing biological solution that can cope with this demand. Sometimes, the current treatment method is not fully capable to treat the wastewater, presumably due to changes in the wastewater constituents. One of the alternatives is to have a compact biological treatment system that is capable to withstand the nature of this wastewater and the changes in the load with minimum pre-treatment and effective treatment capability.

Biological treatment processes are known to be economical and efficient method that can be used for treating wastewater from oil and gas industry. Technologies that can treat large quantities of wastewater with relatively small site requirements are, therefore, of particular importance.

Petroleum refinery wastewater (PRW) compositions are complex and thus specific treatments are required to remove contaminants prior to discharge or for recycling and reuse. Strict legislation, cost savings, sustainable development and public image are the principal motivators for refineries to improve their effluent treatment processes. Some refineries are moving to minimize their discharge to zero level whereby the volume that is discharged from a wastewater reuse system is further treated and sent back to the refinery for recycle (IPIECA, 2010).

Due to the ineffectiveness of purification systems, wastewaters may become seriously hazardous, leading to the accumulation of toxic substances (such as heavy metals, benzene, toluene, ethylbenzene, xylene and phenol) in the receiving environment with potentially serious consequences on the ecosystem (Beg et al., 2001). The organic and inorganic pollutants of environmental concern found in petroleum refinery wastewater include ammonia, oil, phenol, sulphur-based

contaminants and heavy metals (Vohra et al., 2006). High concentrations of phenol, oil and grease, and ammonia were observed in water and sediment at the point of effluent discharge due to accumulation over long period of time (Otokunefor and Obiukwu, 2005).

The quantity of petroleum refinery wastewaters generated and their characteristics depend on the refining process configuration and complexity of the process (Al Zarooni and Elshorbagy, 2006). In general, the volume of wastewater generated is in the range of 3.5 to 5 m^3 per ton of crude oil when cooling water is recycled (WBG et al., 1998), and in some type of refineries the volume of wastewater generated is 0.4 to 1.6 times the volume of crude oil processed (Coelho et al., 2006). During normal operation and efficient refining process, the typical petroleum refinery wastewater contains approximate range of concentrations for biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) of 150-250 mg/L and 300-600 mg/L, respectively and other pollutants could also be found (WBG et al., 1998). In some petroleum refineries and at some times the COD concentration could reach 1020 mg COD/L as reported by Diya'uddeen et al. (2011), and could reach more than ten times the above mentioned values (PPTSB, 2009). This is a large volume of generated polluted wastewater equivalent to 65-90 gallons of water per barrel of crude oil processed in some types of refineries (Alva-Argáez et al., 2007).

Many refineries do not use anaerobic treatment in their wastewater treatment processes and the conventional aeration processes are commonly used which are among the most costly operational expense; however, the volatility of some compounds often results in a significant amount of removal by stripping during aeration or in physical processes such as gas stripping which simply transfers the problem from one medium to another rather than converting the contaminants into innocuous products as would be achieved with biodegradation (Ma, 1999).

Pollution prevention, abatement and control as well as environmental enhancement are the key objectives of wastewater effluent standards as they set the limits of allowable pollutant discharge levels to receiving water bodies (BOBLME, 2011). Because of more stringent effluent requirements for ammonia,

many refineries seek to improve their existing treatment methods (Wang et al., 2006). Also, new regulations imposed by related authorities include effluent limits on ammonia as well as nitrate. Hence, the treatment system of refinery wastewater should be upgraded if those regulations are enforced on industrial effluents.

Enhancing the treatment efficiency on a lab scale process without interfering with the refinery current treatment process was important in order to determine the best compact biological treatment system. The following points are also addressed accordingly:

a. Compact treatment system to save land usage.

b. Biological treatment system to ensure desired efficiency with minimum cost.

c. Pre-treatment step, if needed, to prevent system upset.

d. Sequencing batch reactor for initial treatability to save cost.

e. Integrated treatment process to suit influent characteristics.

f. Apply different loads to the system to identify the optimum.

1.1 Problem Statement

Petroleum refineries generate large amount of wastewater during refining process of crude oil that are highly contaminated and requires advanced multiple treatment systems. Even though there exist several methods for treating petroleum refinery wastewater, improving treatment system performance in terms of better effluent quality, cost effectiveness, and to cope with the current development of technology, the search for alternative treatment methods is required (Rahman, 2004).

Although activated sludge treatment processes are economical and efficient methods and are being used to treat the wastewater from petroleum refinery (Izanloo et al., 2007), but sometimes not fully capable due presumably to changes in the constituents and loads. Also, volatile organic compounds such as BTEX

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(benzene, toluene, ethylbenzene and xylene) and other hazardous substances such as phenol are of concern during selection of the treatment method to ensure that no stripping takes place during aeration as well as not being toxic to the microorganisms used in the biological treatment.

Biological nutrient removal systems could be one of the alternatives as the first stage in the treatment process involved an anaerobic stage which minimizes the volatilization and helps reduce the organic load to subsequent stages. However, they require skilled operators and many recycling lines, and often have difficulties in maintaining the reaction conditions and system control (Makaya et al., 2007).

1.2   Objectives of the Study

The goal of this study was to develop an integrated biological treatment system to treat petroleum refinery wastewater. The study also aimed to achieve the following objectives:

1. To determine the biodegradability of the petroleum refinery wastewater and to determine its degradation percentage.

2. To investigate the treatability of the petroleum refinery wastewater in different configuration of sequencing batch reactor.

3. To develop an integrated multi-stage biological reactor that incorporates different biological conditions in a single compact reactor for effective treatment.

4. To develop a performance simulation mathematical model for the multi-stage biological reactor.

1.3 Scope of the Study

The scope of the study involved the following:

1. In the biodegradability batch study, the degradation was monitored for 28 days in terms of chemical oxygen demand (COD).

2. The treatability of the petroleum refinery wastewater was conducted using sequencing batch reactor (SBR) in two stages:

   a. Three SBR configurations, aerobic, anaerobic-aerobic and aerobic mixed influent were operated in parallel to determine the most suitable configuration.

   b. Parameters such as COD, nitrate and ammonia were monitored on a single operation cycle to identify the optimum reaction time.

3. In the multi-stage anaerobic-anoxic-aerobic SBR, Benzene, Toluene, Ethylbenzene and Xylene (BTEX) were monitored to determine the removal efficiency achieved by this configuration.

4. Development of an integrated multi-stage biological reactor to treat petroleum refinery wastewater and operate it under different loads.

5. Artificial neural network mathematical modeling tool was used to model and simulate the performance of the multi-stage biological reactor.

1.4 Thesis Organization

This thesis has been organized into the following five chapters:

Chapter 1 is an introduction on petroleum refinery and petroleum refinery wastewater. It also tells the problem statement, objectives of and the study the scope.

Chapter 2 is a literature review on effluent standards, petroleum refinery wastewater constituent and treatment, biological treatment system and reactions. The

chapter also contains brief review on sequencing batch reactor, up-flow anaerobic sludge blanket reactor, multi-stage biological process and artificial neural network and its application in wastewater treatment.

Chapter 3 describes the four phases of the study and sampling and characteristics of the petroleum refinery wastewater. The chapter also contains the materials, methods and experimental procedure for each phase and includes brief summary of procedures for measurement of parameters.

Chapter 4 presents the results of the four phases of the study. In phase 1, the biodegradability batch study was conducted in aerobic and anaerobic batch mode. In phase 2, the results of three sequencing batch reactor configurations for the treatment of petroleum refinery wastewater are shown in addition to a monitoring study. In phase 3, three-stage (anaerobic, anoxic and aerobic) sequencing batch train reactor was investigated to treat petroleum refinery wastewater with emphasis on benzene, toluene, ethylbenzene and xylene (BTEX). The results of phase 4 study on the performance of the multi-stage biological reactor under different loads and modeling and simulation of the reactor performance are presented.

Chapter 5 gives the conclusions and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.0 Chapter Overview

In this chapter, the literature review on effluent standards, petroleum refinery wastewater (PRW) constituent and treatment, biological treatment system and reactions are presented. The chapter also contains brief review on sequencing batch reactor, up-flow anaerobic sludge blanket reactor, multi-stage biological process and artificial neural network and its application in wastewater treatment.

2.1 Effluent Standards for Petroleum Refinery Wastewater

The effluent standards values for process effluents in petroleum refineries are indicative of good industry practice and are similar relevant standards of countries with recognized regulatory frameworks (IFC, 2007). The effluent standards are assumed to be for final discharge after treatment to receiving water bodies and should be practicable under normal operating conditions in properly operated facilities and are presented in Table 2.1 for range of concentration as reported by Diya'uddeen et al. (2011), typical concentration as per IFC (2007) and local discharge limits set by the Environmental Quality Act 1974 (Environment, 2009).

2.2 Petroleum Refinery Wastewater Constituent and Treatment

Petroleum refinery wastewater contains a range of toxic and recalcitrant organic compounds such as alkanes, alkenes, polyaromatic hydrocarbons, monocyclic aromatics-benzene, toluene, ethylbenzene, xylenes, naphthenes and phenol (Metcalf and Eddy, 2003). Table 2.2 shows the concentration of the main parameters

for PRW from the literature in terms of range of concentration as reported by Diya'uddeen et al. (2011) and typical concentrations as reported by the World Bank Group (WBG et al., 1998).

Petroleum refining industry will continue to grow, and because refining of oil will continue to be accompanied by the generation of highly polluted wastewater, it is essential to develop effective treatment systems (Al-Khalid and El-Naas, 2011). Although petroleum refineries have various wastewater treatment systems, but the process units involved have a variety of operational limitations and constraints, even though they have been in operation over a long period of time. It also needs proper expertise in the operation as well as maintenance of the process. There is a growing interest to provide effective biological treatment system for the degradation of PRW as it is environmentally friendly and cost-effective alternative (Al-Khalid and El-Naas, 2011). This interest is motivated by the growing concern of environmental quality and protection supported by strict legislation. This research was aimed to investigate the feasibility of having an integrated biological reactor which would give higher operational flexibility and less maintenance. It was essential to investigate the elements that control the petroleum refinery wastewater treatment process in order to develop an integrated biological reactor for effective treatment of petroleum refinery wastewater. The developed reactor should have better mixing, closer contact and higher operational flexibility.

Table 2.1: Effluent discharge standards for PRW

Parameter	pH	COD	BOD$_{5\,d,\,20°C}$	Phenol	Benzene	O&G	SS	Ammonia	Reference
Unit	-	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	-
Typical	6 - 9	150	30	0.2	0.05	10	30	10	(IFC, 2007)
Range	6 - 9	100 - 200	10 - 40	3.7	-	10 - 23	30 - 70	15 - 70	(Diya'uddeen et al., 2011)
Local	5.5 - 9	50 - 100 (80 - 200)	20 - 50	0.001 – 1.0	-	1 - 10	50 - 100	10 - 20	(Environment, 2009)

Table 2.2: Typical and range of composition of PRW

Parameter	pH	COD	BOD$_{5\,d,\,20°C}$	Phenol	Benzene	O&G	SS	Lead	Chrome	Ammonia	Reference
Unit	-	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	-
Typical	-	300 - 600	150 - 250	20 - 200	1 - 100	100 - 300	-	0.2 - 10	0.1 - 100	-	(WBG et al., 1998)
Range	7 - 10.3	80 - 1020	0.2 - 570	0.85 - 200	1 - 100	1.1 - 3000	22.8 - 650	-	-	0.21 - 70	(Diya'uddeen et al., 2011)

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Several studies investigated different methods for treatment of PRW; the application of solar oxidation process in PRW treatment by using $Fe(III)/H_2O_2/Solar-UV$ resulted in 58% removal of COD as maximum reduction, although the use of oxidation agent was minimized but the final reduction was low (Parilti, 2010). Similarly, maximum 75% PRW sour water dissolved organic carbon removal was achieved from Fenton stirred reactor and photo-Fenton reactor in series (Coelho et al., 2006). A recent study using a photocatalytic reactor showed that the maximum COD removal achieved was 83% (Shahrezaei et al., 2012). Electrocoagulation was also assessed as a possible technique for the reduction of COD in PRW with low removal of 63% (El-Naas et al., 2009); the method was reported as ineffective method due to the high amount of soluble organic pollutants and low amount of suspended solids contained in PRW (Yavuz et al., 2010). Another approach is electrochemical treatment of PRW with three-dimensional multi-phase electrode which resulted in 92.8% COD removal efficiency (Yan et al., 2011) but it comes with some complications such as the reactor, pH control and cost. Electrofenton process followed by the electrochemical oxidation was found to achieve COD removal of 75.71%, but energy consumption and set-up were among the disadvantages of the process (Yavuz et al., 2010). A combined physical process dissolved air flotation and activated carbon adsorption improved the COD removal efficiency from 16–64% to 72–92.5% for influent COD values of 110–200 mg/L (Hami et al., 2007); these influent concentrations are considered as low values. All these methods shared disadvantages such as the disposal of the spent contaminated sludge, appropriate reaction conditions control, low efficiencies, low reaction loading rates and narrow pH operation range (Shahrezaei et al., 2012).

Biological treatment processes are known to be economical and efficient in treating wastewater from oil industry (Jou and Huang, 2003), as they are well-established method for remediation of this wastewater . They are preferred over physicochemical processes as they are cost effective, efficient and environmentally friendly (Hamza et al., 2012). They are less expensive compared to advanced oxidation processes that can also give complete mineralization of the compound. In recent years, more attention has been paid to biological treatment processes which can

results in a complete mineralization unlike the most common physical-chemical processes (solvent extraction and adsorption) which 'concentrate' the compound in a solid or liquid phase (Tomei and Annesini, 2008).

Other studies investigated effectiveness of biological methods for treatment of end-of-pipe PRW and the removal was highly inconsistent in the range of 25-46% by utilizing group of microorganisms in rotating biological contactor (Martinez, 1979), and 35% in fluidized bioreactors (Diya'uddeen et al., 2011), increased to 52-56% by utilizing bacterial isolates (Hamza et al., 2012). The application of moving bed bioreactors increased the treatment efficiency to 62% (Wong, 2001), while 64% removal achieved when PRW mixed with other wastewater (Ochieng et al., 2003); 70% COD removal was achieved by aerobic batch treatment (Sarathy et al., 2002), and increased to 90% when nutrient was added to PRW mixed with other type of wastewater (Ochieng et al., 2003). The removal was better at 80-90% with new technology called vertical shaft bioreactors (Wang et al., 2008) and reached 93% by using cross-flow membrane system which is not suitable for high volume of wastewater (Diya'uddeen et al., 2011).

Despite the advantages of conventional biological methods and recently reported development, recalcitrant compounds found in PRW are not adequately eliminated; therefore, complete degradation by biological methods proves difficult, as supported by higher effluent COD values observed in some treated effluents (Diya'uddeen et al., 2011). Many studies have selected one or some of the compounds found in PRW and acclimatized single microbial species to degrade it/them. This practice may have limitations in field application for real PRW due to the presence of different contaminants which might be inhibitory (Busca et al., 2008). However, some developments focused on acclimatization of suitable sludge, higher biomass concentrations and mass transfer, immobilization on an inert support in fixed bed and biologically activated carbon but the removal was below 60%. Other problems of high sludge generation, low tolerance to toxic load and organic shock coupled with a slow degradation rate (Diya'uddeen et al., 2011) need to be resolved.

2.3 Biological Treatment System

In the selection of the suitable biological treatment process for petroleum refinery wastewater, volatilization would be a key element. During refining process the wastewater with hazardous components and petroleum hydrocarbons with varying degree of solubility depending on the temperature is produced. Benzene, toluene, ethylbenzene and xylene (BTEX) are monoaromatic hydrocarbon compounds which are relatively highly soluble in water when compared to the other hydrocarbons such as aliphatic hydrocarbons (AlSalka et al., 2010). The exposure to these compounds is generally associated with significant health implications on human and ecological livings (Ma and Love, 2001a). Volatile organic compounds and other hazardous substances are of concern during selection of the treatment method to ensure no emissions to the atmosphere takes place and sufficient time is given to these VOCs to be degraded.

BTEX compounds are one of these VOCs that produced from crude oil with great mobility abilities and toxicity that with major concern for environment and human health (Texier et al., 2012). Many biological attempts have been reported for the treatment of these volatile organic compounds from the environment (Texier et al., 2012). They have been shown to be biodegradable as sole carbon and energy sources under aerobic conditions; however, during aeration the volatility of these compounds often results in removal by stripping (Ma and Love, 2001a). Although all of the BTEX compounds are rapidly biodegraded under aerobic conditions (Schreiber and Bahr, 2002), but the losses due to aeration could reach up to 30% of their content (Texier et al., 2012). Anoxic condition could be a solution to avoid striping due to aeration (Ma and Love, 2001b), as researchers have found that BTEX can be biodegraded using this condition (Norris, 1995). BTEX have been successfully removed by anoxic condition simultaneously with nitrogen and carbon compounds (Texier et al., 2012). However, high concentration of BTEX can adversely affect the COD removal efficiency as reported by Wong and Gerhardt (2002). BTEX were removed by supporting anoxic and microaerobic redox conditions in SBR lab scale reactor (Ma and Love, 2001b). This lowered the overall oxygen demand when microaerobic conditions were used to

achieve aerobic metabolism of constituents in wastewater. The SBR was operated with a 24-hr cycle consisting of fill (0.5 hr), react (21.5 hr), settle (1.5 hr) and draw (0.5 hr). The experiment was conducted in the SBR with three redox phases: anoxic (9 hr), microaerobic (2 hr, 0.2 mg/L DO) and aerobic (10.5 hr, 4 mg/L DO) (Ma and Love, 2001b). Anaerobic degradation appeared to be promising alternative for BTEX pretreatment (Texier et al., 2012), as minimum agitation involved and as it can lower the overall load. BTEX degradation under anaerobic condition varies from one compound to another, with maximum removal efficiency between 95-99% (Farhadian et al., 2008). Benzene degradation is usually slow, incomplete and subject to long lag times, while toluene is the most readily degraded compound, at the same time as xylene and ethylbenzene appear to be biodegradable (Foght, 2008). There was a degree of removal under each condition and therefore the combination of the three conditions will result in more effective treatment.

Phenol is also one of the important compounds found in petroleum refinery wastewater. It is also one of the most common hazardous organic pollutant that is toxic even at low concentrations (Nair et al., 2010), and frequently has been chosen as a model pollutant in wastewater research (Busca et al., 2008). It exhibit a degree of solubility in water at room temperature, and completely soluble above 68°C (Al-Khalid and El-Naas, 2011). Phenol could be degraded by utilizing anaerobic as well as aerobic microorganisms as has been reported by many researchers (Al-Khalid and El-Naas, 2011). Anaerobic treatment of phenol in synthetic wastewater under thermophilic (55°C) condition showed that the removal was 99% at 40 hr of HRT for a wastewater containing 630 mg/L of phenol, corresponding to concentration of 1500 mg/L of chemical oxygen demand (COD) and a loading rate of 0.9 g COD/L·d (Fang et al., 2006). Synthetic phenol wastewater (varying from 550 to 1150 mg/l) was treated by using anoxic SBR. Cycle length was varied from 24 to 6 hr with settling period 2 hr. Maximum removals for phenol and COD were reported at 12 hr cycle 6-3 hr fill. At 6 hr cycle 2 hr fill the system reported removal ranged from 80% to 56% (Sarfaraz et al., 2004). The aerobic degradation of phenol was extensively studied, Al-Khalid and El-Naas (2011) reported different aerobic systems used to degrade different concentrations (1-10000 mg/L) of synthetic phenol with removal efficiency of as low as 25% up to 100%. Aerobic SBR treated a synthetic

wastewater with a 1300 mg/L phenol concentration; the 4-hr cycle SBR operation achieved 97% removal efficiency. There was little or no stripping of phenol which confirmed that the pathway for phenol removal in this biological system was wholly through biodegradation (Yoong and Lant, 2001). This might be challenged with the fact that the aeration and agitation may cause stripping to the atmosphere and volatilization (Ma and Love, 2001b).

Combination of anaerobic and aerobic treatment processes in continuous or batch systems were reported to be effective at treating strong wastewater (O'Neill et al., 2000). When high strength wastewater pre-treated in anaerobic condition, that will break down the biodegradable substances and reduce the overall organic load (Rebah et al., 2010). As a result, anaerobic pretreatment is essential for load reduction followed by anoxic as it may serve as a viable alternative for biodegrading those volatile constituents, and final stage aerobic for polishing and to support the anoxic condition. It is important to decide which treatment process, or combination of processes, will best perform the treatment of the wastewater effluent involved, because wastewater treatment facilities contribute significantly to the total cost of a capital project which involves land and operation (Bush, 1980).

2.4   Biological Treatment Reactions

Biological treatment reactions are the reactions that occur in nature when group of naturally occurring microorganisms degrade organic matters or when a treatment technology uses them to consume organic matters resulting in the removal of pollutants and elimination of contaminants (WBG et al., 1998). These organic redox reactions occur in several conditions and are carried out by different types of microorganisms depending on the oxygen form and availability.

2.4.1   Anaerobic Reaction

Anaerobic reactions occur in the absence of significant amount of oxygen, nitrate, nitrite and sulphate, and the electron acceptor is other than oxygen such as carbon

dioxide (Norris, 1995). In general, there are three distinct phases of digestion involved in the anaerobic oxidation, namely hydrolysis where solublization of particulate matter occurs and volatile acids are formed, the second step is fermentation (acidogenesis), in which, there is conversion of organic substrates to acetate, hydrogen and CO_2, and organic compounds serve as the electron acceptor as well as the electron donor (Kumar et al., 2012); the third step is methanogenesis in which acetate and hydrogen produce methane and carbon dioxide (Metcalf and Eddy, 2003).

Anaerobic fermentation and oxidation processes are used primarily for the treatment of high-strength organic wastewaters such as petroleum wastewater. Anaerobic digestion processes are advantageous because of the lower biomass yield, higher volumetric loading, elimination of off-gas air pollution and less energy and nutrient requirement; and energy in the form of methane can be recovered from the biological conversion of organic substrates. Which make anaerobic treatment suitable to industrial wastewater as it usually lack of sufficient nutrient (Metcalf and Eddy, 2003).

For treating high-strength industrial wastewaters (generally COD >1000 mg/L) (Behling et al., 1997), anaerobic treatment has been shown to provide a very cost effective alternative to aerobic processes with savings in energy, nutrient addition and reactor volume. Many toxic and recalcitrant organic compounds found in petroleum wastewater such as phenol and toluene are degraded under anaerobic conditions, with the compound serving as a growth substrate (Metcalf and Eddy, 2003). Wong (2000) presented an overview on the application of anaerobic digestion to the petrochemical wastewaters as a successful pretreatment stage.

2.4.2 Anoxic Reaction

Anoxic reactions occur in low oxygen level environment as the microorganisms use chemically combined oxygen such as that found in nitrate and the electron acceptors are the nitrate and nitrite which will be converted to nitrogen gas and water (Norris, 1995). In the case of pre anoxic reactor where wastewater provides the

electron donor, an anoxic reactor receives the influent wastewater and it is followed in the treatment system by an aerobic reactor where nitrification occurs. Heterotrophic bacterial growth occurs in both the anoxic and aerobic zones with nitrate and oxygen consumption, respectively (Metcalf and Eddy, 2003). Anoxic condition degrades recalcitrant compounds and the VOCs as well as the compounds that could be stripped during aeration (Ma and Love, 2001b). Researchers have found that benzene, toluene, ethylbenzene and xylene in addition to other compounds can be biodegraded using nitrate as electron acceptor in anoxic condition (Norris, 1995).

2.4.3 Aerobic Reaction

Aerobic reactions are widely used to degrade organic materials in aerobic respiration in the presence of oxygen which acts as an electron acceptor (Norris, 1995). Aeration is often required to increase the dissolved oxygen and provide the mixing to bring the microbes together with the oxygen and pollutant. A wide range of toxic organic compounds found in petroleum refinery wastewater have been found to serve as growth substrates for aerobic heterotrophic bacteria (Metcalf and Eddy, 2003). Almost all petroleum hydrocarbons are biodegradable under aerobic conditions, but in many cases when dissolved hydrocarbon is greater than 2 to 4 mg/L, biodegradation may be incomplete (Norris, 1995), and volatilization due to aeration will occur (Ma and Love, 2001b).

2.5 Sequencing Batch Reactor (SBR)

Sequencing Batch Reactor (SBR) is a variant of the biological activated sludge process that utilizes a fill-and-draw reactor with complete mixing during the batch reaction step (after filling) and the aeration and clarification occur in the same tank. All SBR systems have five steps in common, which are carried out in sequence as follows: (1) fill, (2) react, (3) settle (sedimentation/clarification), (4) draw (decant), and (5) idle. A unique feature of the SBR system is that there is no need for a return activated-sludge (RAS) system. The aeration and settling occur in the same chamber and no sludge is lost in the react step and none has to be returned to maintain the

solids content in the aeration chamber. The system advantages include (1) simplified operation; final clarifiers and RAS pumping are not required, (2) compact facility, (3) flexible operation; nutrient removal can be accomplished by operational changes; (4) can be operated as a selector process to minimize sludge bulking potential, (5) quiescent settling enhances solids separation (low effluent SS), and (6) applicable for a variety of plant sizes (Metcalf and Eddy, 2003). The system is usually operated in aerobic mode; but also can be operated in anaerobic or even anoxic mode (Ma and Love, 2001b).

The feature of SBR design is its inherent variant of the cyclic phasing, providing different operating modes (Silva et al., 2004). Although SBR may need more than one treatment unit working alternately and skilled operators are also needed (Al-Khalid and El-Naas, 2011), but there is a degree of flexibility associated with working in a time rather than in a space sequence (Norcross, 1992). As SBR is time oriented, the relation between filling and reaction phase time length leads to favorable productivity alterations (Lee et al., 1997). The SBR technology allows upgrading of the existing earthen lagoon treatment systems in petroleum refineries without the need for any additional substantial concrete structures and provided substantial process flexibility (Wong and Gerhardt, 2002).

2.6   Up-flow Anaerobic Sludge Blanket (UASB) Reactor

One of the most notable developments in anaerobic treatment technology was the upflow anaerobic sludge blanket (UASB) reactor in the late 1970s. The UASB reactor is most commonly used, with over 500 installations, for treating a wide range of industrial wastewaters. The UASB reactor is a high rate system that can retain biomass with high treatment capacity and low site area requirement (Zinatizadeh et al., 2007). Upgrade of a petrochemical wastewater treatment plant by adding an UASB reactor to the aerobic treatment provided expected performance and the advantages of the anaerobic pretreatment had been clearly shown in practice (Wong, 2000). The aerobic biodegradability performance can be increased by 20-30% after the petrochemical wastewater had been pretreated by the anaerobic process

(Wong, 2001). A UASB reactor treated a canning factory effluent in an experimental study investigating the influence of organic loading rate (OLR) on the treatment efficiency; the chemical oxygen demand (COD) was increased stepwise from 2300 to 4000 mg/L. The hydraulic retention time was kept constant at 24 hr and the OLR increased from 2.28 to 3.95 kg COD/m^3·d. The highest COD removal (92 %) was reported at OLR 2.5 kg COD/m^3·d (Trnovec and Britz, 1998).

Petroleum refinery wastewater was treated in four UASB reactors that were operated at low organic loading rate (0.05-0.1 kg COD/m^3·d). The organic loading rate was then gradually increased to 2, 1.5, 0.5 and 1.5 kg COD/m^3·d for the four reactors, at an influent COD concentration of 220 mg/L and hydraulic retention times of 2.5, 4.5, 8.5 and 4.5 hr, respectively (Ghavipanjeh and Shayagen, 2004). The COD removal percentage was always below 60% and the average removal was in the range of 30-40%. Petroleum refinery wastewater was treated in a UASB reactor operated at 48 hr HRT and influent COD 500 mg/L at a constant OLR of 0.4 kg/m^3·d and the COD removal was 81%. The biogas production rate was 559 mL/hr at HRT of 40 hr and an influent COD of 1000 mg/L; it was noted that the rate of biogas production increased when HRT increased (Rastegar et al., 2011).

2.7 Multi-Stage Biological Process

In recent decades, many studies investigated the effect of wastewater discharged without sufficient treatment with regards to phosphorus and nitrate nitrogen. The need for ammonia nitrogen removal (nitrification) in wastewater treatment arises from water quality concerns over the effect of ammonia nitrogen on receiving water as it results in depletion of dissolved oxygen (DO) and cause toxicity to aquatic life (Metcalf and Eddy, 2003). Nitrate-nitrogen is removed through biological reduction of nitrate to nitric oxide, nitrous oxide and nitrogen gas in a process termed denitrification (Metcalf and Eddy, 2003). Nitrogen and phosphorus discharged to receiving waters can result in eutrophication as these nutrients can accelerate the growth of algae and phytoplankton.

Various biological treatment processes have been proposed to reduce the nutrients concentration in the final effluent discharged to water bodies. Biological nitrogen removal (BNR) process and biological phosphorus removal (BPR) process are combined in multi-stage biological process to achieve the nutrient removal which could be achieved by the alternate phases of anaerobiosis and aerobiosis, and this phenomenon is used in nutrient removal (Brett et al., 1997).

Multi-stage biological reactor employ anaerobic condition followed by anoxic and aerobic, and works on the basis of biological COD, N and P removal which is achieved by manipulating three sets of biochemical reactions; nitrification, denitrification and biological excess phosphorus removal processes (Oldham and Rabinowitz, 2002). Although anaerobic, anoxic and aerobic treatment conditions all have degradation limitations, but when combined as one process would enhance the degradation for a wide range of pollutants in a single process (Perri, 1997). These processes are applied widely in wastewater treatment plants, their advantages as reported by Metcalf and Eddy (2003) and Jiang et al. (2012) are:

    a. high efficiency of pollutant removal,

    b. stable performance,

    c. ability to stand shock loading,

    d. phosphorous removal,

    e. nitrification and denitrification,

    f. the alkalinity produced in preanoxic process by denitrification is made available to offset the alkalinity depleted by nitrification, almost half of the alkalinity used for nitrification can be provided by preanoxic,

    g. recovery of alkalinity reduces the amount of alkalinity that have to be added at significant cost to maintain an acceptable pH for the nitrification process,

    h. aeration energy savings,

    i. the ability to produce a sludge that settles well,

    j. by using nitrate to oxidize influent BOD, the preanoxic process requires less oxygen for aeration, and

    k. preanoxic process eliminate the cost of methanol addition.

Current configurations of multi-stage biological processes are varying in term of the number of stages, the nature and location of recycles and the operation of the process (Group et al., 2010). A number of activated sludge related processes have been developed, as described below.

A. University of Cape Town (UCT) Process

The UCT process was developed at the University of Cape Town and is hence called the UCT process (Brett et al., 1997) and commercialized in the 1980s and operating up to date (Morse et al., 1998). The feature and detail of the process are described in Figure 2.1. Recycled activated sludge from clarifier and aeration basin passes through anoxic basin prior to entering anaerobic basin for residual NO_3^- removal; thus, provide an additional barrier to the entry of NO_3^- into the anaerobic basin. In fact, the finding that the removal efficiency of anaerobic stage could be negatively affected by nitrate-nitrogen entering the anaerobic stage, this finding led to the development of the UCT process (Wang et al., 2010). Problems associated with the UCT process is related to process control as recycling must be carefully controlled to just under load the primary anoxic basin with nitrate to avoid a nitrate discharge to the anaerobic basin. Under full-scale operation, such careful control of recycling is not possible due to uncertainty of the actual concentrations.
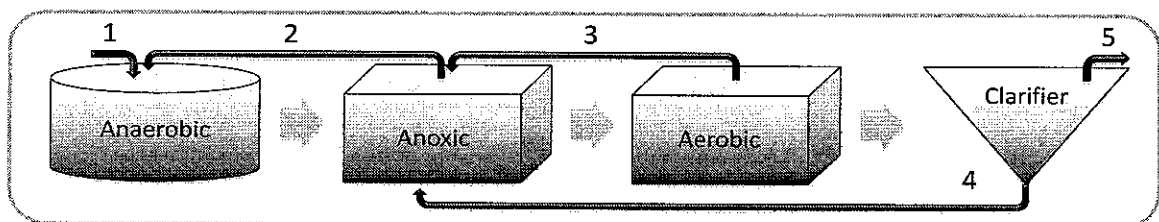
Figure 2.1: Schematic diagram of the UCT process

(1. Influent, 2. Recycle to anaerobic, 3. Recycle to anoxic, 4. Sludge recycle to anoxic, 5. Effluent).

B. Virginia Initiative Plant (VIP) Process

The VIP process was developed in the 1980s (Jeyanayagam, 1997) with multiple complete mix cells for the anaerobic, anoxic and aerobic treatment basins as shown in Figure 2.2. It is similar to the UCT process, but the anoxic basin is baffled into two or more sections to increase the rate of reaction in the first section, thereby firmly establishing the desired anaerobic and anoxic condition (Group et al., 2010).
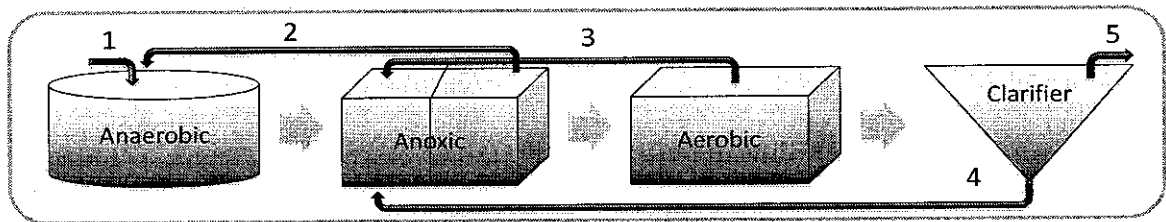
Figure 2.2: Schematic diagram of the VIP process

(1. Influent, 2. Recycle to anaerobic, 3. Recycle to anoxic, 4. Sludge recycle to anoxic, 5. Effluent).

C. Modified UCT (MUCT) Process

It is difficult to achieve the level of denitrification in the anoxic basin required to protect the anaerobic zone from nitrates when the zone is receiving both the recycled activated sludge and high internal nitrate recycle flows (Group et al., 2010). The MUCT is a modified UCT process commercialized in the 1990s (Morse et al., 1998) by having separate anoxic basins which reduce the need to careful control of recycling from aerobic basin as shown in Figure 2.3. The first anoxic zone is designed to reduce only the nitrate nitrogen in the return activated sludge and the second anoxic zone is designed for a much higher quantity of nitrate nitrogen removal as mixed liquor is recycled to it from the nitrification aerobic zone (Brett et al., 1997).
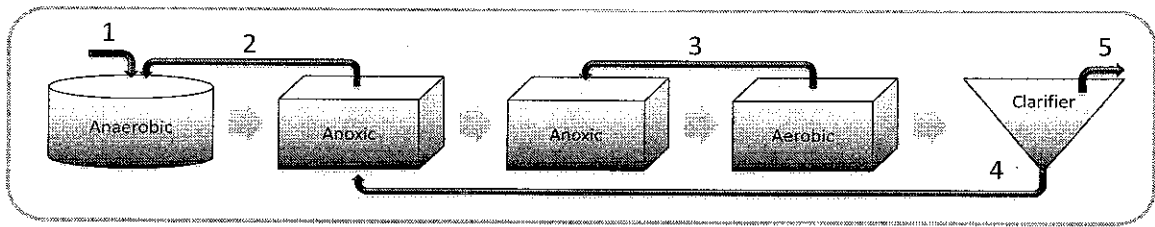
Figure 2.3: Schematic diagram of the MUCT process

(1. Influent, 2. Recycle to anaerobic, 3. Recycle to anoxic, 4. Sludge recycle to anoxic, 5. Effluent).

2.8 Artificial Neural Network

The use of software to simulate existing historical data and predict unknown data based on a model representing the process, help to minimize efforts and creates more data which do not exist. The modeling and simulation of processes have been developed using ever more complex deterministic models, due to the recent evolution of personal computers (Gontarski et al., 2000). Artificial neural network (ANN) is one of these modeling and simulation tools that commonly used in many areas of science and engineering and it represent a set of methods that may be useful in solving the complexity of modeling of complex process (Kasiri et al., 2008).

ANN is a mathematical modeling tool used to simulate complex relationships following a simplified level of the activity of the human brain through a large number of highly interconnected processing elements (neurons). ANN network consists of neurons grouped into layers in relation to each other by parallel connections (Kasiri et al., 2008). Typically, ANN first layer called the input layer with the independent variables, the second layer called the hidden layer to interpret any input-output structure and the last layer called the output layer with dependent variables. The number of input and output neurons represents effectively the number of variables used in the prediction and the number of variables to be predicted, respectively. The desired prediction accuracy is determined by the number of neurons in the hidden layer and considered as a parameter for the optimum structure. ANN has been used in the application of artificial intelligence that has shown quite a promise in engineering, pattern recognition and analysis (Hamed et al., 2004). ANN

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modeling has been widely and effectively used to reproduce experimental data and simulate the process to predict its behavior (Kasiri et al., 2008).

Wastewater treatment systems are complex and non-linear processes which require a non-linear control strategy; whereby artificial neural network is the choice when a large amount of data are available but no reliable model and little knowledge of how the process works (Ward et al., 2008) and (Caraman et al., 2007). Artificial neural network has been used to model existing data and simulate for predicted behavior in many wastewater treatment processes to ease the operation activities. ANN is claimed to have a distinctive advantage over some other nonlinear estimation methods used for bio-processes as they do not require any prior knowledge about the structure of the relationships that exist between important controlling variables (Holubar et al., 2002).

Anaerobic biological treatment of wastewater was modeled based on integrated fuzzy systems and neural network for the simulation and control of complex anaerobic treatment system consisting of anaerobic fluidized bed reactor and upflow anaerobic sludge blanket (Tay and Zhang, 1998). Several feed-forward backpropagation neural networks (FFBP) were trained in order to model, and subsequently control, methane production in four anaerobic continuous stirred tank reactors. The model was able to predict gas production and avoid shock loadings (Holubar et al., 2002). Utilizing a neural network simulation, anaerobic wastewater treatment process has been modeled to define the potentially damaging events that occur during disturbances to an anaerobic digestion. The neural network was capable of rapid recognition of disturbances that in the form of an increase in influent COD concentration and by utilizing data from an on-line bicarbonate alkalinity sensor (Wilcox et al., 1995).

ANN has been used to simulate full working wastewater treatment plant using a model that was developed using laboratory data for ten months (Hamed et al., 2004). Modeling of this wastewater treatment process used a configuration with tangent sigmoid activation function for the input and hidden layers, while the linear activation function was used as the output activation function, resulted in R^2 values ranged from 0.63 to 0.81 for BOD, and from 0.45 to 0.65 for SS. Using the same mentioned

configuration, COD removal was modeled using ANN in a wastewater treatment process for the prediction and simulation of degradation (Elmolla et al., 2010). The configuration of the backpropagation neural network with 14 neurons and Levenberg–Marquardt backpropagation training algorithm (TRAINLM) predicted the actual experimental results with correlation coefficient (R^2) of 0.997 and MSE of 0.000376.

Optimum results derived from artificial neural networks software should be able to generalize the pattern of the data that used to train the model and not over trained (over-fitting problem) when the R^2 values from testing set are not similar to R^2 from training set (Jeon and University, 2007). The root mean square error (RMSE) is a measure of skill and is computed from the difference between the predictions and the measurements whereby, the larger the RMSE, the poorer is the forecast (Benestad et al., 2008). Variance accounted for (VAF) is another performance parameter where maximum value is targeted and computed from the vector of expected outputs (collecting successive time-varying values) and the vector of NN's outputs (Beirao et al., 2007). The correlation coefficient (R^2) has a value between 0 and 1; when it is close to 1, it implies that there is perfect linear correlation; when close to 0, it indicates no correlation (Jeon and University, 2007). The mean absolute percentage error (MAPE) evaluates the total estimation error, because it is dimensionless and unaffected by the number of observation, it provides a good measure of the total variation between the observed and estimated values, whereby, the lowest MAPE score is recommended. MAPE is computed by first determining the deviation between the observed and estimated values. The deviations are then divided by the observed values and multiplied by 100 to give the percentage error. Negative signs are dropped to yield absolute percentage errors. The absolute percentage errors are then summed and divided by the number of observations to yield the mean absolute percentage error (Klosterman, 1990).

One of the important steps to gain best model is normalization of data to make the variance of all components more homogeneous whereby, when some vector components have a variance that is significantly higher than the variance of other components, those components will dominate; hence, data normalizations are

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typically performed on data to reduce the variance of the vector components (Beccali et al., 2004).

2.9 Originality and Significance of the Study

Treatment of petroleum refinery wastewater of wide range of strength in terms of COD from 700 mg/L to over 7000 mg/L by multi-stage biological treatment system has not been reported. Also, this combination of different biological conditions (anaerobic, anoxic and aerobic) in a single multi-stage biological reactor has not been reported.

2.10 Summary

The literature on effluent standards, petroleum refinery wastewater constituent and treatment, biological treatment system and reactions are presented. The chapter also reviews briefly on sequencing batch reactor, up-flow anaerobic sludge blanket reactor, multi-stage biological process and artificial neural network and its application to wastewater treatment.

CHAPTER 3

METHODOLOGY

3.0 Chapter Overview

Sampling and characteristics of PRW is described. The experimental study was conducted in four main phases as follows:

- Phase 1: Biodegradability Batch Study: This study was performed to determine the degradation percentage and the feasibility of treating petroleum refinery wastewater and the overall durations for start up and maximum degradation. This study involved aerobic and anaerobic batch treatment for single run over 28 days.

- Phase 2: Sequencing Batch Reactor Treatability Study. SBR was used to investigate the treatability of the petroleum refinery wastewater in two stages.

  o Three SBR configurations. Aerobic SBR, anaerobic-aerobic SBR and aerobic mixed influent SBR were operated in parallel to determine the most suitable configuration out of the three.

  o SBR Monitoring Study. Monitoring for different parameters on a single operation cycle was carried out to identify the optimum reaction time.

- Phase 3: Three-Stage SBR Study. Anaerobic-anoxic-aerobic SBR train study investigates on the three stages SBR train configuration feasibility to achieve efficient treatment.

o BTEX treatment and monitoring study. To monitor BTEX as the volatile component under the three stages SBR to determine the degree of degradation.

- Phase 4: Integrated Multi-Stage Biological Reactor. Two continuous-flow anaerobic-anoxic-aerobic reactors operated in parallel to treat petroleum refinery wastewater in two steps.

  o Determination of multi-stage biological reactor performance under different loads.

  o Modeling and simulation of multi-stage biological reactor performance under different loads using ANN mathematical software tool.

3.1 Sampling and Characteristics of Petroleum Refinery Wastewater

The wastewater for this study was collected from a local petroleum refinery facility that discharges its treated effluent to the sea. The refinery processes the Malaysian light sweet crude oil and also includes a condensate splitter unit for naphtha condensates. The effluent generated from the refinery is treated in an effluent treatment system (ETS). Prior to that, the wastewater generated is stored in two equalization balancing tanks. The first tank, high strength equalization tank (HSEQ), receives its contents from the slop tank and from recycled off-site slops. The second tank, final equalization tank (FEQ), receives the HSEQ effluent combined with the wastewater from caustic neutralization vessel, sour water stripper, oily contaminated drain (OCD) collection and process drain collection. The discharge from the refinery is then treated in the dedicated ETS.

The ETS consists of a balancing tank, an induced gas flotation unit (IGF), a BTEX stripper, an accidental contaminated drain (ACD) effluent pond, a dissolved air flotation unit (DAF) and a final pond. The effluent from the plant and ETS configuration at the time of this study is illustrated in Figure 3.1 (PPTSB, 2009). The discharge from the FEQ to the ETS is estimated to be 216 m^3/d, while the ACD

receives addition discharge from the boiler and utilities plant effluent in addition to storm water and surface run-off at the rate of 120 m³/d.
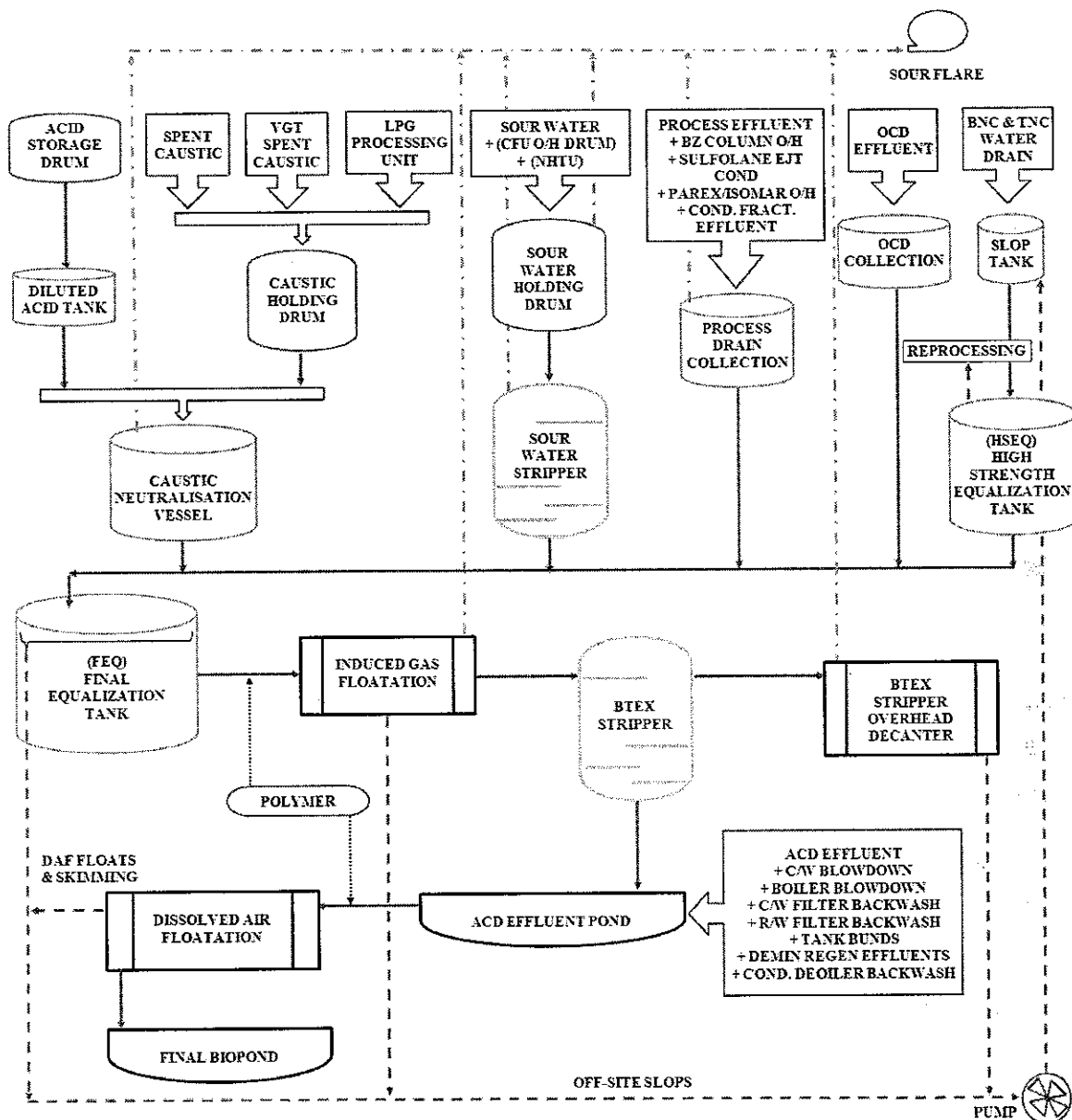
Figure 3.1: Current wastewater generation sources and treatment process.

Several site visits were made to the petroleum refinery facility that was selected for the study. PRW was collected from the final equalization balancing tank (FEQ) that receives the effluent raw wastewater prior to treatment from the slop tank and the

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recycled off-site slops, combined with the wastewater from caustic neutralization vessel, sour water stripper, oily contaminated drain collection and process drain collection as in Figure 3.1.

The wastewater for the entire study was collected from the FEQ and the pH of the wastewater was in the range of pH 6-7. The wastewater was stored in the cold room (4°C) prior to testing and treatment. The average wastewater COD concentration for PRW was found to be 712 mg/L for the first sampling batch which was used for the biodegradability study. There were different batches of wastewater collected from the petroleum refinery facility during this study with different characteristics as shown in Table 3.1 and described in each section.

Table 3.1: Petroleum refinery wastewater batches

Parameter	Unit	Batch 2 (Treatability Study)	Batch 3 (Three-Stage SBR)	Batch 4 (Multi-Stage Biological Reactor)
pH	-	6	8.13	8.48
COD	mg/L	1066	1260	7896
Ammonia-N	mg/L	7.8	5.94	13.5
Nitrate-N	mg/L	0.47	6.0	2.23
Sulfate	mg/L	22.6	12	-
Phosphorous	mg/L	5	4.77	10.2
TSS	mg/L	189.9	190	-
VSS	mg/L	65	65	-
TOC	mg/L	359.74	360	-
TN	mg/L	23.1	-	-
$BOD_{5\ d,\ 20°C}$	mg/L	390	350	3378
Alkalinity	mg/L	-	3188	990
TKN	mg/L	-	70	40.6
VFA	mg/L	-	497	198
Benzene	mg/L	-	17.919	106.709
Toluene	mg/L	-	1.983	106.045
Ethyl benzene	mg/L	-	0.024	2.749
m-Xylene	mg/L	-	0.383	5.0625
p-Xylene	mg/L	-	0.370	5.0625
o-Xylene	mg/L	-	0.273	3.017
Phenol	mg/L	-	25.1	14.458

The average characteristics of the untreated wastewater in the final equalization tank during normal operation at the local petroleum refinery facility are shown in Table 3.2, while the characteristic at the time of collection is described in each study.

Table 3.2: Petroleum refinery wastewater characteristics

Parameter	Unit	Final Equalization Tank (FEQ)	
		1st 12 hr*	2nd 12 hr*
pH	-	6.5	6.7
BOD$_{5\ d,\ 20°C}$	mg/L	1482	1303
COD	mg/L	2781	2933
Suspended solids	mg/L	32	30
Mercury (Hg)	mg/L	<0.001	<0.001
Cadmium (Cd)	mg/L	<0.001	<0.001
Chromium, Hexavalent (Cr^{6+})	mg/L	<0.05	0.08
Copper (Cu)	mg/L	<0.01	<0.01
Arsenic (As)	mg/L	<0.05	<0.05
Cyanide (Cn)	mg/L	<0.05	<0.05
Lead (Pb)	mg/L	<0.05	<0.05
Chromium, Trivalent (Cr^{3+})	mg/L	<0.05	<0.05
Manganese (Mn)	mg/L	0.33	0.32
Nickel (Ni)	mg/L	0.01	<0.01
Tin (Sn)	mg/L	<0.1	<0.1
Zinc (Z n)	mg/L	0.21	0.18
Boron (B)	mg/L	<0.2	<0.2
Iron (Fe)	mg/L	11.9	8.8
Phenol	mg/L	22	28.2
Free Chlorine (Cl)	mg/L	<0.1	<0.1
Sulphide	mg/L	0.047	0.027
Oil and Grease	mg/L	40	23.3
Total Dissolved Solid	mg/L	1516.7	1343.3
Chloride	mg/L	482.7	458
Alkalinity	mg/L	159.7	181.7
Benzene	mg/L	29.5	31.4
Toluene	mg/L	16.5	18.2
Ethyl benzene	mg/L	35.8	41.0
Xylene	mg/L	18.6	17.8

*Average concentrations as adopted from local petroleum refinery unpublished data (PPTSB, 2009).

3.2 Phase 1: Biodegradability Batch Study

This study was conducted to determine the biodegradability of petroleum refinery wastewater in a batch single run for 28 days in aerobic and anaerobic condition following Zahn-Wellens/EMPA test (EPA, 1998).

3.2.1 Experimental Procedure

Three cylindrical glass reactors each with a volume of 2 L, equipped with a magnetic stirrer were used. Two reactors were operated in aerobic mode, while the third was in anaerobic mode. A supply of compressed air (for the aerobic reactors only) was passed through a filter delivering air free from dust, oil, and organic impurities at adjustable rate to maintain a minimum concentration of dissolved oxygen of 2 mg/L. Activated sludge from a sewage treatment plant was used as seed biomass in the reactors.

In each of the reactors, a mixture containing the wastewater, mineral nutrients, and a seed biomass in aqueous medium was agitated at 20-25°C in diffused light for 28 days. Each of the reactors consisted of 500 mL of wastewater, 500 mL of inoculum and 1 L of mineral medium solution. The blank control (Reactor 2) consisted of the seed biomass and mineral nutrients without wastewater which was replaced with mineral nutrient. The three reactors were operated in parallel as in following Figure 3.2, 3.3 and Table 3.3. The petroleum refinery wastewater was collected from the final equalization tank (FEQ) and used in this study and the average COD concentration for PRW was found to be 712 mg/L.
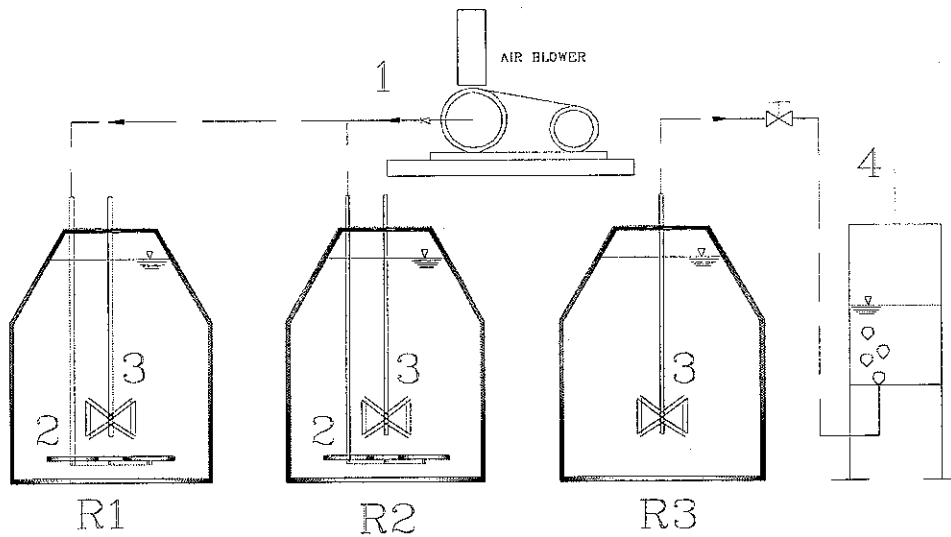
Figure 3.2: Schematic diagram of the biodegradability experimental set-up

(1. Compressed air, 2. Diffuser, 3. Stirrer, 4. Vent).

Table 3.3: Biodegradability batch study

Reactor	Influent	Type	Mode	Content
R1	PRW	Aerobic	Aeration and mixing	Inoculum and wastewater
R2	Blank	Aerobic	Aeration and mixing	Inoculum blank
R3	PRW	Anaerobic	mixing	Inoculum and wastewater
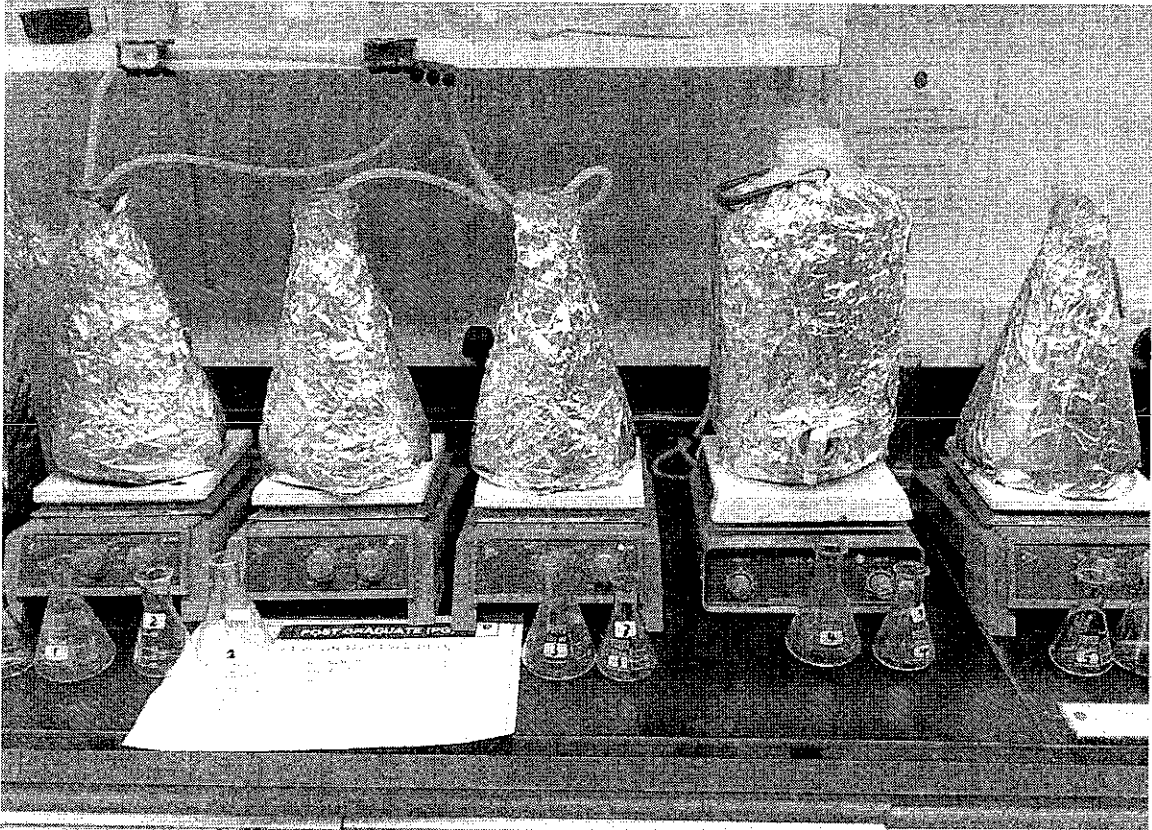
Figure 3.3: The batch reactors for biodegradability study.

The mixture consists of the biomass (seed sludge) and mineral nutrients (calcium chloride, ferric chloride, magnesium sulfate, and potassium phosphate dibasic). The mineral medium was prepared by dissolving the nutrients in distilled water. One liter of the mineral medium solution was then fed to each of the three reactors. The mineral medium solution was also used to top up to replace losses due to wastewater evaporation and sampling.

The biodegradation process was monitored by determining the average triplicate soluble chemical oxygen demand (sCOD) in filtered batch samples taken (15 mL) at daily intervals of 24 hr for 28 days. The ratio of eliminated COD, corrected for the blank, after each interval, to the initial COD value was expressed as the percent biodegradation at the sampling time. The percent biodegradation was then plotted against time to give the biodegradation curve.

3.2.2 Calculation for Degradation in the form of COD

Degradation percentage was calculated at time t from the following:

$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}}\right] \times 100 \tag{3.1}$$

where, D_t is the percent degradation at time t; C_A is the concentration of COD in the test suspension measured after 3 hr $\pm$ 30 min of incubation and expressed as mg/L; C_t is the mean concentration of COD in the test suspension at time t and expressed as mg/L; C_{BA} is the mean concentration of COD in the blanks measured after 3 hr $\pm$ 30 min of incubation and expressed as mg/L; C_B is the mean concentration of COD in the blanks at time t and expressed as mg/L.

3.3 Phase 2: Sequencing Batch Reactor Treatability Study

SBR was used to investigate the treatability of the petroleum refinery wastewater in two stages. In the first stage, the treatability of petroleum refinery wastewater was conducted in three SBR configurations (aerobic SBR, anaerobic-aerobic SBR and aerobic mixed influent SBR), operated in parallel to determine the most suitable configuration. The second stage was the SBR monitoring study whereby the three SBR configurations were monitored on a single operation cycle to determine the optimum reaction time.

3.3.1 Three SBR Configurations Treatability Study Experimental Procedure

In this stage, three different parallel batch configurations of sequencing batch reactors were set up to treat the PRW. The configurations included aerobic mode SBR to treat PRW, coupled anaerobic-aerobic mode SBR to treat PRW and aerobic mode SBR to treat PRW mixed with domestic wastewater as shown in the following Table 3.4 and Figures 3.4 and 3.5. All the four 3-L reactors (2 L sample volume) each equipped with a mechanical stirrer were operated in a 24 hr cycle. A supply of compressed air was provided for the reactors operated in the aerobic mode. One liter of activated

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sludge biomass from a sewage treatment plant was used as seed in all the reactors in treating 2 L of the wastewater samples.

Table 3.4: SBR treatability study

Reactors	Mode	Influent	Operation Cycle (hr)				
			Feed	Mix	Aerate	Settle	Decant
R1	Aerobic	PRW	0.5	21		2	0.5
R2	Anaerobic	PRW	0.5	21	None	2	0.5
R3	Aerobic	R2	0.5	21		2	0.5
R4	Aerobic	PRW mixed	0.5	21		2	0.5
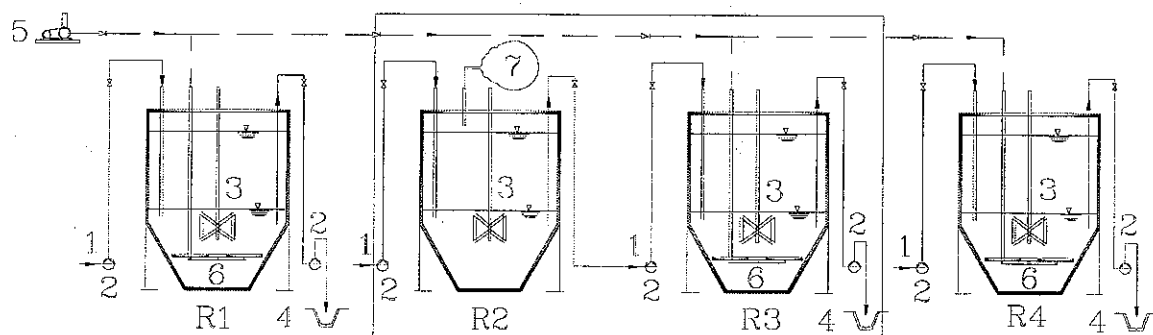
Figure 3.4: Schematic diagram of the SBR experimental set-up

(1. influent point, 2. peristaltic pump, 3. stirrer, 4. treated effluent, 5. air pump, 6. diffuser, 7. vent).
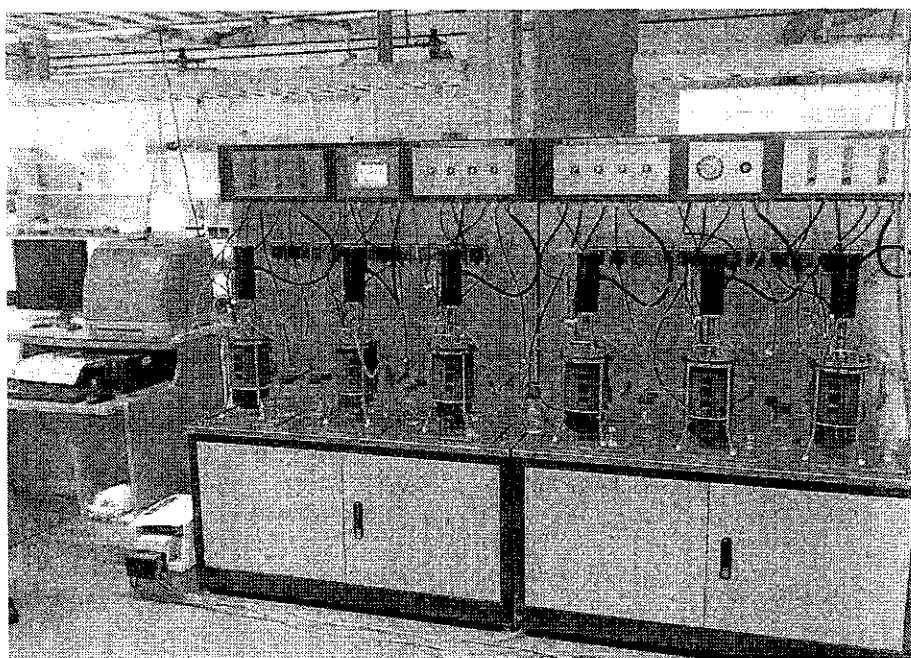
Figure 3.5: Sequencing batch reactor (SBR) systems set up to treat the petroleum refinery wastewater.

Reactors R1, R3 and R4 were operated in the aerobic mode. Feeding time, aeration period, settling and decanting was set at 30 min, 21 hr, 2 hr, and 30 min, respectively. Two liters of wastewater was decanted at the end of the cycle period. The reactors were then fed with fresh 2-L of wastewater for the next batch cycle. Parameter measurements were conducted on the decanted liquid in triplicate at the end of the 24 hr cycle.

Reactor R2 was operated in the anaerobic mode treating PRW. The feeding time, mixing period, settling and decanting was set at 30 min, 21 hr, 2 hr, and 30 min, respectively. Effluent from reactor R2 (treating PRW) was fed into reactor R3 which was operated in the aerobic mode. Reactor R4 treated wastewater from PRW mixed with domestic wastewater.

3.3.2 SBR Monitoring Study Experimental Procedure

In this stage, the three SBR configurations experiment in Section 3.3.1 were repeated in treating wastewater from PRW to monitor different parameters on a single

operation cycle consisted of 24 hr duration as shown in Table 3.5. This monitoring was carried out to identify the optimum reaction time. This study was carried out by sampling over 24 hr and later sampling intervals were shortened to 7 hr of the cycle. Samples were collected, filtered (for soluble) and measured for COD, sCOD, ammonia, nitrate, MLSS and MLVSS at regular intervals.

Table 3.5: SBR monitoring study

Reactor	Configuration	Mode	Influent
R1	Aerobic	Aerobic	PRW
R2	Coupled	Anaerobic	PRW
R3		Aerobic	Reactor 2 effluent
R4	Aerobic	Aerobic	PRW mixed with domestic

3.4 Phase 3: Three-Stage SBR Study

In phase 3, the petroleum refinery wastewater was treated in a Three-Stage SBR train which consisted of anaerobic-anoxic-aerobic mode, each operated as SBR. In this study, BTEX was also monitored as well as the other parameters such as COD, ammonia, nitrate, MLSS and MLVSS. The three modes were operated in separate reactors, whereby the first SBR reactor (R1) was operated in anaerobic mode and received the raw petroleum refinery wastewater, while the second SBR reactor (R2) was operated in anoxic mode and received the anaerobic effluent and fifty percent of the aerobic effluent, and the third SBR reactor (R3) was operated in aerobic mode and received the anoxic effluent. The mode of operation for the Three-Stage SBR is summarized in Table 3.6.

Table 3.6: Three-Stage SBR treatability study

Reactor	Influent	Type	Recycle
R1	Raw PRW	Anaerobic (mixing)	n/a
R2	R1 effluent	Anoxic (mixing)	50% R3
R3	R2 effluent	Aerobic (aeration and mixing)	n/a

All reactors were operated in 24 hr batch cycle. The feeding time, mixing period, settling and decanting was set at 30 min, 21 hr, 2 hr, and 30 min, respectively as shown in Table 3.7. The average mixed liquor suspended solids (MLSS) for reactor R1, reactor R2, and reactor R3 were 1940, 617, and 2820 mg/L respectively. The average mixed liquor volatile suspended solids (MLVSS) for the reactors were 1265, 348 and 1836 mg/L respectively.

Table 3.7: Three-Stage SBR cycle

Reactor	Mode	Influent	Operation Cycle (hr)				
			Feed	Mix	Aerate	Settle	Decant
R1	Anaerobic	PRW	0.5	21	None	2	0.5
R2	Anoxic	R1 and R3	0.5	21	None	2	0.5
R3	Aerobic	PRW mixed	0.5	21		2	0.5

The anaerobic reactor effective volume was 2.2 L, feeding was 1.4 L/d, and sludge zone was 0.8 L. Gas was collected by gas-liquid displacement in a column filled with alkaline solution containing 5% (w/v) NaOH to absorb carbon dioxide and thymol blue as an indicator of absorption capacity of the solution (Zakarya et al., 2008). The collected gas was then used to replace the decanted volume of the treated wastewater during discharge phase and before filling. As all the three reactors were operated as SBR and automated by timers to control the cycles, the volume of all reactors were the same and only half of the effluent from the anaerobic and aerobic reactors were used as influent to the anoxic reactor. The anoxic reactor volume was 1.9 L, feeding was 1.4 L/d, and sludge zone was 0.5 L. Gas was collected by air bag, and the collected gas was then used to replace the decanted volume of the treated wastewater during discharge in the decanting phase and before filling phase. The aerobic reactor volume was 1.9 L, feeding volume was 1.4 L/d, and sludge zone volume was 0.5 L.

A supply of air was passed through a stone diffuser, and the flowrate was adjusted to the minimum to avoid stripping of the volatile compounds. The mixtures

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containing the wastewater and sludge was agitated at room temperature (24-29 °C) in diffused light as in Figure 3.6 and Figure 3.7.
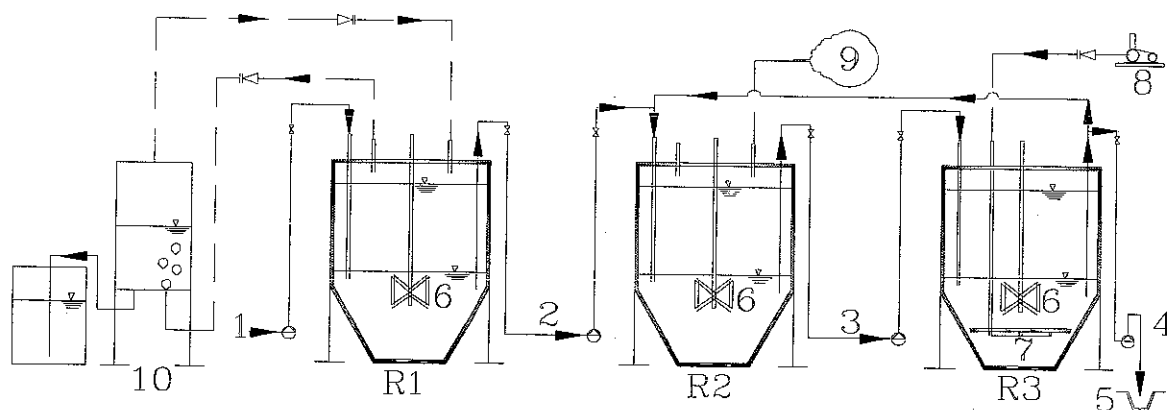
Figure 3.6: Schematic diagram of the Three-Stage SBR experimental set-up

(1. Influent, 2. R1 effluent, 3. R2 effluent, 4. Final effluent, 5. Discharge, 6. Stirrer, 7. Diffuser, 8. Air pump, 9. Air bag, 10. Gas collection set-up).
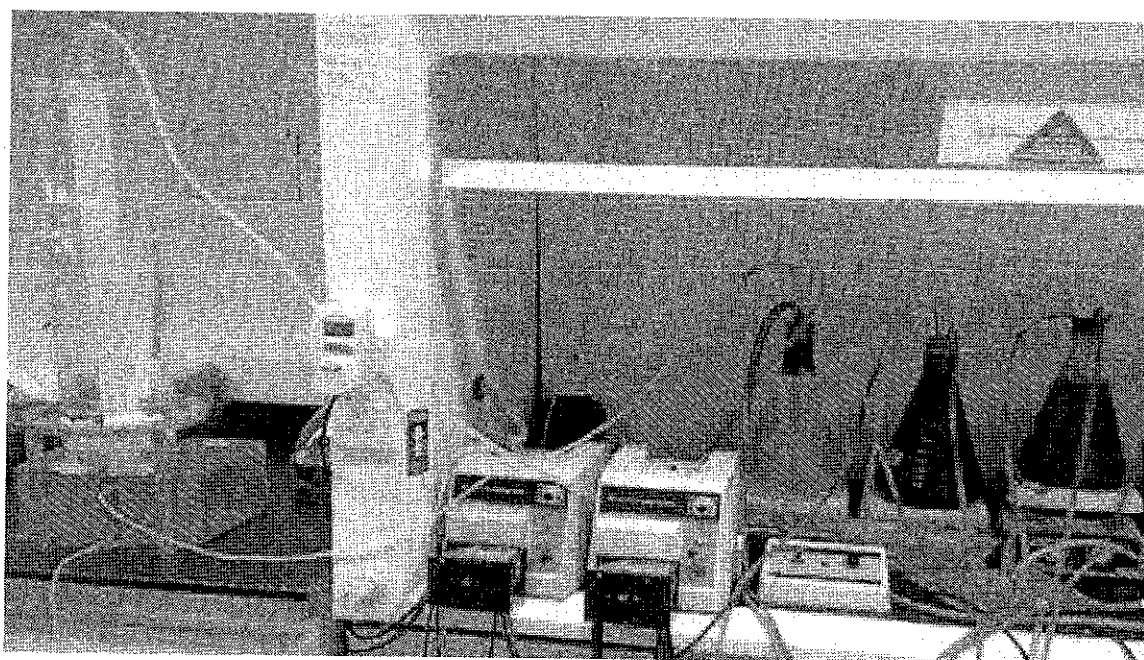
Figure 3.7: Three-Stage SBR, anaerobic, anoxic and aerobic reactors.

This study involved monitoring volatile components under the anaerobic, anoxic and aerobic stages of the SBR. BTEX group of volatile compounds were monitored throughout the treatment system to identify the degradation percentage in the three stages of treatment process. Samples were collected and analyzed for BTEX using

gas chromatography-mass spectrometry (GC-MS) with selected ion method (SIM) and the sample were injected as liquid to purge and trap (P&T) equipment which was necessary to concentrate the sample in gas form prior to be injected to the GC.

3.5 Phase 4: Multi-Stage (Anaerobic, Anoxic and Aerobic) Biological Reactor Study

In this phase, an integrated multi-stage biological reactor (MSBR) that consisted of anaerobic, anoxic and aerobic compartments was developed and operated in continuous flow in two parallel reactors. Determination of reactor performance under different loads was carried out. Modeling and simulation of reactor performance using mathematical software tool (Neural Network in MATLAB, R2009a) was performed to predict the reactor behavior.

3.5.1 Multi-Stage Biological Reactor (MSBR)

An integrated compact biological reactor that consisted of three stages biological process was developed and fabricated for treatment of petroleum refinery wastewater. The three stage biological process consisted of anaerobic, anoxic and aerobic zones within a single unit to accommodate effective treatment.

Anaerobic treatment is important in the first stage to break down the major compounds and prevent volatilization. Hence, the developed reactor received the influent in the anaerobic compartment which operated on the basis of up-flow anaerobic sludge blanket (UASB) reactor. Energy recovery in the form of methane is an advantage of this step. The anaerobic compartment is the tallest and in the core of the reactor to provide gravity flow to the subsequent compartments and reduces the piping and area requirements. Wastewater influent flowrate to the anaerobic chamber was 1.4 L/d; equivalent to 1.69 d HRT. Anaerobic reactor volume, diameter and height were 2.36 L, 94 mm and 430 mm, respectively. The anaerobic reactor was operated with an internal effluent recycle ratio of 1:1 to well distribute the influent and provide better mixing.

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Then the wastewater was released to the anoxic denitrification compartment which was designed to remove recalcitrant compounds. Anoxic stage removes refractory compounds and minimizes the nutrient in the final discharge to eliminate harmful effects on the environment. This compartment is baffled and higher than the subsequent compartment to provide gravity flow of the water and reduces the cost. The anoxic reactor was operated with recycled flow from the aerobic effluent and the biomass was recycled internally. Anaerobic effluent combined with recycled aerobic effluent enters the anoxic zone as influent with joint flowrate of 22.4 L/d while anoxic zone volume was 4.14 L and the HRT was 0.18 d.

Aerobic nitrification stage polishes the wastewater before it goes to the clarifier to separate the biomass from the treated final effluent. Anoxic effluent enter aerobic zone which was of 6.64 L volume and the HRT was 0.3 d. Aerobic effluent goes through an external clarifier (2.1 L volume) to separate the sludge from the liquid before it gets discharged. The aerobic reactor received recycled biomass from the clarifier.

Recycle pump transfers back a portion of the aerobic effluent to the anoxic compartment. The reactor has a gas collection system that works on the basis of water displacement for the collection of biogas produced in the anaerobic compartment. The following Figure 3.8 shows the details of the reactor and water flow.

In the startup period, each of the zones in the both reactors were analyzed for COD, ammonia, nitrate, MLSS, MLVSS, pH and dissolved oxygen (DO) for the influent and effluent samples following the standard methods until reaching steady state condition. Then, different loadings were applied to the reactors.
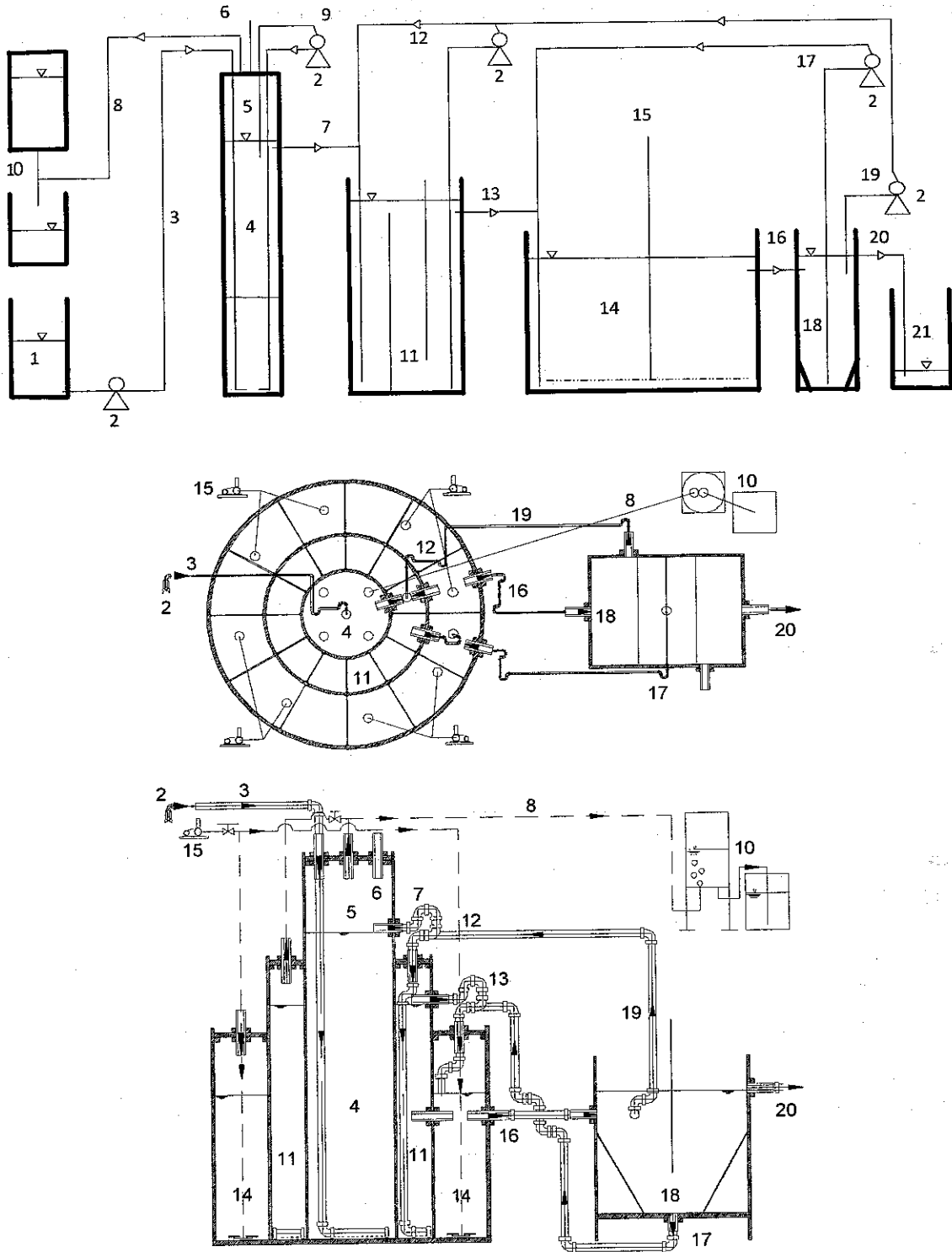
Figure 3.8: Schematic diagram, top view and side section view of the MSBR

1.Influent tank, 2.Pump, 3.Influent, 4.Anaerobic compartment, 5.Gas zone, 6.Sampling point, 7.Anaerobic effluent, 8.Gas line, 9.Internal recycle, 10.Gas collection, 11.Anoxic compartment, 12.Internal recycle, 13.Anoxic effluent, 14.Aerobic compartment, 15. Aeration, 16.Aerobic effluent, 17.Sludge recycle, 18.Clarifier, 19.Recycle to anoxic tank, 20.Effluent, 21.Effluent tank.

3.5.2 Multi-Stage Biological Reactor (MSBR) Performance Determination Procedure

A loading test study for the treatment process was carried out using the MSBR by applying different organic loading rates (OLR). OLR is equivalent to the amount of organic matter to be stabilized by microorganisms (Wang et al., 2010). The study results were used in the performance prediction and optimization of the treatment of petroleum refinery wastewater. This was necessary to correlate the biomass growth rate and substrate utilization rate to the biomass concentration and the specific growth rate and the specific substrate utilization rate, which is dependent on the substrate concentration. Two reactors (made of transparent Perspex material), MSBR A and MSBR B were used for this experiment as shown in Figure 3.9.
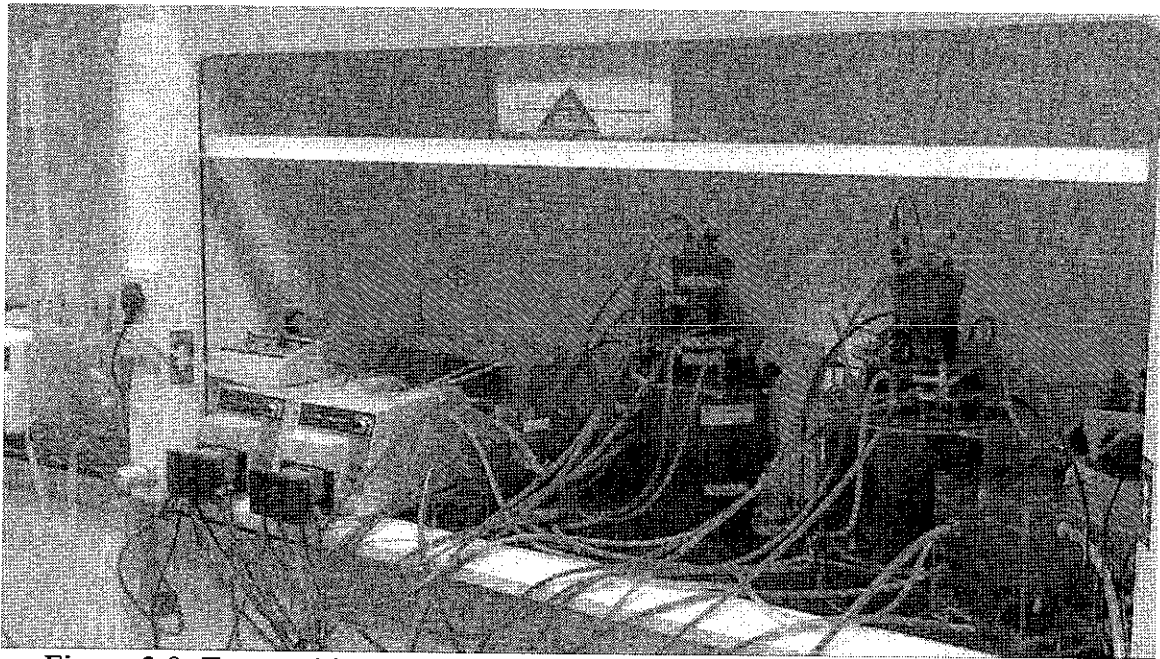
Figure 3.9: Two multi-stage biological reactors inside a fume hood in the lab in operation during experimental work.

The substrate was varied in six different organic loading by dilution with distilled water mixed with BOD mineral nutrients (calcium chloride, ferric chloride, magnesium sulfate, and potassium phosphate dibasic). Six different influent organic loadings were applied at a constant flowrate of 1.4 L/day, three loadings for each

reactor operating in parallel at room temperature (25-29°C). Both reactors were operated at the respective organic loadings until steady state conditions were achieved.

The influent was pumped continuously to the system by a peristaltic pump, while the effluent exit the anaerobic (UASB) reactor through a water-seal tube to prevent any atmospheric air from entering the system. The anaerobic effluent flowed to the anoxic reactor and the anoxic effluent flowed to the aerobic reactor. The gas was collected by water displacement method and the volume was monitored every 24 hr for actual total gas production. Gas samples were collected and analyzed for gas composition for methane and carbon dioxide by using gas chromatograph with flame ionization detector. Theoretical methane production rate is estimated at 35°C as 0.4 L CH_4/g COD (Metcalf and Eddy, 2003) and was corrected for average 27°C operating temperature as follows:

$$M_c = M_t \frac{T_{ac}}{T_t}$$

(3.2)

where, M_c is the corrected methane production rate and was calculated and found to be 0.39 L CH_4/g COD, M_t is the theoretical methane production rate; T_{ac} is the actual temperature in Kelvin (273.15 + T°C); T_t is the operating temperature in Kelvin (273.15 + T°C).

The theoretical methane gas production volume per day was estimated (Metcalf and Eddy, 2003) from the following:

$$M_v = 0.39 \times \left(S - (1.42 \times 0.08 \times S)\right) \times Q$$

(3.3)

where, M_v is the methane volume in L; S is the COD removed in anaerobic treatment stage in g/L; solids yield by 0.08 g VSS / g COD removed; the COD of the cells is equal to 1.42 times the concentration of cells as VSS; Q is the flowrate in L/d. The theoretical total gas production was estimated by dividing the theoretical calculated methane by the methane percentage.

The anaerobic seed biomass was obtained from a local petroleum refinery site and palm oil mill effluent treatment plant for better acclimatization and sufficient

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concentration. The anoxic and aerobic seed biomass was obtained from a local sewage treatment plant and petroleum refinery site. The hydraulic retention time (HRT) was maintained at 40, 4 and 7 hr for anaerobic, anoxic and aerobic reactors respectively.

After six different loads were applied successfully to the reactors, the two parallel MSBR reactors were in steady state operation with diluted influent prior to introducing the full actual real load without dilution. MSBR A was operated with 0.26 kg COD/m^3·d while MSBR B with 0.74 kg COD/m^3·d. The reactors were in steady state condition before the feeding of raw influent to the system which was 0.77 kg COD/m^3·d. Volumetric organic loading rates (L_{org}) for each stage were calculated based on the flowrate to each stage and the volume of that stage. For the overall L_{org} calculation, the MSBR volume was consider as one unit and the flowrate was 1.4 L/d. Specific substrate removal rates were also followed these considerations; furthermore, the biomass concentration for MSBR was determined as mass (mg) in each stage then divided by MSBR volume. All six loadings and the full load to both MSBR reactors are described in Table 3.8.

Table 3.8: Multi-stage biological reactor loadings

Operation days	Loads		Average COD loading (kg/m^3·d)		Average COD concentration (mg/L)	
			MSBR			
	A	B	A	B	A	B
0 - 60	1	3	0.10	0.22	982	2048
60 - 120	2	5	0.16	0.42	1504	3944
120 - 172	4	6	0.26	0.74	2476	6972
172 - 179	PRW		0.77		7273	

3.6 Multi-stage Biological Reactor Modeling and Simulation

The multi-stage biological reactor monitoring results during different loading were used for modeling for phase 4. Artificial neural network was used as mathematical tool to simulate and predict the pattern of the reactor.

Optimal generalization was targeted from this tool, therefore, Feed-forward backpropagation network type was selected and Levenberg–Marquardt (TRAINLM) backpropagation algorithm (TRAINLM) was used as training function as it is usually able to have smaller mean square error (MSE) compared to other backpropagation algorithms (Elmolla et al., 2010) and has been proved to be the fastest and most robust (Hamed et al., 2004). Batch gradient descent with momentum backpropagation algorithms (LEARNGDM) as adaption learning function was used in this study. The number of neurons has to be determined as it is related to the converging performance of the output error function during the training process. Increasing the number of neurons usually results in a better learning performance, as too few number of neurons limit the ability of the neural network to model the process, but too many number of neurons may result in losing the generalization and learning the noise present in the database used in training (Holubar et al., 2002).

Neural Network in MATLAB (R2009a) software was used with feed-forward backpropagation neural network three layers. There are several activation functions in MATLAB, but few of them were preferable and used in wastewater treatment modeling with low error level (Tezel et al., 2010), namely, sigmoid (hyperbolic tangent and logarithmic) (Hamed et al., 2004) and linear (PURELIN) (Jami et al., 2012). Two configurations were compared to each other, first, with log sigmoid transfer function (LOGSIG) at hidden layer and a linear transfer function (PURELIN) at output layer. Second, with tangent sigmoid transfer function (TANSIG) at hidden layer and a linear transfer function (PURELIN) at output layer. The linear activation function (PURELIN) was used for both configurations for the output neuron since it is appropriate for continuous valued targets (Hamed et al., 2004).

The set of data obtained from the impact of different organic loads in phase 4 was used in the modeling. The data covered approximately 180 days and with 160 entries for input and output. Half of the data were used to train the model and the other half was used for validation. The data were organized by selecting the single entries in term of order as training set and even entries in term of order as validation set.

Normalization of input data was performed by dividing all the input data with the maximum input; this resulted in the data to be in the range of 0 to 1. Output data were normalized by dividing all the output data with the maximum output; this resulted in the data to be in the range between 0 and 1.

Neurons were tested and varied the number of neurons in the range from 5 up to 35 neurons. For better initialization of the model, the model was run 100 times at every neuron tested. The optimum number of neurons of the training set was determined based on:

- Minimum root mean square error (RMSE)

- Maximum variance accounted for (VAF)

- Maximum correlation coefficient (R^2)

- Minimum mean absolute percentage error (MAPE)

3.7   Procedures for Measurement of Parameters

pH, alkalinity, mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solids (MLVSS), biochemical oxygen demand ($BOD_{5 \ d, \ 20°C}$) were determined in accordance with Standard Methods (APHA, 1992). Chemical oxygen demand (COD), volatile fatty acids (VFA), ammonia nitrogen, nitrate nitrogen, phosphorus, were determined by colorimetric method using a HACH DR 2000 spectrophotometer. Other parameters measurement procedures are also detailed as followed:

3.7.1 pH Measurement

pH was measured in samples to determine either it were acid, neutral or alkali. A pH meter (Hach Sension 4) with a pH electrode (Hach platinum series pH electrode model 51910, from Hach company) was used for pH measurement. The pH meter was calibrated with pH 4.0, 7.0 and 10.0 buffers before it was used. 100 mL of wastewater sample was collected in a beaker; pH meter electrode was rinsed with

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distilled water and dried before it was placed in the sample. The pH value was recorded when the display was staple.

3.7.2 Alkalinity Measurement

The alkalinity was measured for wastewater samples to determine its quantitative capacity to neutralize a strong acid to a designated pH. The determination of alkalinity levels at various points in a treatment plant aids understanding and interpretation of the treatment process and management of digesters and biological nutrient removal. The experiment was performed by collecting 50 mL wastewater sample and adding three drops of methyl orange indicator and then the sample was titrated with 0.1 N sulfuric acid (H_2SO_4) until color changed to red. The amount of acid used was determined and total alkalinity concentration was then calculated.

3.7.3 Mixed Liquor Suspended Solid (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) Measurement

Mixed liquor suspended solid (MLSS) and Mixed liquor volatile suspended solids (MLVSS) were determined according to the Standard Methods (APHA, 1992). Glass fiber filter papers (Advantec GC 50, 47mm) were rinsed with distilled water and placed into oven overnight and kept in a desiccator and weighted before been used. Wastewater samples were collected and diluted and filtered in the filter papers. Dried at 103-105°C for 1 hr and placed into desiccator to cool down to room temperature and then weighted. In MLVSS measurement, the filter paper with residue from the MLSS measurement was ignited at 550°C in the furnace (Nabertherm L15/12/P320) and placed into desiccator and then weighted for Fixed and Volatile Solids. Suspended solid (TSS) and volatile suspended solids (VSS) were done using the same procedure.

3.7.4 Sludge Volume Index (SVI) Measurement

Sludge volume index (SVI) is the volume of 1 g of sludge after 30 min of settling (Metcalf and Eddy, 2003), and was determined according to the Standard Methods (APHA, 1992). The SVI (mL/g) was determined by placing a mixed-liquor sample in a 10 mL measuring cylinder and measuring the settled volume after 30 min and the corresponding sample MLSS concentration. The numerical value was computed by multiplying the settled volume with 100 to correct the measurement as mL/L, and then was divided by the MLSS concentration (g/L).

3.7.5 Biochemical Oxygen Demand (BOD$_5$) Measurement

Biochemical oxygen demand (BOD$_5$) was determined by measuring the amount of dissolved oxygen (DO) that used by microorganisms in five days at a constant temperature of 20°C to degrade the organic matter that present in the wastewater sample. BOD$_5$ was measured according to the Standard Methods (APHA, 1992). Wastewater samples were collected and diluted and poured into the 300 mL BOD bottles. Bacterial seed was obtained from a local sewage treatment plant (UTP-STP) and mixed with acclimatized biomass before been added together with aerated distilled water that was prepared overnight with BOD nutrient. Initial DO concentration was measured and bottles were capped and sealed and placed in a refrigerator at 20°C for 5 days. DO initial and final were measured by DO probe that equipped with a stirring mechanism (YSI 5000 dissolved oxygen meter). Results were calculated for the DO difference divided by sample dilution and corrected with the seed and blank and multiplied by the dilution factor.

3.7.6 Chemical Oxygen Demand (COD) Measurement

Chemical oxygen demand (COD) is equivalent of the organic matter in wastewater sample that can be chemically oxidized using dichromate in acid solution. COD was measured according to HACH method (Method 8000) using HACH reagent (HACH, 2002). Wastewater samples were collected and diluted and 2 mL was

poured into COD vial. The vial was shaken and placed into the digester for 2 hr. Blank was used as zero and colorimetric determination of COD was carried out using HACH spectrophotometer DR 2000 and multiplied by the dilution factor. Soluble COD measurement was done using the same procedure using filtered sample.

3.7.7 Volatile Fatty Acids (VFA) Measurement

The method is using Hach reagents based on esterification of the carboxylic acids present in the sample and subsequent determination of the esters by the ferric hydroxamate reaction (HACH, 2002). Wastewater samples were collected and filtered or centrifuged before 0.5 mL of sample was placed into 25 mL sample cell. Ethlylene glycol and sulfuric acid were added and the cell was heated for 3 min. The cell was cooled and hydroxylamine hydrochloride, sodium hydroxide, ferric chloride sulfuric acid and deionized water were added and reading was recorded corrected to blank deionized water using Hach spectrophotometer. All volatile acids present are reported as their equivalent mg/L as acetic acid.

3.7.8 Ammonia-Nitrogen Measurement

Ammonia nitrogen (NH_3-N) was measured by the Nessler Method (HACH Method 8038) (HACH, 2002). Wastewater samples were collected and diluted and 25 mL was used. Three drops of mineral stabilizer were added which complexes hardness in the sample. Three drops of polyvinyl alcohol dispersing agent were added which aids the color formation in the reaction of nessler reagent with ammonium ions. Nessler reagent was added and one minute reaction took place and yellow color was formed proportional to the ammonia concentration. HACH spectrophotometer was used to read the sample corrected to the blank.

3.7.9 Nitrate-Nitrogen Measurement

Nitrate nitrogen (NO_3-N) was measured following the cadmium reduction method (High Range) using HACH powder pillow (HACH, 2002). Cadmium metal reduces nitrates in the sample to nitrite ion, which reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt, which couples with gentisic acid to form an amber colored solution. 10 mL of wastewater samples were collected and poured into sample cells. Nitrate reagent powder pillow (NitraVer 5) was added and shaken for 1 min and left to react for 5 min. HACH spectrophotometer was used to read the sample corrected to the blank.

3.7.10 Phosphorus Measurement

Total phosphorus (PO_4^{3-}) was measured by using HACH powder pillow method (PhosVer 3) (HACH, 2002). Wastewater samples were collected and diluted and 5 mL was added to test vial together with potassium persulfate powder pillow and heated for 30 min then cooled to room temperature. Sodium hydroxide was added and the vial was used to set the instrument to zero. PhosVer 3 powder pillow was added and 2 min reaction took place. Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) were converted to reactive orthophosphate. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates were converted to orthophosphates by heating with acid and persulfate, which then reacted with molybdate in an acid medium to produce a mixed phosphate/molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. HACH spectrophotometer was used to read the sample corrected to the blank.

3.7.11 Total Organic Carbon (TOC) Measurement

A total organic carbon (TOC) analyzer (SHIMADZU TOC-V$_{CSH}$) equipped with auto sampler (SHIMADZU ASI-V) was used for determining total carbon (TC) and total inorganic carbon, and the difference between total carbon (TC) and total inorganic

carbon is equal to total organic carbon (TOC). Wastewater samples were collected and filtered before they were placed into sample cells and loaded to the auto sampler for injection to the analyzer.

3.7.12 Total Kjeldahl Nitrogen (TKN) Measurement

Total Kjeldahl nitrogen (TKN) was measured according to the Standard Methods (APHA, 1992). Wastewater samples were collected and 20 mL poured into 300 mL test tubes together with 20 mL of sulfuric acid and 10 tablets of catalyst and digested using Buchi K-435 digestion unit equipped with Buchi B-414 scrubber unit. Distillation and titration for digested samples and blank were conducted using Buchi auto Kjeldahl unit K-370 unit.

3.7.13 Phenol Measurement

High Performance Liquid Chromatograph (HPLC Agilent 1100 series) equipped with a micro-vacuum degasser (Agilent 1100 Series), quaternary pump, diode array and multiple wavelength detectors (DAD) (Agilent 1100 Series) at wavelength 254 nm was used. The data were recorded by a Chemistation software. The column used was Zorbax SB-C18 (3 mm ID x 250 mm, 5 μm). The mobile phase was 75% methanol and 25% ultra pure water at a flow rate of 0.60 mL/min. The temperature was 28°C and sample injection volume was 1 μL. The following Figure 3.10 shows the peak and retention time obtained from running 30 mg/L standard.
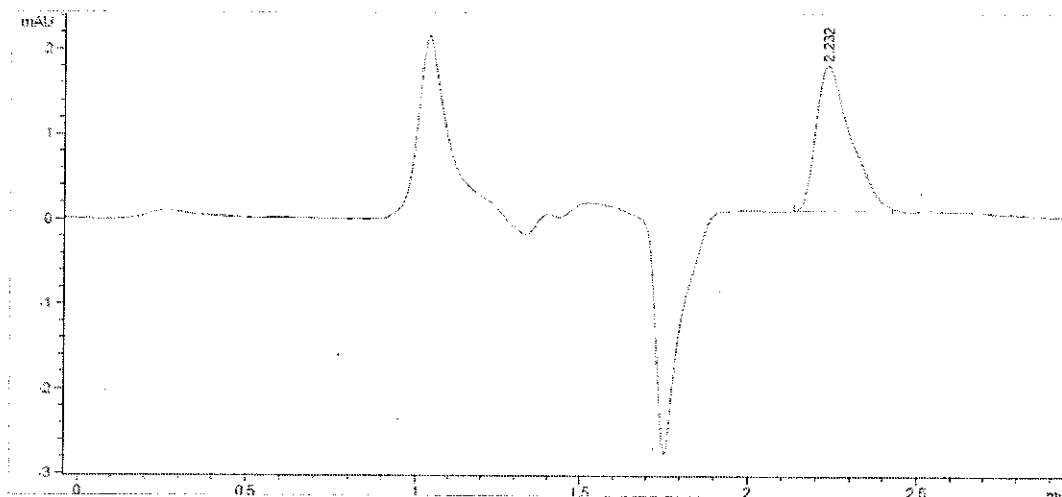
Figure 3.10: Phenol peak and retention time in HPLC.

3.7.14 Gas Composition Measurement

Gas Chromatograph-Flame Ionization Detector (GC-FID) model SHIMADZU GC-2010 was used for analyzing gas composition. Samples were collected and analyzed for methane and carbon dioxide. The column was GS-Q J&W (25 m, 0.32 mm I.D.). The analytical line temperature was 150°C and the pressure was 30 kPa and the carrier gas was nitrogen. The column flow was 0.99 mL/min. The oven temperature was 60°C for 1 min. The detector channel (TCD) temperature was 200°C and the makeup flow was 30.0 mL/min. The following Figure 3.11 shows peaks and retention time for gas in GC-FID.
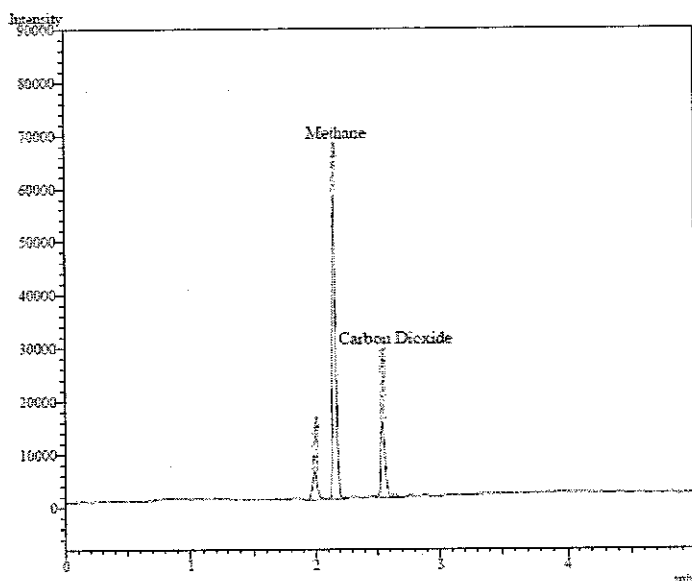
Figure 3.11: Gas peaks and retention time in GC.

3.7.15 BTEX Measurement

Gas chromatograph-mass spectrometer (GC-MS) model SHIMADZU GC-17A (GCMS-QP5050A) was used for BTEX measurement. Samples were collected and filtered and analyzed for BTEX using GC-MS with selected ion method (SIM). The samples were injected as liquid to purge and trap (P&T) equipment (Tekmar Dohrmann 3100 sample concentrator) which was necessary to concentrate the sample in gas form prior to be analyzed in GC. The column was SGE-BP1 (30 m, 0.25 mm I.D., 0.25 μm thickness). The interface temperature was 260°C and the analysis time was 10 min. The gas carrier was purified Helium (99.999). The column pressure was 56.7 kPa and the column flow was 1 mL/min. The oven temperature was 60°C for 2 min and increased to 100°C at 5°C/min. Sample injection volume was 1 mL to P&T and the purging time was 11 min under temperature of 30°C and the line temperature was 150°C. The following Figure 3.12 shows peaks and retention time for BTEX in GC-MS.

57
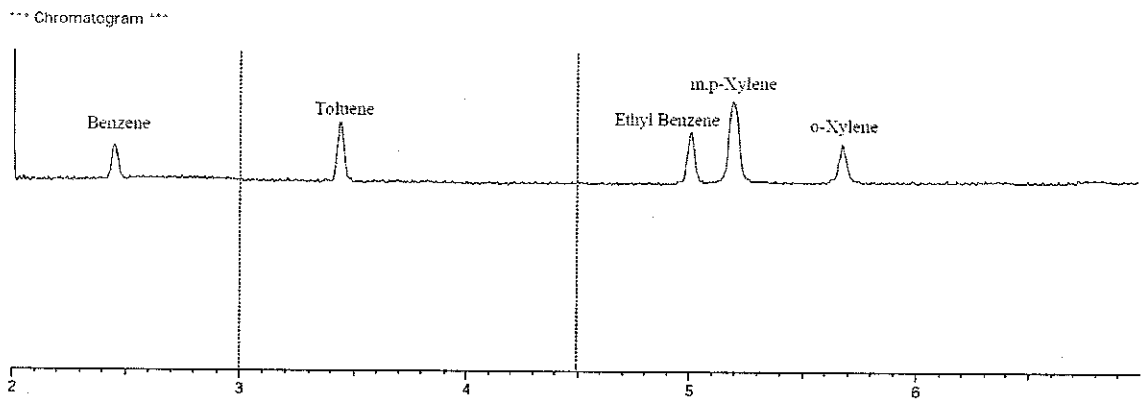
Figure 3.12: BTEX peaks and retention time in GCMS.

CHAPTER 4

RESULTS AND DISCUSSION

4.0 Chapter Overview

This section presents the results for the four phases in the study:

- Phase 1: Biodegradability batch study. This section presents the results for determination of degradation percentage in treating petroleum refinery wastewater. The results cover the aerobic and anaerobic batch treatment for single run over 28 days.

- Phase 2: Sequencing batch reactor treatability study. This section presents the results for SBR that was used to investigate the treatability of the petroleum refinery wastewater in two stages.

  o Three SBR configurations treatability. The results determine the most suitable configuration out of the three reactors (aerobic SBR, anaerobic-aerobic SBR and aerobic mixed influent SBR) that were operated in parallel.

  o SBR monitoring study. The results for monitoring different parameters on a single operation cycle that was carried out to identify the optimum reaction time.

- Phase 3: Three-Stage SBR study. This section presents the results for anaerobic-anoxic-aerobic SBR train study that investigated the feasibility of the three-stage SBR train configuration to achieve effective treatment.

o BTEX treatment and monitoring study. The results cover the monitoring of BTEX as volatile components under the three stages SBR to determine the degree of degradation.

- Phase 4: Integrated multi-stage biological reactor. This section presents the results for two continuous anaerobic-anoxic-aerobic reactors operated in parallel.

    o The results for determination of reactor performance under different loads.

    o The results for modeling and simulation of multi-stage biological reactor performance using ANN software.

4.1 Phase 1: Biodegradability Batch Study

This section presents the result for the study that was conducted to determine the biodegradability of petroleum refinery wastewater in a batch single run for 28 days in aerobic and anaerobic condition. The biodegradability batch study was conducted according to Table 4.1 for influent PRW average COD concentration of 712 mg/L.

Table 4.1: Biodegradability study sampling

Reactor	Influent	Test Type	Content	Sampling
R1	PRW	Aerobic	Inoculum and wastewater	Daily
R2	Blank	Aerobic	Inoculum blank	Daily
R3	PRW	Anaerobic	Inoculum and wastewater	Daily

4.1.1 Aerobic Biodegradability Batch Study

Reactor R1 was operated in aerobic batch mode to treat PRW. The initial sampling for test suspension was conducted immediately after preparing the reactors with the mixture and pH adjustment. The initial soluble COD concentration (sCOD) for test suspension was 159 mg/L which was less than the original concentration due to

dilution from mixing PRW with the mineral solution and seed biomass. Second reading was conducted after 24 hr; it shows 99% degradation in R1. The sCOD concentration was approximately 22 mg/L showing maximum degradation over 24 hr. As the experiment continued, the concentration remained approximately at this level, it can be observed that the sCOD of the test suspension plateau at an average sCOD of 40 mg/L until end of the study as shown in Figure 4.1.
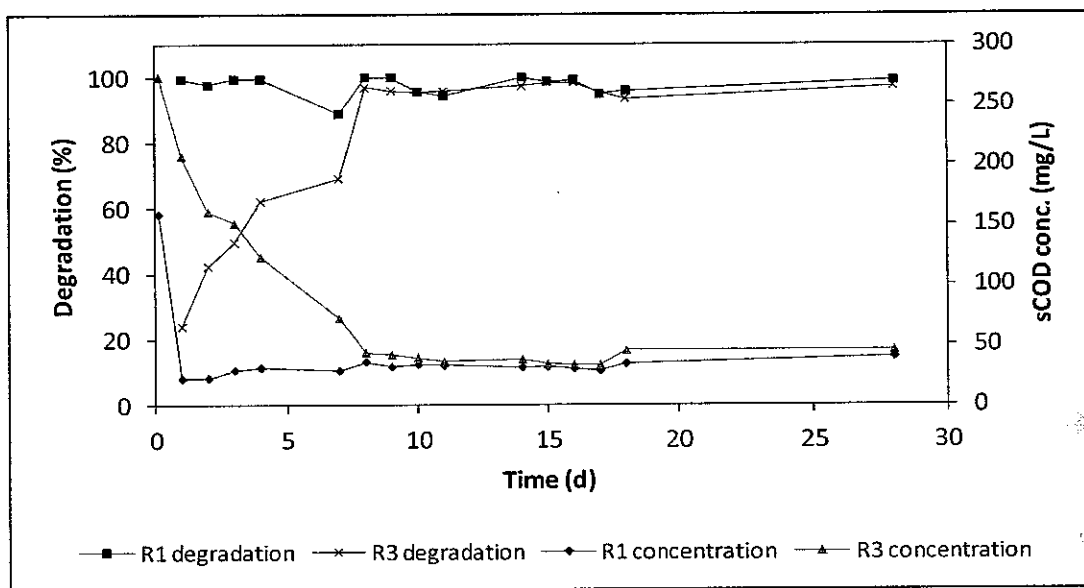
Figure 4.1: COD degradation and COD soluble concentration versus days for aerobic and anaerobic biodegradability batch treatment for PRW.

It can be observed that test suspension in aerobic treatment of PRW can achieve below 50 mg/L after one day of treatment with 99% degradation indicating immediate degradation.

4.1.2 Anaerobic Biodegradability Batch Study

For reactor 3 which was operated in anaerobic batch mode to treat PRW. The initial reading was taken immediately after preparing the reactor with the mixture and pH adjustment. The initial soluble COD concentration (sCOD) in test suspension was 273 mg COD/L which was less than the original concentration of 712 mg/L due to

dilution occurring from mixing PRW with the mineral solution and seed biomass. The sCOD concentration was approximately 44 mg/L at the 9th day of sampling showing slow degradation over the study period. As the experiment continued, the concentration remained approximately at this level, it can be observed that the sCOD of the test suspension plateau at an average sCOD of 46 mg/L until end of the study as shown in Figure 4.1.

Reactor R3 operated in the anaerobic mode treating PRW reached more than 90% COD removal after 9 days of treatment. COD concentration reached below 50 mg/L after 9 days of treatment indicating slow degradation.

4.1.3 The Overall Results of the Biodegradability Study

From the overall results of the biodegradability study as presented in Figure 4.1, this illustrates the COD degradation and the COD soluble concentration in test suspension versus days for both type of wastewater for aerobic and anaerobic mode. It can be observed that aerobic degradation of PRW achieved more than 90% removals after one day of treatment.

Biodegradability batch study was conducted to determine the degradation percentage. From the biodegradability study results, it was shown that the PRW was ultimately biodegradable using both aerobic as well as anaerobic mode of degradation, with more than 90% COD removal. However, it was also found that wastewater treatment achieved better COD removals when treated aerobically. It can be observed that sCOD concentration in test suspension in aerobic treatment of PRW can reach below 50 mg/L after one day of treatment. However, anaerobic treatment of the same source of wastewater resulted in sCOD concentration in test suspension below 50 mg/L after 9 days of treatment. It should be noted that initial COD concentrations varied due to dilution of the wastewater with the biomass and nutrients.

4.2 Phase 2: Sequencing Batch Reactor Treatability Study

This section presents the results for phase 2 SBR study that was used to investigate the treatability of the petroleum refinery wastewater in two stages. The results for the first stage determine the most suitable configuration out of the three reactors (aerobic SBR, anaerobic-aerobic SBR and aerobic mixed influent SBR) that were operated in parallel. In the second stage the results show the monitoring of different parameters on a single operation cycle that was carried out to identify the optimum reaction time. The average influent COD concentration was found to be 712 mg/L for PRW. The SBR treatability study was conducted according to Table 4.2 below.

Table 4.2: SBR treatability study details and sampling

R	Configuration	Mode	Influent	Cycle	Sampling interval		
					Steady state	Monitoring	
						1st	2nd
1	Aerobic	Aerobic	PRW	24 hr	Daily	7 hr	1.5 hr
2	Coupled	Anaerobic	PRW	24 hr	Daily	7 hr	1.5 hr
3		Aerobic	Reactor 2	24 hr	Daily	7 hr	1.5 hr
4	Aerobic	Aerobic	mixed PRW	24 hr	Daily	7 hr	1.5 hr

4.2.1 Three SBR Configurations Treatability Study

4.2.1.1   Overall Results for Three SBR Configurations Treatability Study

In this study, the three SBR reactors treating PRW with 24 hr cycle are shown in Figure 4.2 and Figure 4.3 below which shows COD concentration (mg/L) versus days for PRW treated under the aerobic and anaerobic mode.

63
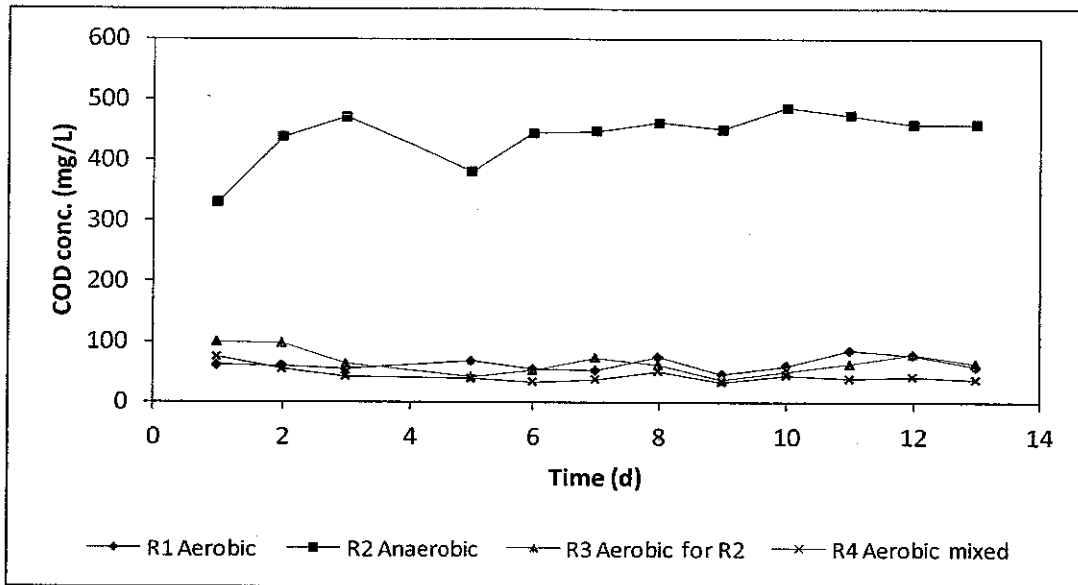
Figure 4.2: COD concentration versus days for aerobic and anaerobic SBR treatment of PRW.
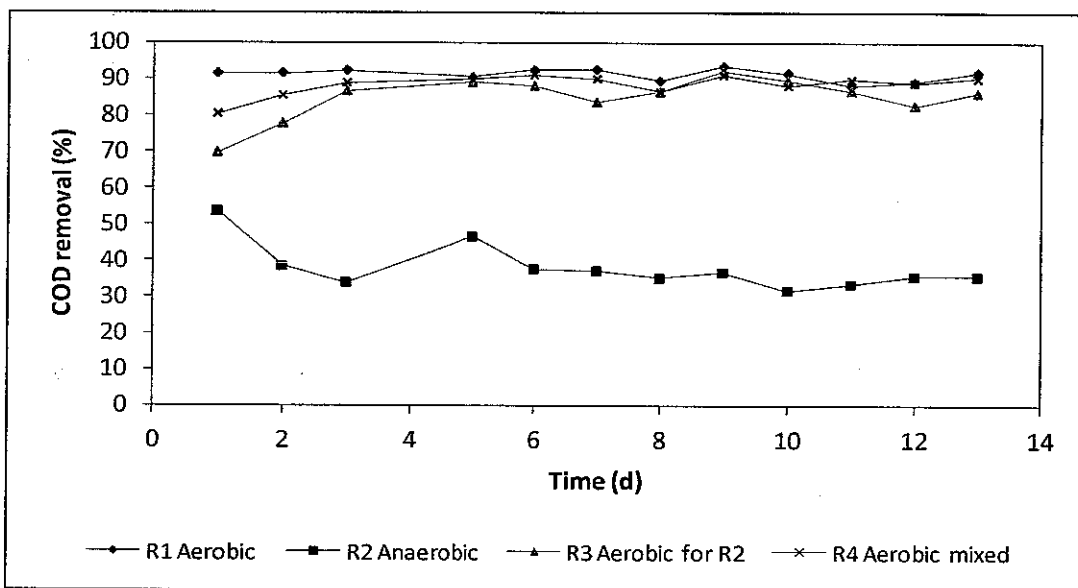
Figure 4.3: COD removal percentage versus days for aerobic and anaerobic SBR treatment of PRW.

It can be observed from COD removal percentage versus days for PRW wastewater operated under the aerobic and anaerobic mode, that anaerobic SBR treatment of PRW wastewater achieved COD removal in the range of 30-40% at the end of the study, which consist of 22 days acclimatizing and 14 days continuous

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operation and monitoring. However, aerobic SBR treatment of PRW wastewater achieved COD removals of 80-90% after the third cycle.

4.2.1.2 Aerobic SBR Treatability Study

Reactor R1 was operating as SBR treating PRW in aerobic mode with 24 hr cycle. It can be observed from Figure 4.2 and Figure 4.3 that the effluent concentration was stable throughout the study period. The average PRW influent COD concentration was 712 mg/L at the time of experiment. Effluent concentration was 61 mg/L in the first cycle with 91% removal efficiency. This performance was maintained until the end of the study. The lowest and highest concentration recorded was 46 mg/L and 85 mg/L, respectively; and never exceeded 100 mg/L.

The average effluent COD concentration was 63 mg/L, while the average COD removal percentage was 91% which was much better than 36% removal in fluidized bed reactor (Ochieng et al., 2003) and 77% removal for influent concentration of 510 mg/L in batch reactor (Sarathy et al., 2002).

4.2.1.3 Anaerobic-Aerobic SBR Treatability Study

SBR reactor R2 was operated in anaerobic mode with 24 hr cycle to treat PRW. Effluent COD concentration was measured and found to be 330 mg/L on the first day of sampling. The average influent PRW COD concentration was 712 mg/L at the time of study. The effluent concentration started to increase in the first week after which it was stable with average concentration of 441 mg/L as shown previously in Figure 4.2 and Figure 4.3. It can be observed also from removal percentage versus days that an average COD removal of approximately 40% was achieved.

Effluent from the above anaerobic SBR reactor R2 was fed to be further treated in aerobic SBR reactor R3 with 24 hr cycle. This enhanced the final effluent treatment as shown in Figure 4.4. Influent COD concentration was approximately 441 mg/L which was representing the effluent from R2. Average effluent COD concentration

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was found to be approximately 65 mg/L with average COD removal of 85%. The overall average COD removal of this combined treatment was found to be approximately 91%. This removal was much higher than reported for this system which was not able to give effluent concentration below 100 mg/L (Perri, 1997).
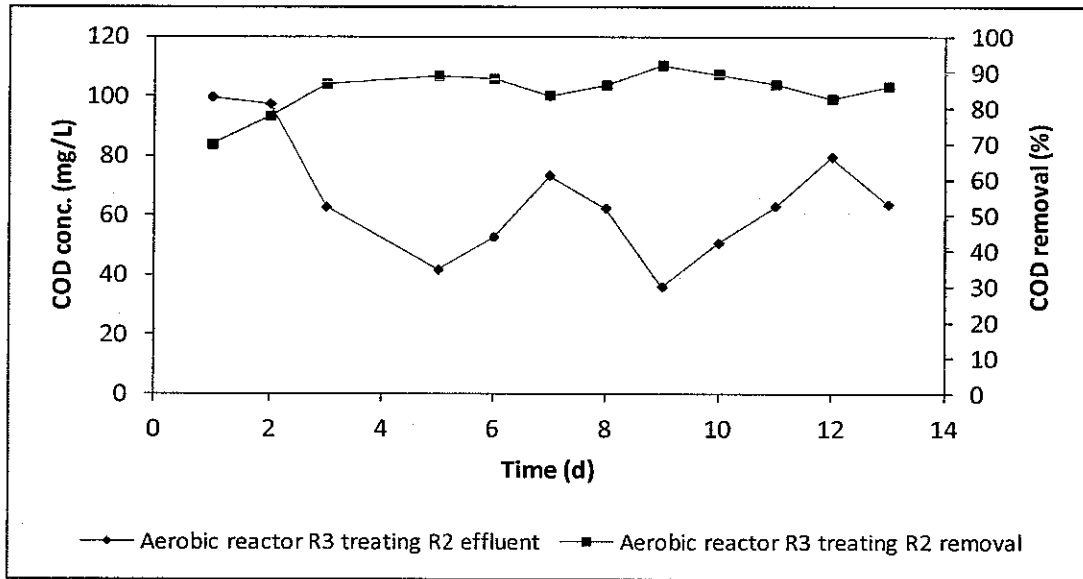
Figure 4.4: COD concentration and removal percentage versus days for SBR aerobic treatment for anaerobic effluent.

When considering this two stages treatment as one system, then the anaerobic R2 reactor influent will be considered as the system influent, and the effluent from reactor R3 is the system effluent then the removal efficiency will be 91% as shown in Figure 4.5.
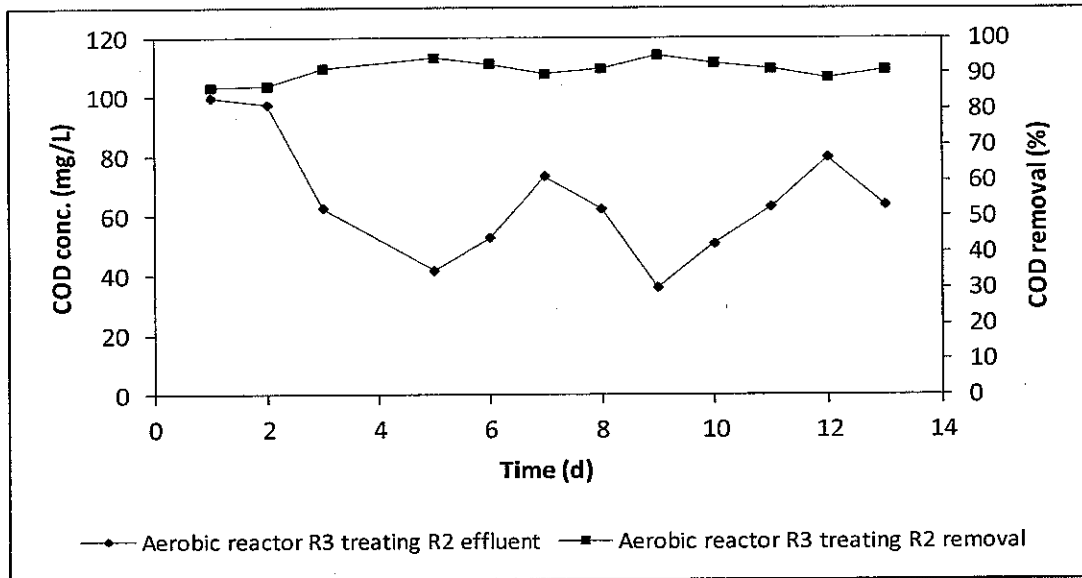
Figure 4.5: COD concentration and removal percentage versus days for SBR anaerobic-aerobic treatment of PRW.

4.2.1.4 Aerobic SBR (Influent Mixed with Domestic) Treatability Study

Another treatment approach conducted was operating an aerobic SBR reactor R4, treating PRW combined with domestic wastewater. The results are shown in the Figures 4.2 and 4.3. Influent COD concentration was found to be approximately as 378 mg/L after dilution with the domestic wastewater compared to the original concentration of 712 mg/L and the average effluent COD concentration was found to be approximately 44 mg/L with an average COD removal of 88%. This result was better than that achieved by mixing PRW with other type of wastewater which enhanced the removal efficiency from 36% to 64% (Ochieng et al., 2003).

4.2.1.5 Comparative Results for SBR Systems

Figure 4.6 and Figure 4.7 below show the results for aerobic reactor, combined anaerobic-aerobic reactors and aerobic mixed with domestic wastewater operated over cycle period of 24 hr, 48 hr, and 24 hr, respectively.

67
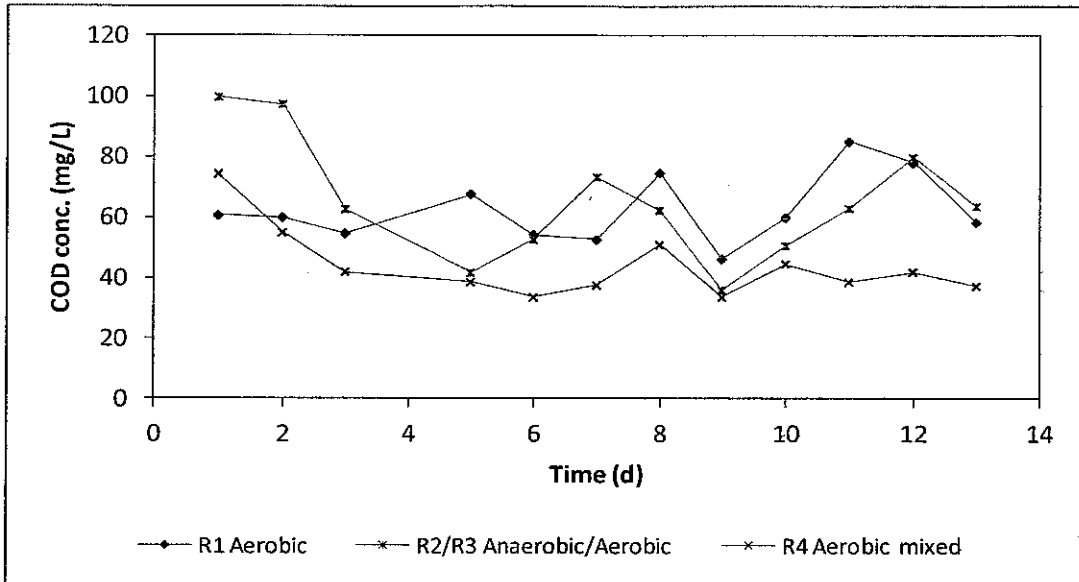
Figure 4.6: COD concentration versus days for SBR systems treating PRW.
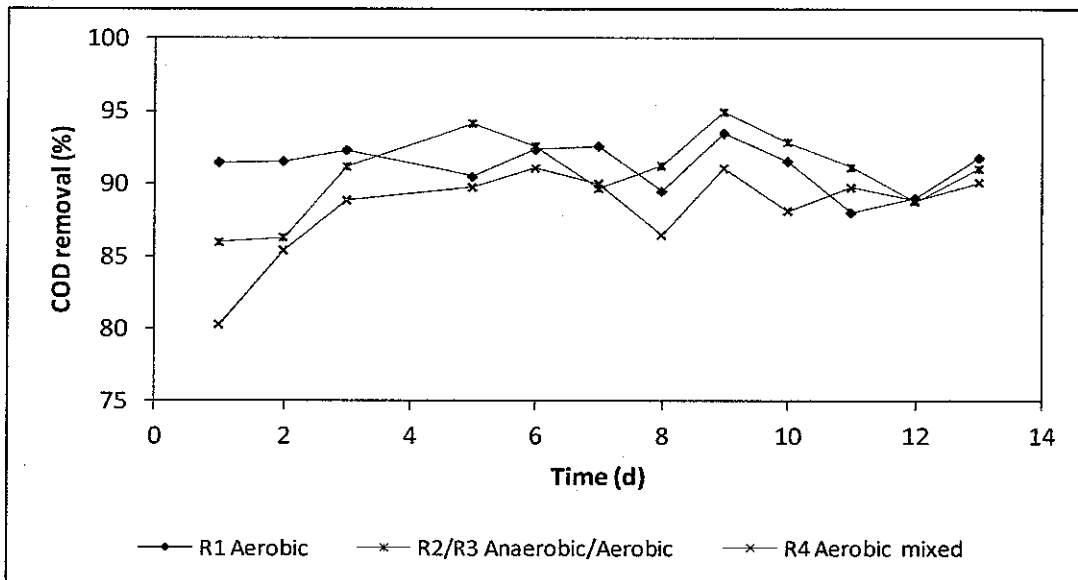
Figure 4.7: COD removal percentage versus days for SBR systems treating PRW.

The average last three measurements COD removals for the aerobic reactor, combined anaerobic-aerobic reactors and aerobic mixed with domestic wastewater achieved was found to be approximately 90% for all of them, however, the average effluent COD was 74 mg/L, 69 mg/L, and 39 mg/L, respectively.

SBR treatability study on aerobic reactor, coupled anaerobic-aerobic reactor, and mixed domestic refinery influent aerobic reactor were tested. When taking into consideration the other aspect such as minimum volatilization takes place and less aeration required, Anaerobic-aerobic reactor achieved similar removal efficiency compared to Aerobic reactor but the effluent quality was relatively better, hence this configuration was favored.

4.2.2 SBR Monitoring Study

This section presents the results for monitoring different parameters on a single operation cycle that was carried out to identify the optimum reaction time. This study was conducted using a batch of petroleum refinery wastewater that has COD and BOD_5 average concentrations of 1066 mg/L and 390 mg/L respectively, and the BOD_5/COD ratio was moderate of about 0.4 (Metcalf and Eddy, 2003). The average characteristics of the raw petroleum refinery wastewater (PRW) and the petroleum refinery wastewater mixed with domestic wastewater (PRW+DW) during this study are tabulated in Table 4.3.

Table 4.3: Influent wastewater characteristics

No.	Parameter	Unit	PRW	PRW+DW
1	pH	-	6	6.5
2	COD	mg/L	1066	770
3	Ammonia-N	mg/L	7.8	9.9
4	Nitrate-N	mg/L	0.47	0.23
5	Sulfate	mg/L	22.6	28.4
6	Phosphorous	mg/L	5	6.8
7	TSS	mg/L	189.9	199.3

4.2.2.1 *Parameters Monitored with Respect to Reactors*

The SBR monitoring study was conducted for single 24 hr cycle and readings were taken every 7 hr. In a later stage there was more focus on the first 7 hr to monitor the

degradation in shorter intervals. The soluble COD overall results that show the combination of the two studies are presented in Figure 4.8.
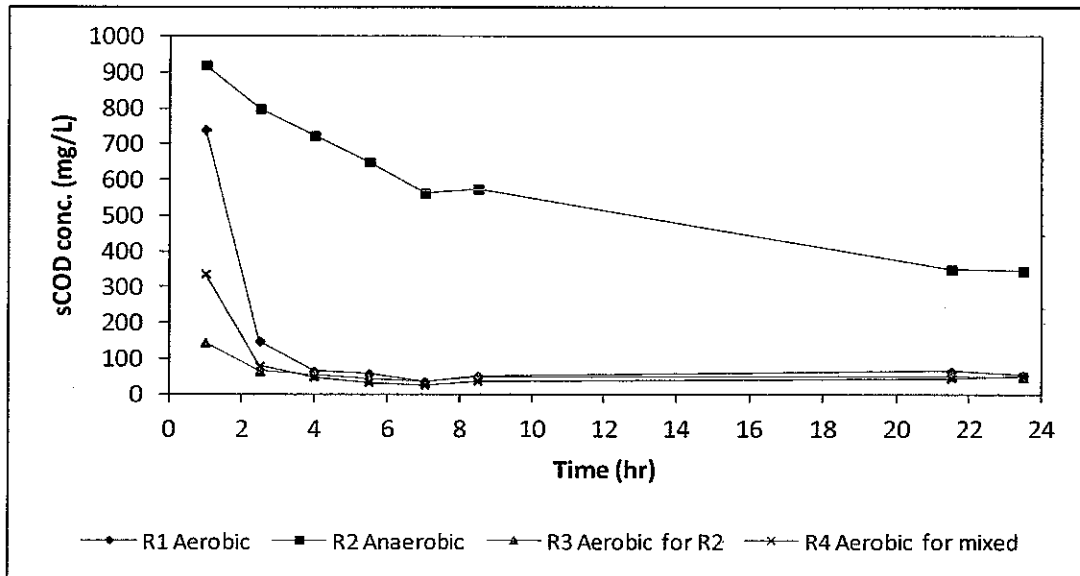
Figure 4.8: sCOD concentration versus time for SBR systems treating PRW wastewater for combined results representing 24 hr monitoring and 7 hr monitoring.

Figure 4.9 and Figure 4.10 present the sCOD concentration in the test suspension for four reactors during 24 hr and 7 hr monitoring. The figures shows that reactor 1, 3 and 4 after 7 hr the COD removal reach 91%, 65% and 81% respectively, corresponding to sCOD concentration of 58, 58 and 49 mg/L; compare to reactor R2 which needs the whole cycle to reach 65% removal corresponding to 350 mg/L. For the second monitoring period (7 hr) the highest removal for the reactors operating in the aerobic mode, was recorded between 4 hr from the beginning of the cycle to 6 hr with removals ranging from 95-75%.
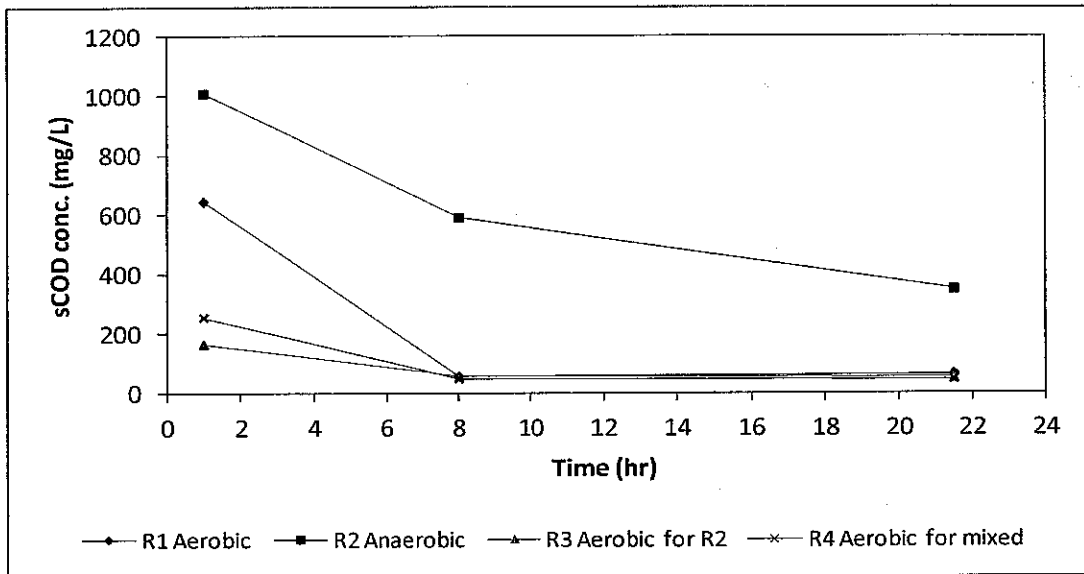
Figure 4.9: sCOD concentration versus time for SBR systems treating PRW wastewater (24 hr).
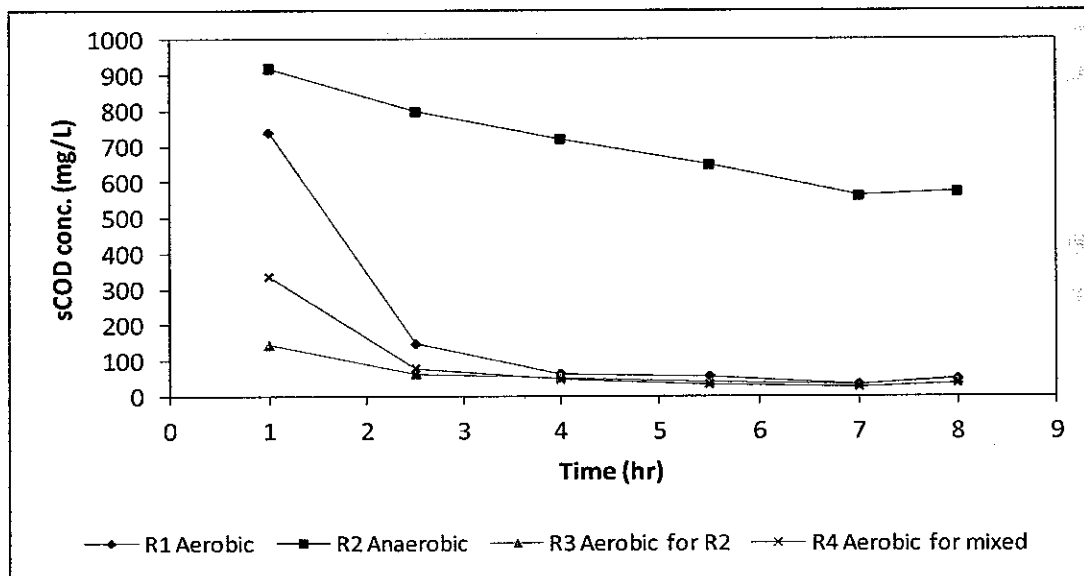
Figure 4.10: sCOD concentration versus time for SBR systems treating PRW wastewater (7 hr).

Figure 4.11 and Figure 4.12 present the ammonia concentration in test suspension for three aerobic reactors and one anaerobic. The first 24 hr monitoring shows increase in ammonia in the anaerobic reactor 2, while aerobic reactors shows mostly decrease. This behavior was confirmed in the second monitoring period (7 hr), in

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which the anaerobic reactor was stable and aerobic reactors 1, 3 and 4 shows removal of 98%, 78% and 48% respectively after 6 hr.
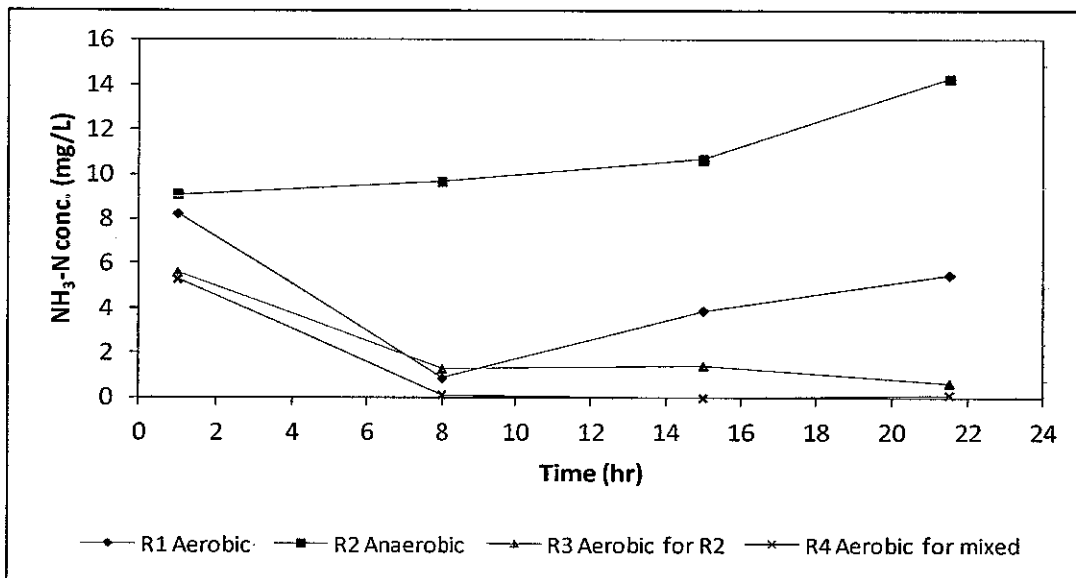
Figure 4.11: Ammonia-N concentration versus time for SBR systems treating PRW wastewater (24 hr).
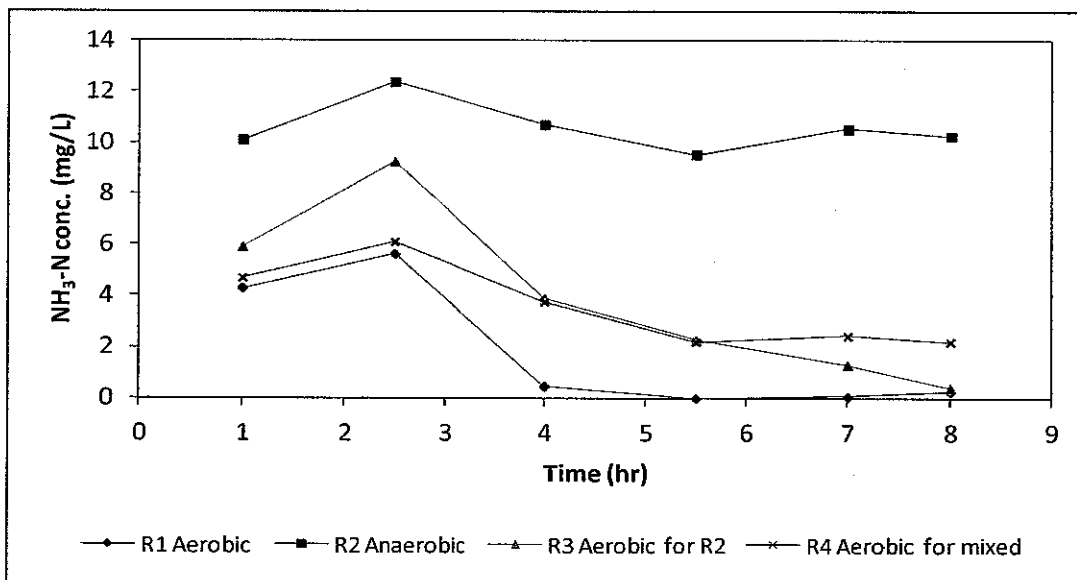
Figure 4.12: Ammonia-N concentration versus time for SBR systems treating PRW wastewater (7 hr).

Figure 4.13 and Figure 4.14 present the nitrate concentration in test suspension for three aerobic reactors and one anaerobic. The first 24 hr monitoring shows slight decrease in nitrate in the aerobic reactors with removal ranging between 60-20% in the second sample, after which it increases, while the anaerobic reactor shows no change. This behavior was confirmed in the second monitoring period (7 hr), in which the anaerobic reactor was stable and aerobic reactors 1, 3 and 4 shows slight increase in concentration indicating the need for denitrification.
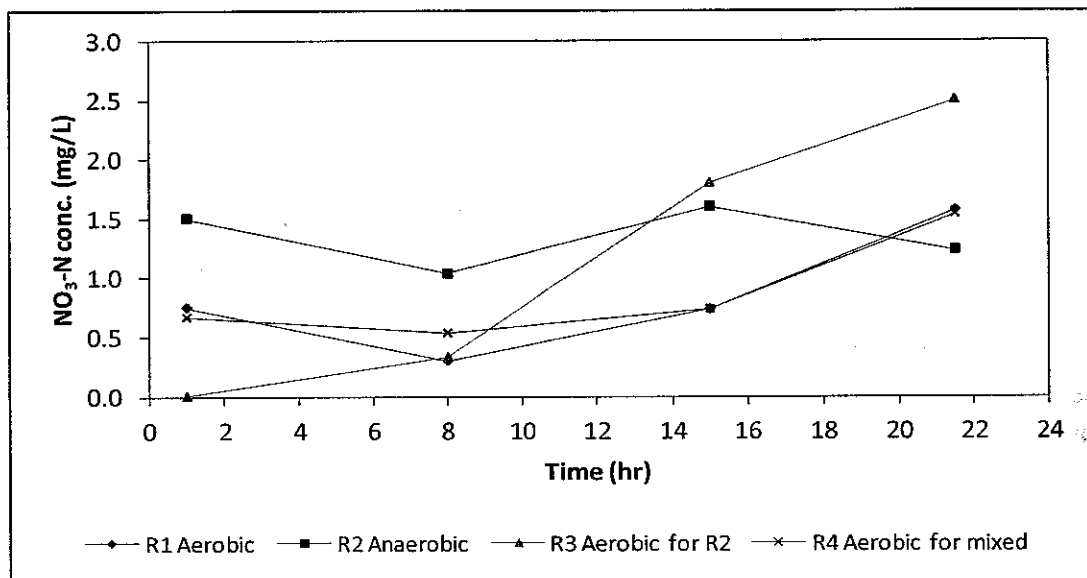
Figure 4.13: Nitrate-N concentration versus time for SBR systems treating PRW wastewater (24 hr).
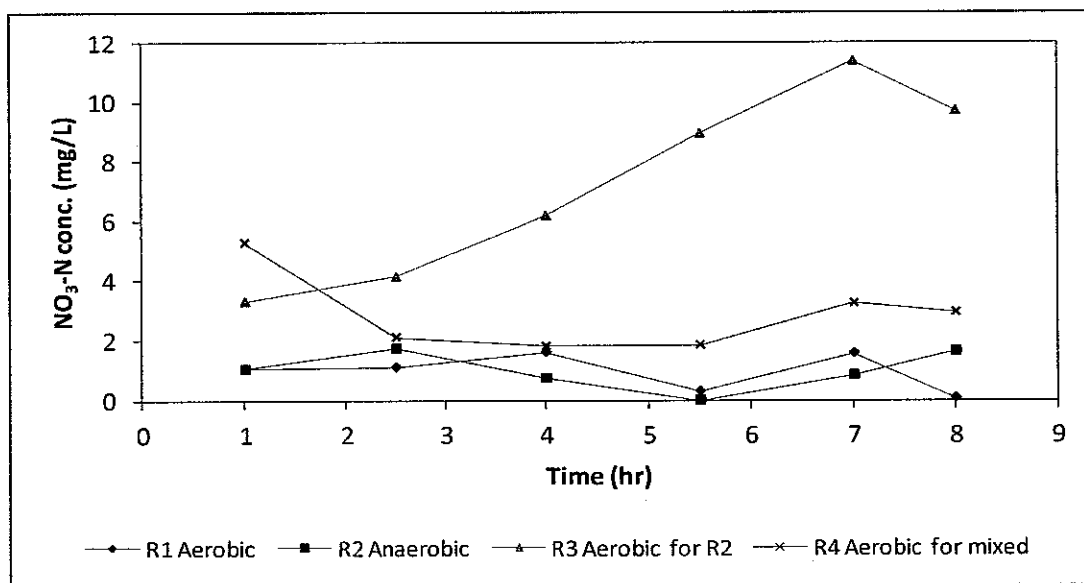
Figure 4.14: Nitrate-N concentration versus time for SBR systems treating PRW wastewater (7 hr).

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Figure 4.15 and Figure 4.16 present the mixed liquor suspended solids concentration in the reactors versus sampling intervals. The first 24 hr sampling period shows that MLSS concentration for reactor 2, 3 and 4 increased to 2750, 1925 and 3242 mg/L respectively, while reactor R1 was losing its content of MLSS and the final concentration was 2308 mg/L. At the end of the second monitoring period (7 hr) there was growth in MLSS in all reactors.
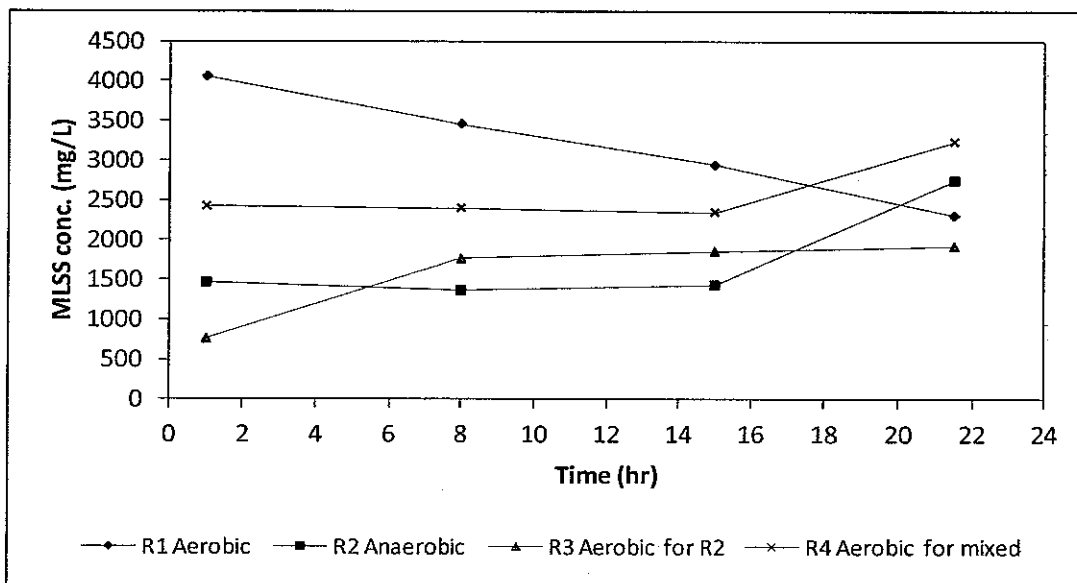
Figure 4.15: MLSS concentration versus time for SBR systems treating PRW wastewater (24 hr).
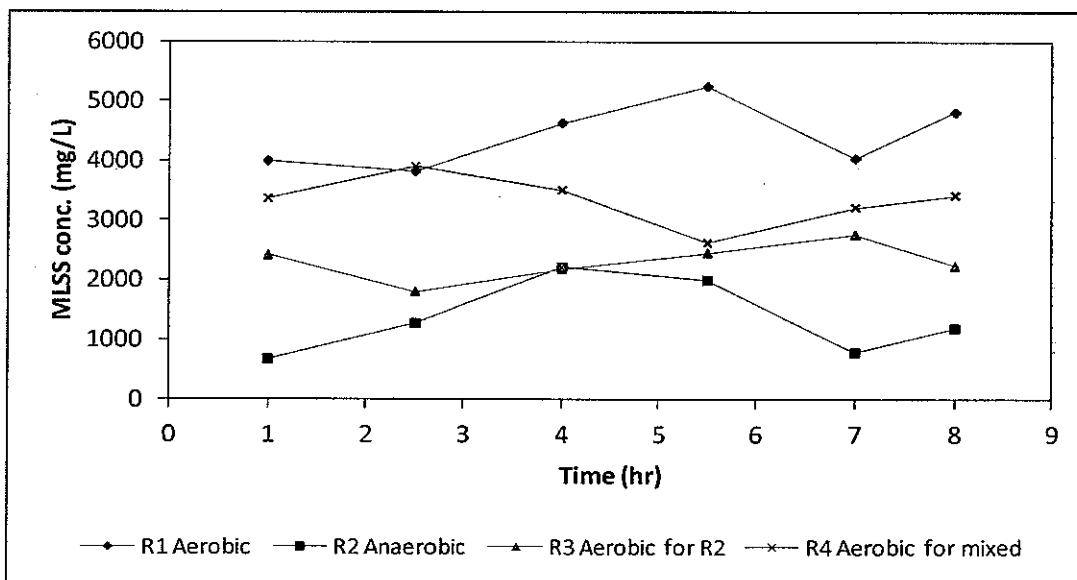
Figure 4.16: MLSS concentration versus time for SBR systems treating PRW wastewater (7 hr).

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Figure 4.17 and Figure 4.18 present the mixed liquor volatile suspended solids concentration in the reactors versus sampling intervals. The first 24 hr sampling period shows that MLVSS concentration for reactor 2, 3 and 4 increased to 1308, 1417 and 2275 mg/L respectively, while reactor 1 was losing its content of MLVSS and the final concentration was 1942 mg/L. For the second monitoring period (7 hr) there was growth in MLVSS in all reactors after 6 hr.
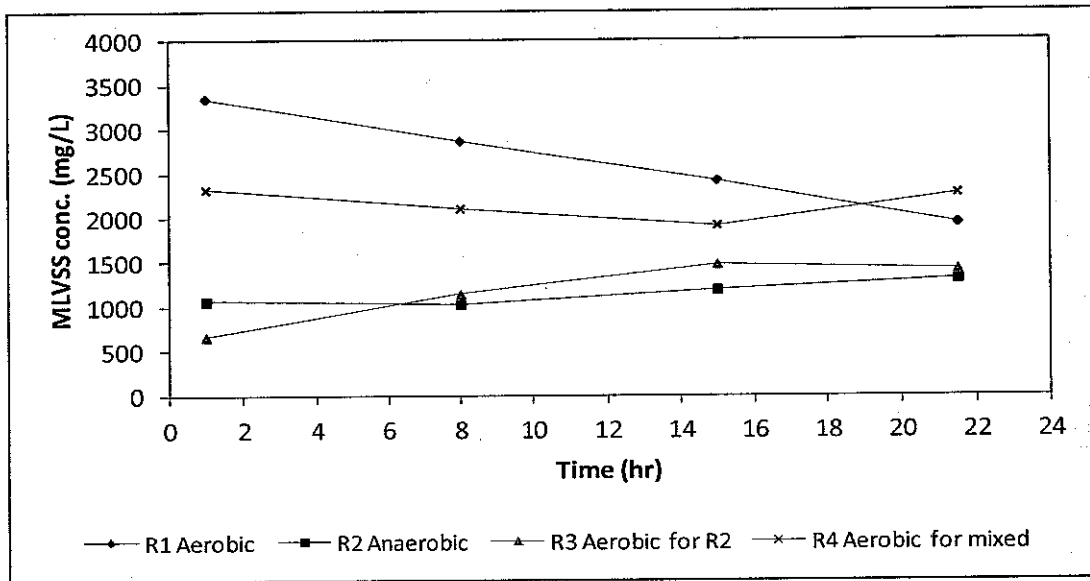
Figure 4.17: MLVSS concentration versus time for SBR systems treating PRW wastewater (24 hr).
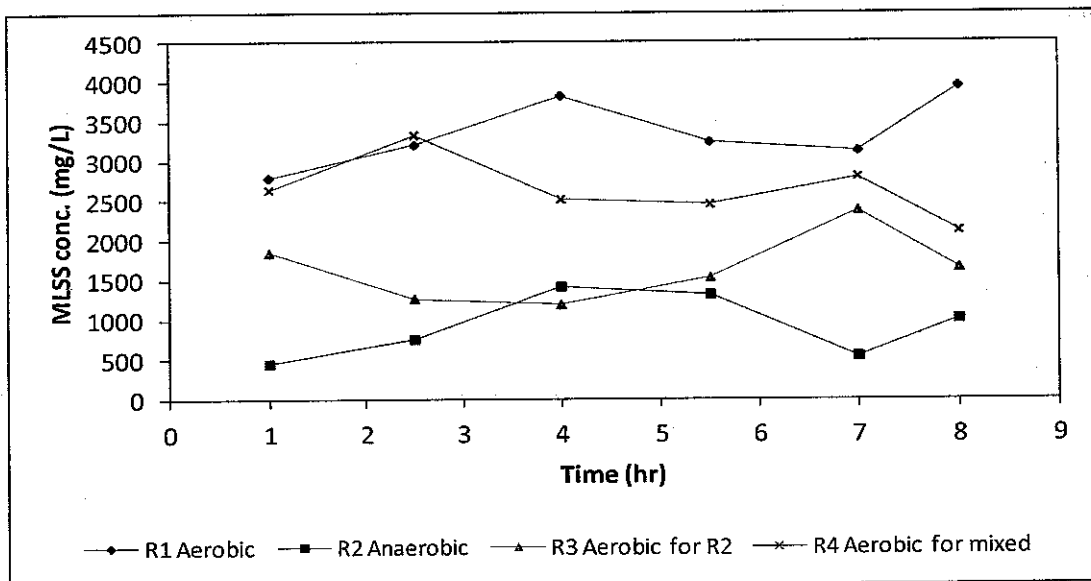
Figure 4.18: MLVSS concentration versus time for SBR systems treating PRW wastewater (7 hr).

The above mentioned results could be represented to describe the behavior of each reactor by looking at all the parameters in each reactor.

4.2.2.2   Aerobic Degradation of PRW

From the aerobic degradation of PRW in reactor R1 as was plotted in the figures presented in Section 4.2.2.1, it can be observed that the biomass concentration in the beginning of the cycle was above 3000 mg MLVSS/L but continued to decline towards end of the cycle to 2000 mg MLVSS/L. It can be observed from the 24 hr monitoring that there was an immediate degradation of ammonia-nitrogen after 8 hr, in which the concentration reached 0.9 mg/L. This due to the degradation of ammonia-nitrogen present in the raw wastewater. This degradation was observed to be in the first 4 hr as can be seen from the 7 hr monitoring period that was done later. However, after 8 hr, the ammonia-nitrogen increased to 5.5 mg/L at the end of the cycle. This may be due to the degradation of biomass through the cycle as the biomass concentration in term of MLVSS decreased gradually from 3350 mg/L to 1942 mg/L at the end of the cycle. This was associated with increase in nitrate concentration and sharp decrease in sCOD concentration. These results indicate that most of the degradation took place in the first 6 hr from the beginning of the 24 hr cycle.

4.2.2.3   Anaerobic Degradation of PRW

In anaerobic reactor R2, the biomass concentration in the beginning of the cycle was above 1000 mg MLVSS/L and continued to increase towards the end of the cycle to MLVSS concentration more than 1300 mg/L as was shown in the figures presented in Section 4.2.2.1. The sCOD degradation was showing gradual removal over the 24-hr period and reached 350 mg/L corresponding to 65% removal; which is considered as low removal percentage and a high amount of substrate was still available in the reactor. However, the ammonification of organic nitrogen during the anaerobic digestion elevated the ammonia-nitrogen inside the reactor. From these results, 24 hr

cycle was not sufficient to achieve the desired effective removal of substrate and longer cycle is needed.

4.2.2.4 Aerobic Degradation of Anaerobic Effluent

Effluent decanted from the anaerobic reactor R2 was further treated aerobically in reactor R3. From the figures presented in Section 4.2.2.1, most of the sCOD was degraded during the first eight hours of aeration. The ammonia-nitrogen concentration was initially high as the effluent was taken from the anaerobic reactor. However, the ammonia-nitrogen was quickly degraded and converted to nitrate-nitrogen in the first eight hours of aeration. It can be seen that the nitrate-nitrogen concentration also increased gradually during the first eight hours of aeration. The nitrate-nitrogen concentration continued to increase towards the end of the study, indicating that sCOD removed produced ammonia-nitrogen which was then degraded into nitrate-nitrogen during the nitrification process. Denitrification was not significant in the reactor as nitrate was not decreasing indicating the need for anoxic condition for complete removal of nitrate. It can be observed also from the results that on average 6 hours duration was sufficient for maximum degradation and removal of substrate.

4.2.2.5 Aerobic Degradation of PRW Mixed With Domestic Wastewater

The PRW was co-treated with domestic wastewater in reactor R4 that was operated in aerobic mode. It can be observed from the figures presented in Section 4.2.2.1, that the sCOD was removed consistently throughout the study period with the MLVSS consistently maintained at 2200 mg/L. It can be observed that the initial ammonia-nitrogen concentration was degraded during the first 8 hr of aeration with the nitrate-nitrogen concentration increasing after the 8 hr.

4.2.2.6   Summary of Results for Parameters Monitored

At the end of this study, the aerobic degradation of PRW results indicated that most of the degradation occurred in the first 6 hr from the beginning of the cycle. From the anaerobic degradation of PRW results, 24 hr cycle was not sufficient to achieve the desired removal and longer cycle is needed. It can be observed also from the aerobic degradation of the anaerobic effluent results that on average 6 hr duration was sufficient for maximum degradation and removal of substrate; which applies also to the aerobic degradation of PRW mixed with domestic wastewater (PRW+DW). However, when considering shortening the cycle to 8 hr or less for the aerobic degradation, it can be observed that the initial ammonia-nitrogen concentration was degraded during the first 8 hr of aeration with the nitrate-nitrogen concentration increasing after the 8 hr, indicating the need for denitrification by introducing anoxic condition.

The average influent and effluent concentration for the final effluent for all the reactors were combined, and the anaerobic-aerobic SBR reactor was favored as shown in the following Table 4.4.

Table 4.4: Influent and effluent for all SBRs

Reactor	Influent	Effluent			Influent	Effluent
	PRW	R1	R2	R3	PRW+DW	R4
Mode	-	Aerobic	Anaerobic	Aerobic	-	Aerobic
pH	6	7	7	7	6.5	7
COD	1066	61	381	60	770	43
Ammonia	7.8	5.87	13.93	0.77	9.87	0.80
Nitrate	0.47	1.47	1.30	3.10	0.23	1.93
Sulfate	22.6	71.78	0.33	81.22	28.44	46.22
Phosphorous	5	3.21	6.82	5.34	6.75	4.08
TSS	189	58.56	109.11	48.67	199.33	41.97
VSS	65	18.89	13.33	16.67	92.00	51.67
TOC	359.74	11.69	77.76	10.64	219.54	10.67
TN	23.1	7.90	20.63	17.50	12.19	20.03

All concentrations, except pH, are in mg/L.

4.3   Phase 3: Three-Stage SBR Study

This section presents the results for anaerobic-anoxic-aerobic SBR train study that investigated the three-stage SBR train configuration treatment performance. The results also cover the monitoring of BTEX as volatile component under the three-stage SBR to determine the degree of degradation.

4.3.1 Anaerobic, Anoxic and Aerobic SBR Train Study

The study was conducted for anaerobic, anoxic and aerobic train of SBR reactors to treat petroleum refinery wastewater. This study was conducted using a batch of PRW that has low BOD_5/COD ratio of about 0.3, indicating the presence of toxic components and the need for acclimated microorganisms (Metcalf and Eddy, 2003). The PRW characteristics during this study are detailed in the following Table 4.5.

Table 4.5: Influent wastewater characteristics

No.	Parameter	Unit	Amount
1	pH	-	8.13
2	DO	mg/L	0.76
3	Alkalinity	mg/L	3188
4	COD	mg/L	1260
5	$BOD_{5\,d,\,20°C}$	mg/L	350
6	Nitrate	mg/L	6.0
7	Ammonia	mg/L	5.94
8	Phosphorous	mg/L	4.77
9	Sulfate	mg/L	12
10	TSS	mg/L	190
11	VSS	mg/L	65
12	TOC	mg/L	360
13	TKN	mg/L	70
14	VFA	mg/L	497
15	Benzene	mg/L	17.919
16	Toluene	mg/L	1.983
17	Ethyl benzene	mg/L	0.024
18	m-Xylene	mg/L	0.383
19	p-Xylene	mg/L	0.370
20	o-Xylene	mg/L	0.273

It can be observed that anaerobic degradation of PRW (average concentration was 1260 mg/L) reached on average 1000 mg/L corresponding to average 20% removal efficiency. The anoxic reactor received the anaerobic effluent and recycled effluent from aerobic reactor, the average influent concentration was 685 mg/L and the effluent was 586 mg/L with average removal of 15%. The aerobic reactor received the anoxic effluent and reduces the final effluent to average 344 mg/L with 39% removal as shown on Figure 4.19.
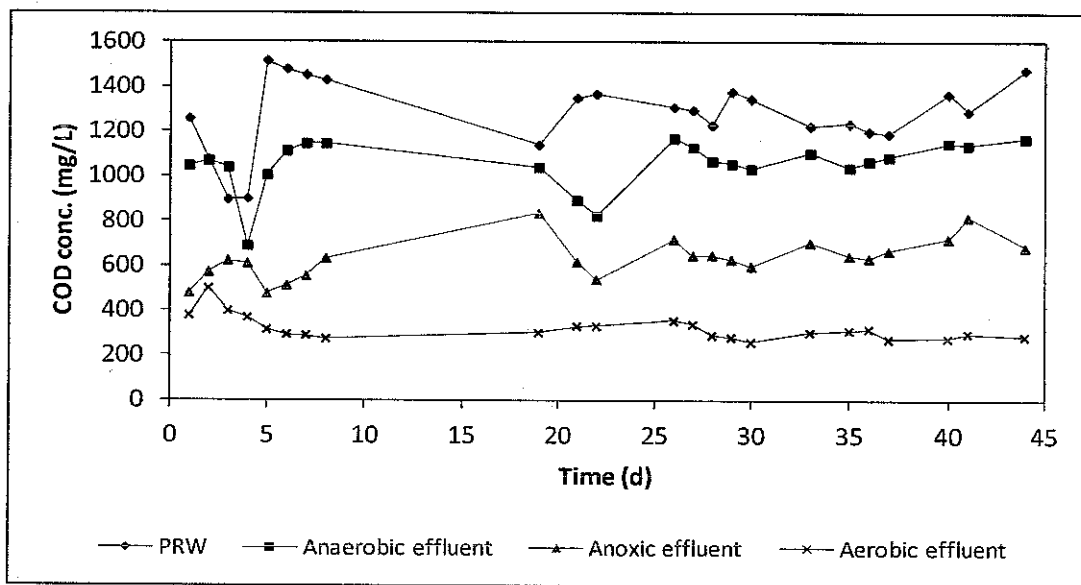
Figure 4.19: COD concentration versus days for anaerobic, anoxic and aerobic sequencing batch reactors treating PRW.

The performance of the anaerobic reactor continued improving after twenty days and reached 39% removal efficiency on twenty second reading which was 823 mg/L. This elevates the anoxic and aerobic removal efficiency and the overall removal was 71% and corresponding to COD concentration of 344 mg/L. After which, influent concentration was increased and the anaerobic reactor started to show increase in effluent concentration and the subsequent stages were affected accordingly. The average concentration for the last six samples was 1294 mg/L for influent, which reduced to 295 mg/L in the final train effluent corresponding to 77% removal.

The collected methane was on average close to the theoretical calculated volume as shown in Figure 4.20 which illustrates the volumes versus days of experiment.
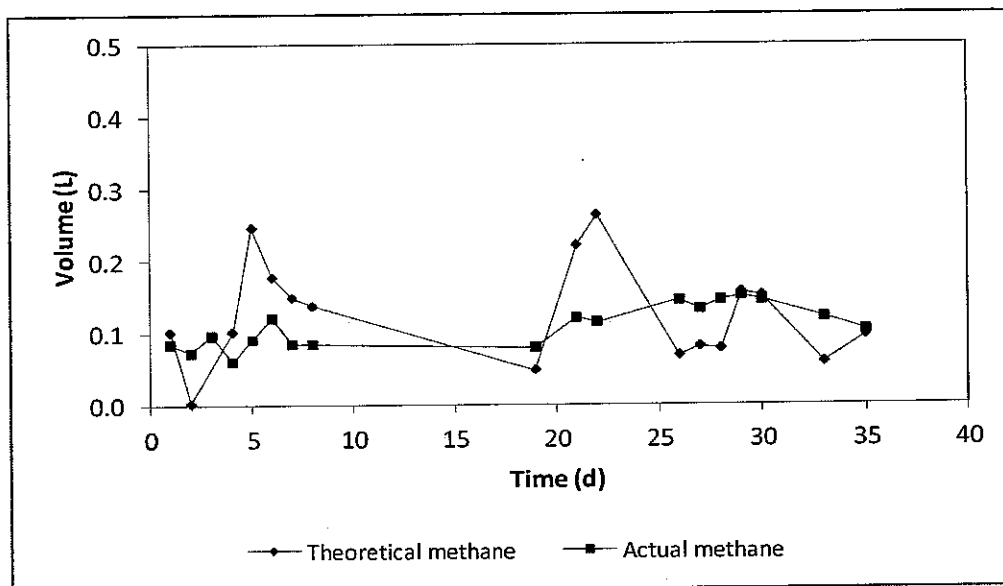
Figure 4.20: Theoretical and actual methane gas versus days for anaerobic reactor in the three-stage SBR treating PRW.

4.3.2 BTEX Treatment and Monitoring

The three-stage SBR reactor was monitored to identify the removal of BTEX throughout the stages. Samples were collected and analyzed for BTEX using GC-MS with purge and trap (P&T) equipment. The SBR train configuration achieved on average almost complete degradation of BTEX from petroleum refinery wastewater as shown in the following Figure 4.21. It can be observed that anaerobic degradation of BTEX reached on average 78% removals. The anoxic reactor received the anaerobic effluent and recycled effluent from aerobic reactor, the average removal was 74% from the concentration received which corresponded to 19% from the overall system performance. The aerobic reactor received the anoxic effluent and removed on average 83% from the concentration received which corresponded to 3% from the overall system performance. Although the BTEX concentration during the

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application of full load was approximately 18 mg/L, but there was no adverse effect as reported in the literature for loads more than 12 mg/L, and the reactor managed to perform (Wong and Gerhardt, 2002).
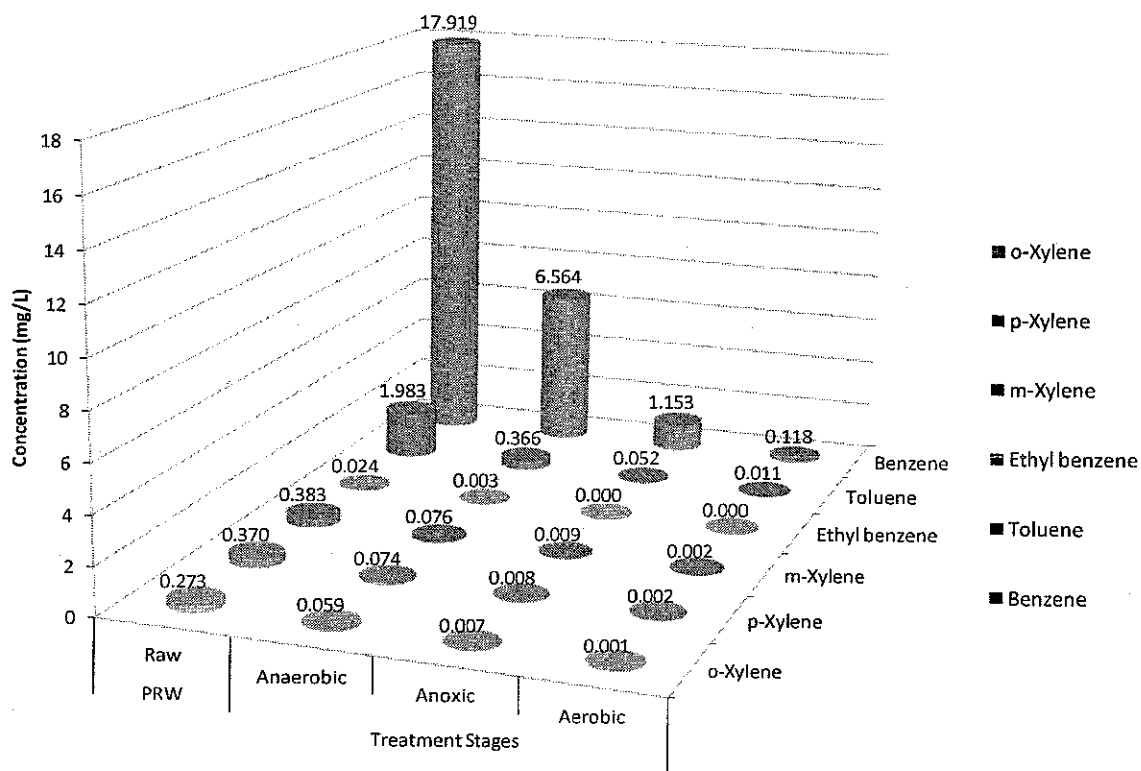
Figure 4.21: BTEX concentration throughout the anaerobic, anoxic and aerobic sequencing batch reactors treating PRW.

The anaerobic-anoxic-aerobic train treatment showed high efficiency for treatment of BTEX from PRW with near complete removal (99%), which makes this configuration essential to in the design of the reactor that proposed in the following phase of study.

At the end of this study, the following Table 4.6 shows summary for the average results obtained throughout the monitoring of the three-stage SBR reactor set-up. The good performance of the anaerobic-aerobic SBR and together with the efficient removal of BTEX showed by the three-stage SBR, all of that led to the design of the multi-stage biological reactor as discussed in the following section.

Table 4.6: Influent and effluent concentration for the three-stage SBR

Parameter	Unit	Influent	Effluent		
		PRW	Anaerobic	Anoxic	Aerobic
pH	-	8.13	8.14	8.88	9.31
DO	mg/L	0.76	1.25	1.24	5.10
Alkalinity	mg/L	4123	5153	5483	4683
COD	mg/L	1260	1001	586	344
$BOD_{5\ d,\ 20°C}$	mg/L	350	344	172	105
Ammonia	mg/L	5.94	6.45	10.35	13.58
Nitrate	mg/L	6.0	1.2	3.3	4.1
Phosphorous	mg/L	4.77	5.91	6.24	8.95
Sulfate	mg/L	12	9	627	1534
MLSS	mg/L	-	1847	1083	2883
MLVSS	mg/L	-	1210	625	1856
TSS	mg/L	190	43	38	89
VSS	mg/L	65	34	33	87
Benzene	mg/L	17.919	6.564	1.153	0.118
Toluene	mg/L	1.983	0.366	0.052	0.011
Ethyl benzene	mg/L	0.024	0.003	0.000	0.000
m-Xylene	mg/L	0.383	0.076	0.009	0.002
p-Xylene	mg/L	0.370	0.074	0.008	0.002
o-Xylene	mg/L	0.273	0.059	0.007	0.001

4.4 Phase 4: Multi-Stage Biological Reactor Performance Determination

This section presents the results that illustrate the overall performance of the integrated multi-stage biological reactor (MSBR). This section also shows the detailed results for anaerobic-anoxic-aerobic reactor that was operated in continuous flow in two parallel reactors. The results for determination of reactor performance under different loads are also presented here. This section also covers modeling and simulation results for the reactor performance by using ANN as a mathematical software tool.

The MSBR employs the multi-stage biological process similar to biological nutrient removal but with significant difference particularly on the anaerobic stage which operates independently by retaining the anaerobic sludge without the need to recycle the sludge from the clarifier, preventing dissolved oxygen and nitrate entering

this zone. Anoxic stage also retains the anoxic sludge and reduces the need for sludge recycling from aerobic and anaerobic stages. The differences could be seen with the latest development such as UCT, VIP and MUCT described in Section 2.7 compared to MSBR configuration illustrated in the following Figure 4.22.
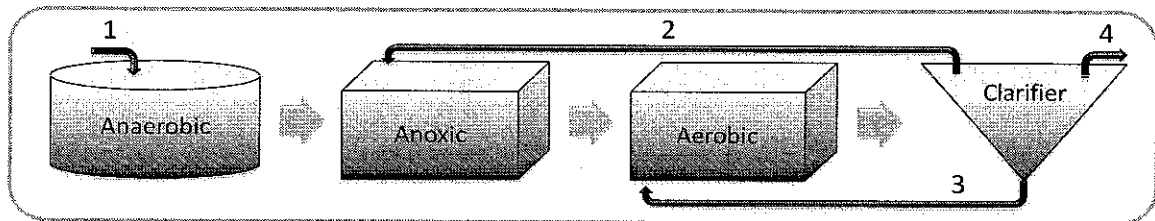
Figure 4.22: Schematic diagram of the MSBR

(1. Influent, 2. Effluent recycles to anoxic, 3. Sludge recycles to aerobic, 4. Effluent).

Incorporating the three stages which were proved to be important to accomplish maximum removal as found during the above mentioned results from these preliminary studies, and also from literature which indicate that anaerobic, anoxic and aerobic treatment all have degradation limitations, but when combined could enhance the degradation to a wide range of pollutants in a single treatment system (Perri, 1997).

MSBR receives the influent in the anaerobic stage which was designed as a cylinder at the core of the system and is also the tallest to provide closer contact which minimizes the piping and offer gravity flow to the subsequent stage. HRT was 40 hr as was observed from the SBR monitoring study and the volume for this stage and others was selected from the available perspex standard tubes during fabrication. Anoxic stage was baffled for better mixing of the reactor content as well as to prevent the flow short-circuiting. It is also at the outer circle and taller than the subsequent aerobic stage to provide closer contact which minimizes the piping and offer gravity flow to the aerobic stage with HRT of 4 hr as was observed from the SBR monitoring study. Aerobic stage is at the outer circle and attached to the clarifier with 7 hr of HRT as was observed from the SBR monitoring study. The detailed flow diagram is

illustrated in Figure 3.8 while the overall top and side view are described in the following Figure 4.23.
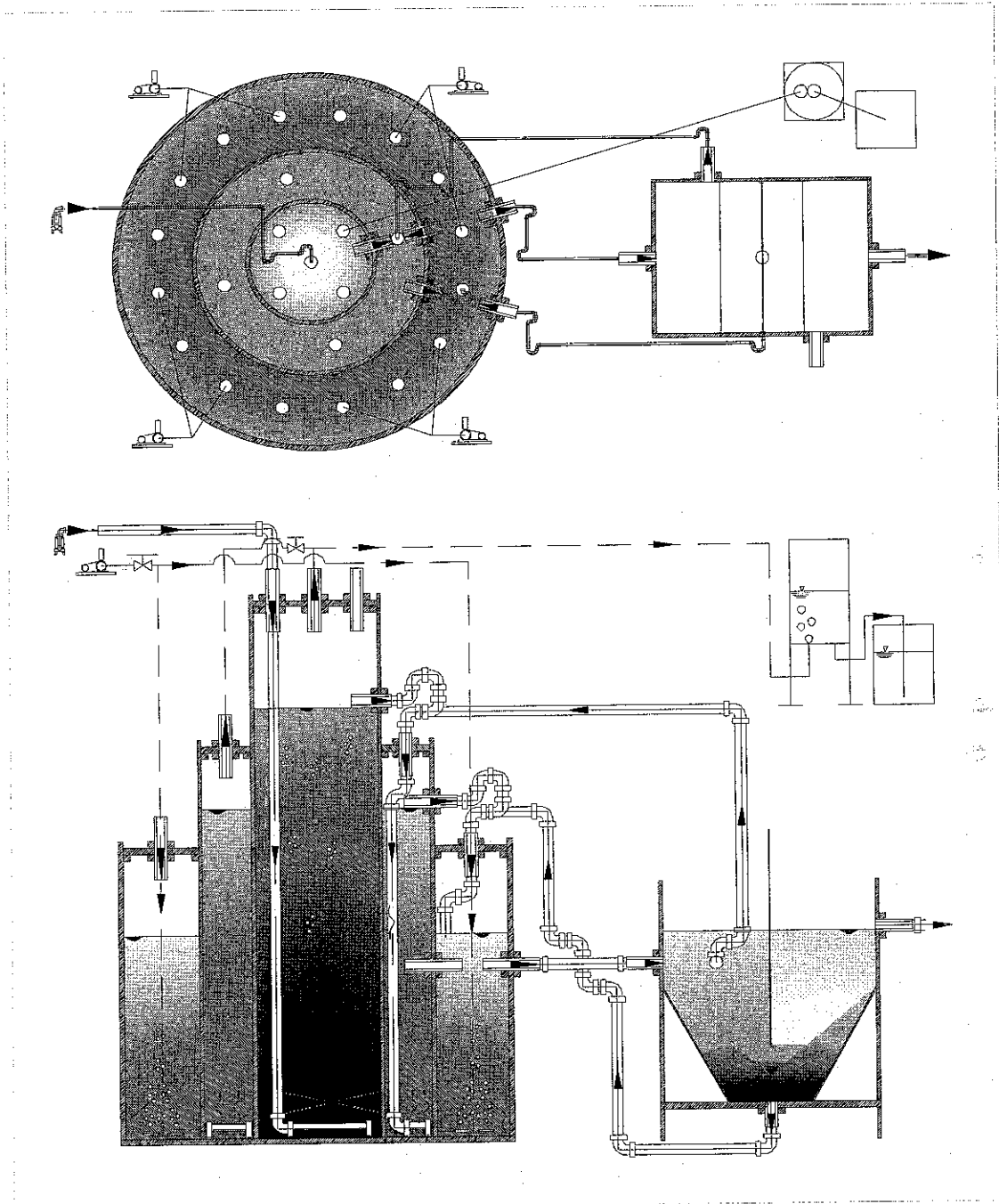
Figure 4.23: Schematic diagram of the anaerobic-anoxic-aerobic reactor, top view (top) and side section view (bottom).

Six volumetric organic loading rates (L_{org}) were applied to the two MSBRs as shown in Table 4.7. Results are presented for every stage versus the L_{org} applied to that stage and overall for MSBR by calculating the L_{org} for the whole reactor.

Table 4.7: MSBR loadings for every stage and overall

MSBR	Mode	Load	Inf. COD mg/L	L_{org} (kg/m³·d)				
				Anaerobic	Anoxic	Aerobic	Anoxic-Aerobic	MSBR
A	Anaerobic	1	982	0.58	-	-	-	0.10
		2	1504	0.89	-	-	-	0.16
		4	2476	1.47	-	-	-	0.26
B		3	2048	1.21	-	-	-	0.22
		5	3944	2.34	-	-	-	0.42
		6	6972	4.14	-	-	-	0.74
A	Anoxic	1	53	-	0.29	-	0.03	-
		2	71	-	0.38	-	0.04	-
		4	102	-	0.55	-	0.06	-
B		3	76	-	0.41	-	0.05	-
		5	165	-	0.90	-	0.10	-
		6	229	-	1.24	-	0.23	-
A	Aerobic	1	64	-	-	0.22	-	-
		2	63	-	-	0.21	-	-
		4	86	-	-	0.29	-	-
B		3	77	-	-	0.26	-	-
		5	153	-	-	0.52	-	-
		6	279	-	-	0.94	-	-

4.4.1 Multi-Stage Biological Reactor Performance under Different Loads

The petroleum refinery wastewater that was used for this study had different characteristics from the previous batches used for the other studies. In fact, each batch of the wastewater samples was different from the other in terms of strength. The present wastewater in this stage represents the extreme strength as it comes after one month from the date the facility resumed work after a shutdown exercise. This study was conducted using a batch of PRW that has moderate a BOD_5/COD ratio of around 0.4 which is considered moderate according to Metcalf and Eddy (2003). Table 4.8 shows the PRW characteristics.

Table 4.8: Influent wastewater characteristics

No.	Parameter	Unit	Amount
1	COD	mg/L	7896
2	$BOD_{5\,d,\,20°C}$	mg/L	3378
3	pH	-	8.48
4	VFA	mg/L	198
5	Ammonia-N	mg/L	13.5
6	Nitrate-N	mg/L	2.23
7	TKN	mg/L	40.6
8	Total P	mg/L	10.2
9	Total alkalinity	mg/L	990
10	Benzene	mg/L	106.709
11	Toluene	mg/L	106.045
12	Ethyl benzene	mg/L	2.749
13	m-Xylene	mg/L	5.0625
14	p-Xylene	mg/L	5.0625
15	o-Xylene	mg/L	3.017
16	Phenol	mg/L	14.458

The two reactors were monitored for approximately 180 days excluding two weeks for startup but including the transition periods whereby the load was changed until a steady state operation was reached. The experimental results were recorded when the reactor reached the steady state period for every load applied. At the end of the study, there were 7 days of operation in which the full load to both reactors was applied. MLSS and MLVSS concentration for both MSBR A and MSBR B under different volumetric organic loading rates applied are presented in Figure 4.24 and Figure 4.25. The sludge volume index (SVI) was the indication of the tendency of aerated activated sludge in the aerobic stage to settle. SVI values below 100 are desired (Metcalf and Eddy, 2003). SVI was on average 52 mL/g for the second load corresponded to MLSS concentration of approximately 1500 mg/L indicating slower settling properties and poorer biomass. The biomass continued to increase to about 3000 mg/L and SVI decreased to 45 mL/g in the fourth load indicated that the biomass was dense and has rapid settling characteristics. This behavior continued as SVI was low in the range of 47 to 39 mL/g for the other loads while the biomass concentration reached approximately 4000 mg/L.
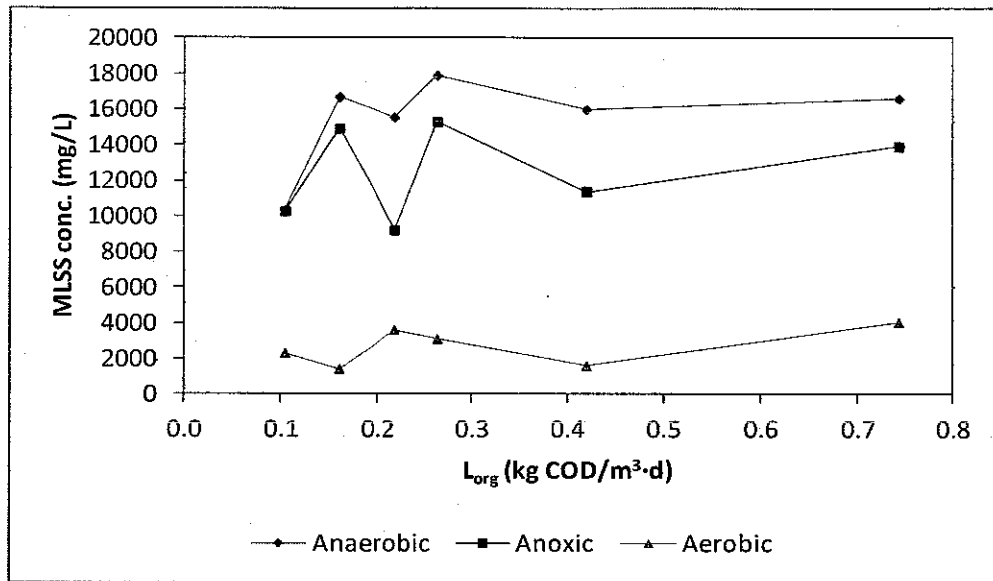
Figure 4.24: MLSS average concentrations versus L_{org} applied.
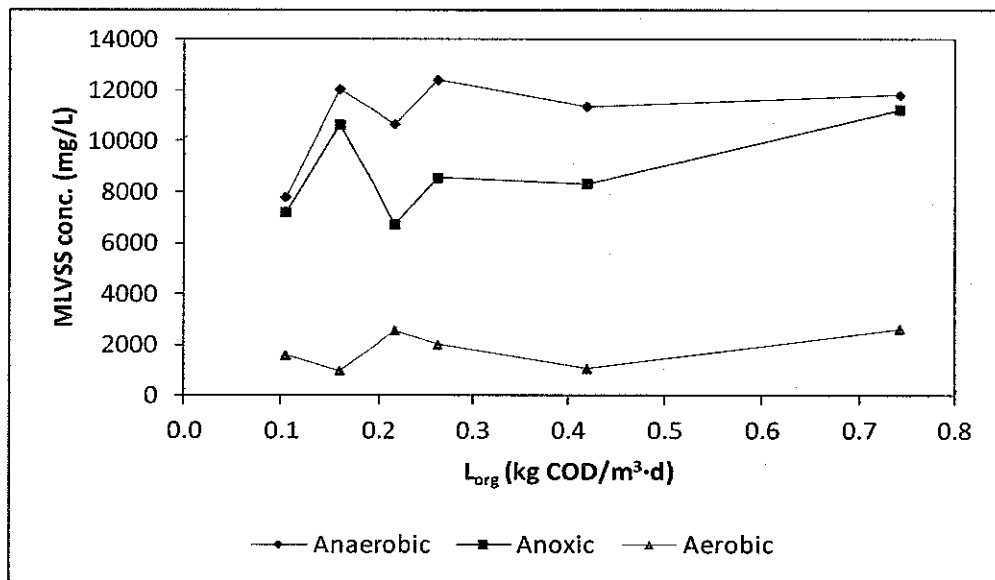
Figure 4.25: MLVSS average concentrations versus L_{org} applied.

4.4.1.1 Volumetric Organic Loading Rate

Six volumetric organic loading rates were applied stepwise by increasing the influent concentration to MSBR reactors, three loadings to each reactor as presented in Table 4.9. Figure 4.26 presents the volumetric organic loading rate applied to two multi-stage biological reactors operating in parallel versus average effluent COD concentration throughout the anaerobic, anoxic and aerobic stages treating PRW.

After the six loads were applied, the full strength actual raw petroleum refinery wastewater was applied. The average effluent concentration was noted when the reactor reached the end of the acclimatization period and comes to steady state condition.

Table 4.9: Volumetric organic loading rates applied

Period (days)	Load	MSBR	L_{org} (kg/m³·d)	COD (mg/L)
0 – 60	1	A	0.10	982
	3	B	0.22	2048
60 – 120	2	A	0.16	1504
	5	B	0.42	3944
120 – 172	4	A	0.26	2476
	6	B	0.74	6972
172 – 179	PRW	A & B	0.77	7273
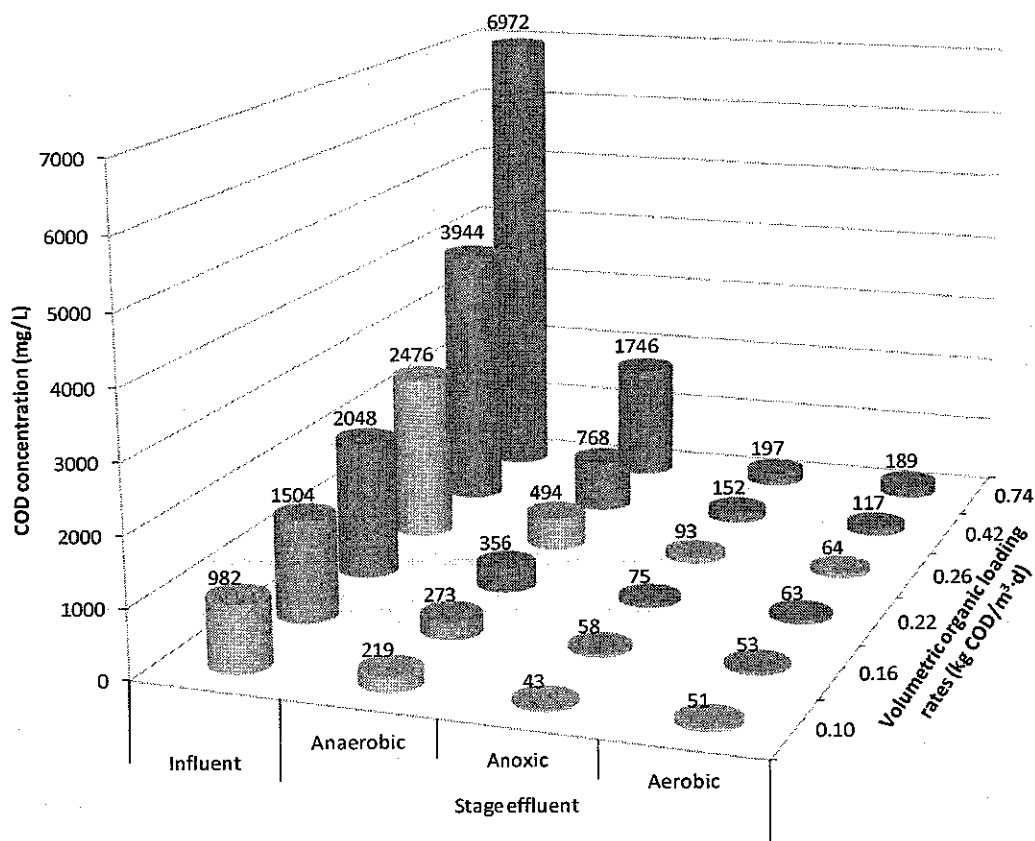
Figure 4.26: Volumetric organic loading rates applied to two multi-stage biological reactors operating in parallel versus average influent and effluent COD concentration throughout the anaerobic, anoxic and aerobic stages treating PRW.

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4.4.1.2 Chemical Oxygen Demand

COD was the key parameter to monitor the performance of the MSBR reactors as it is one of the important parameters for wastewater treatment plant as relatively shorter time is required for its determination (Khan et al., 2006). Figure 4.27 presents the average influent and effluent total COD results throughout the study period for the anaerobic stage in MSBR reactor which was operated on the basis of upflow anaerobic sludge blanket (UASB). L_{org} was calculated for this stage by considering the flowrate to the stage and the volume of the stage. From the beginning of the study period to the 60th day represent the first L_{org} 0.58 and 1.21 kg/m^3·d which were applied to reactors A and B, respectively. The removal efficiency was found to be 78% and 83% respectively. From the 60th day to the 120th day, when the L_{org} of 0.89 and 2.34 kg/m^3·d applied to reactors A and B, respectively, the COD removal efficiency was found to be 82% and 81%, respectively. From the 120th day to the 172nd of the study, L_{org} of 1.47 and 4.14 kg/m^3·d were applied to reactors A and B, respectively. The COD removal efficiency was found to be 80% and 75%, respectively.

From the data obtained, the reactors gave efficient COD removal, which was always above 75% for the entire duration of the study. The highest percentage COD removal was 83% and was achieved by Reactor B at 1.21 kg/m^3·d and influent COD concentration of 2048 mg/L, whilst the lowest effluent COD concentration was 219 mg/L and was achieved by Reactor A at 0.58 kg/m^3·d and influent COD concentration of 982 mg/L.

At organic loading rate (OLR) of 1.21 kg/m^3·d, hydraulic retention time (HRT) of 40 h and influent COD of 2048 mg/L, the COD removal was 83% and found to be better than that recently reported in the literature (Ghavipanjeh and Shayagen, 2004) with 81% COD removal at OLR of 0.4 kg/m^3·d and HRT of 48 h and influent COD of 1000 mg/L.

After all six L_{org} loads were applied, the anaerobic stage was in steady state operation at L_{org} 1.47 and 4.14 kg/m^3·d applied to UASB reactors A and B, respectively. After which, the full load of 4.31 kg/m^3·d was applied to anaerobic

stage in reactors A and B. The reactors coped with the full load at the end of the study and shows high removal efficiencies. For reactor A, the full load represented three times increase in the L_{org}, which might caused a shock load to the microbes but there was significant adjustment with 65% removal efficiency. For reactor B, the removal efficiency was 80% with similar effluent concentration to reactor A in the MSBR as one treatment system.
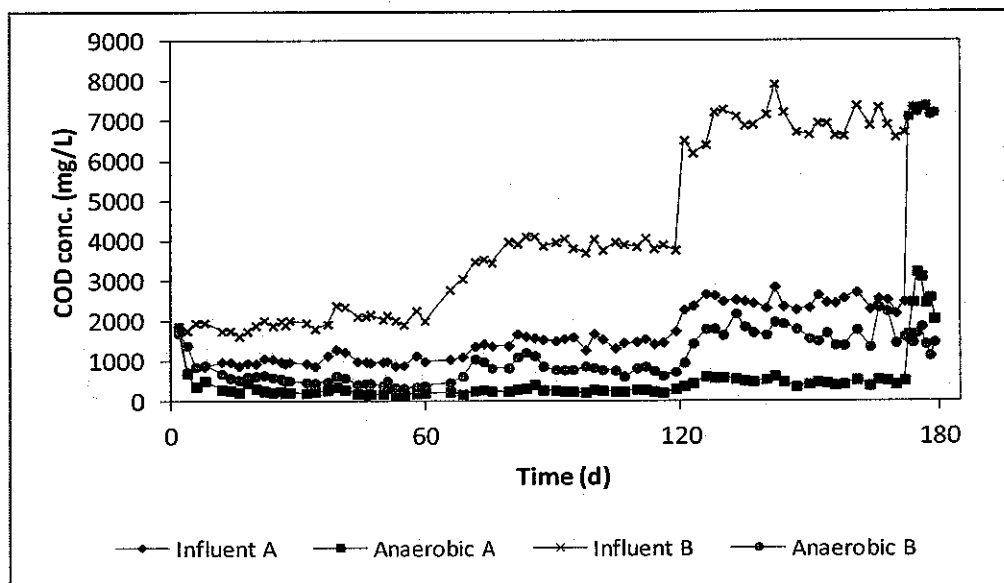
Figure 4.27: COD concentration versus time for anaerobic stage in reactor A and reactor B.

The average influent and effluent COD concentration when the reactor reached the steady state condition for each volumetric organic loading rate (L_{org}) were plotted in Figure 4.28 together with removal percentage versus volumetric organic load (calculated for the stage) applied to reactor. It can be observed that as L_{org} increased the discharge effluent concentration also increased. The removal percentage was initially 78% and continued to increase until the highest was 83%, after which it started to decrease until reaching 72% at the last load as shown in Figure 4.28.

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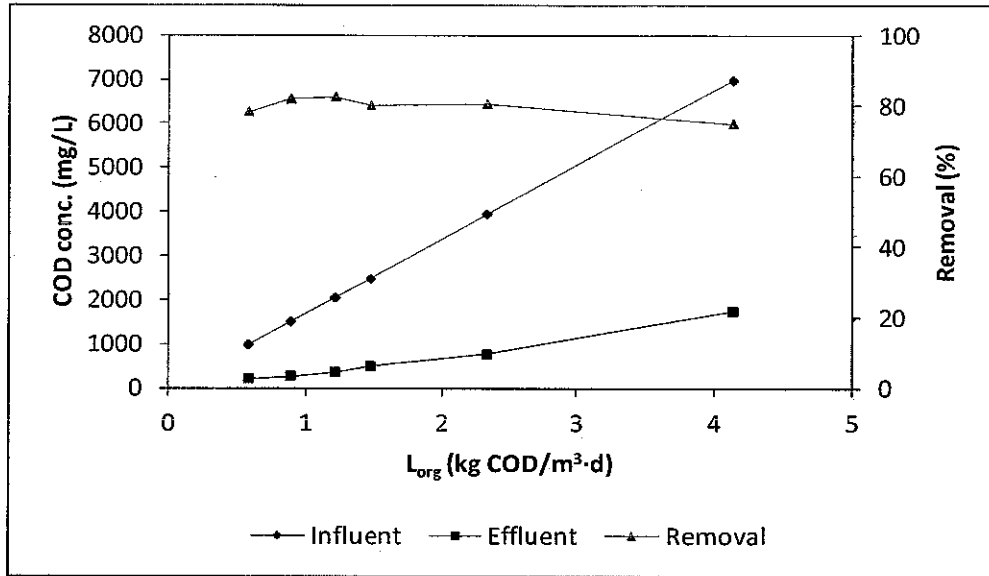
Figure 4.28: Average COD for influent, effluent and removal versus L_{org} for anaerobic stage in reactor A and B.

Figure 4.29, shows the specific substrate removal rate calculated for COD removed per MLVSS concentration in the reactor with respect to reactor volume and flowrate, plotted against reactor effluent COD concentration for the anaerobic stage. It can be observed that the correlation coefficient R^2 was 0.96.
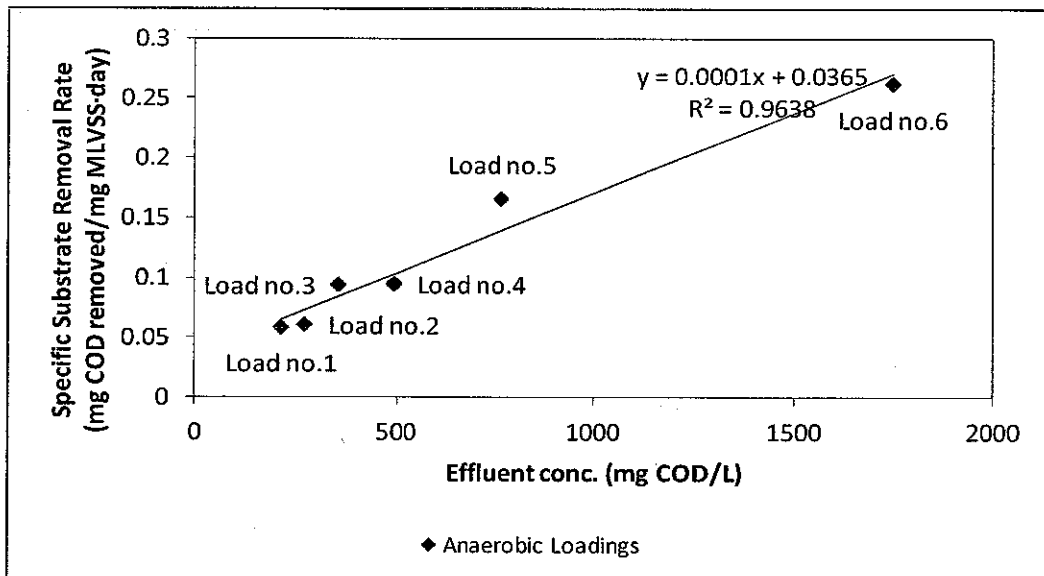
Figure 4.29: Specific total COD utilization rate versus effluent COD concentration for anaerobic stage in reactor A and B.

The average influent and effluent total COD results for the anoxic and aerobic stages are shown in Figure 4.30 and Figure 4.31 respectively. The two stages work with high recycle ratio, thus the influent and effluent are very close to each other. The removal efficiency during the application of all loads for anoxic stage was 11% on average with 19% as maximum recorded. The removal efficiency for aerobic stage was 22% on average with 32% as maximum recorded.
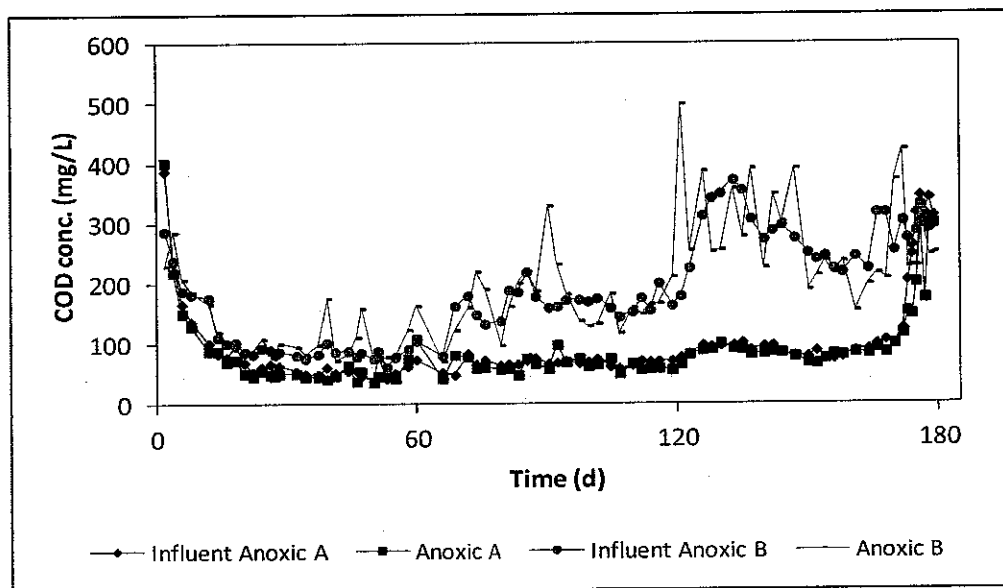
Figure 4.30: COD concentration versus time for anoxic stages in reactor A and B.
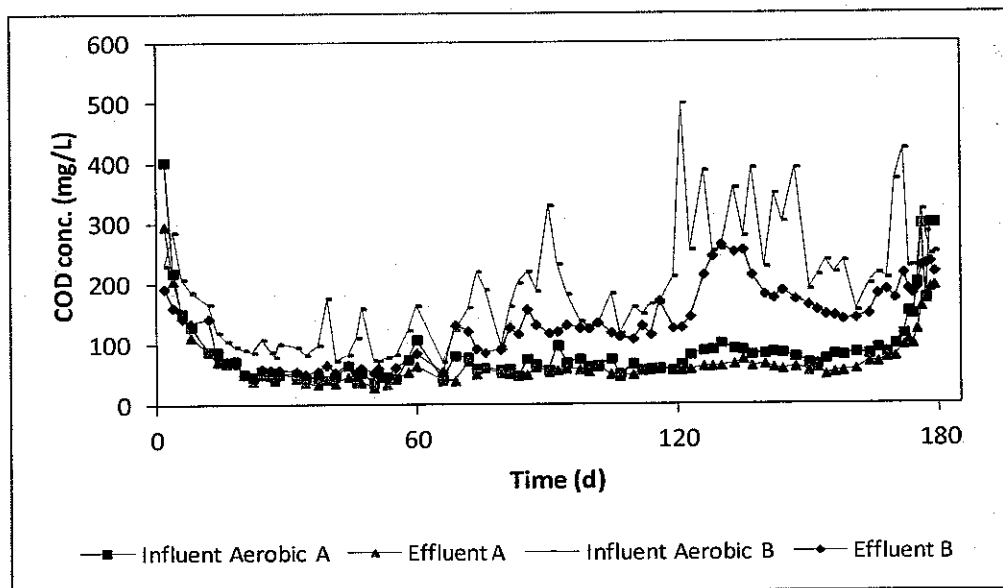
Figure 4.31: COD concentration versus time for aerobic stages in reactor A and B.

The average influent and effluent COD concentration when the reactor reached the steady state condition for each volumetric organic loading rate (L_{org}) was plotted in Figure 4.32 and Figure 4.33 together with removal percentage versus volumetric organic load (calculated for the stage) applied to reactor. It can be observed that as L_{org} increased the discharge effluent concentration also increased. The removal percentage for anoxic and aerobic stages was initially 18 and 19% respectively, and continued to increase until the highest was 19 and 32% respectively.
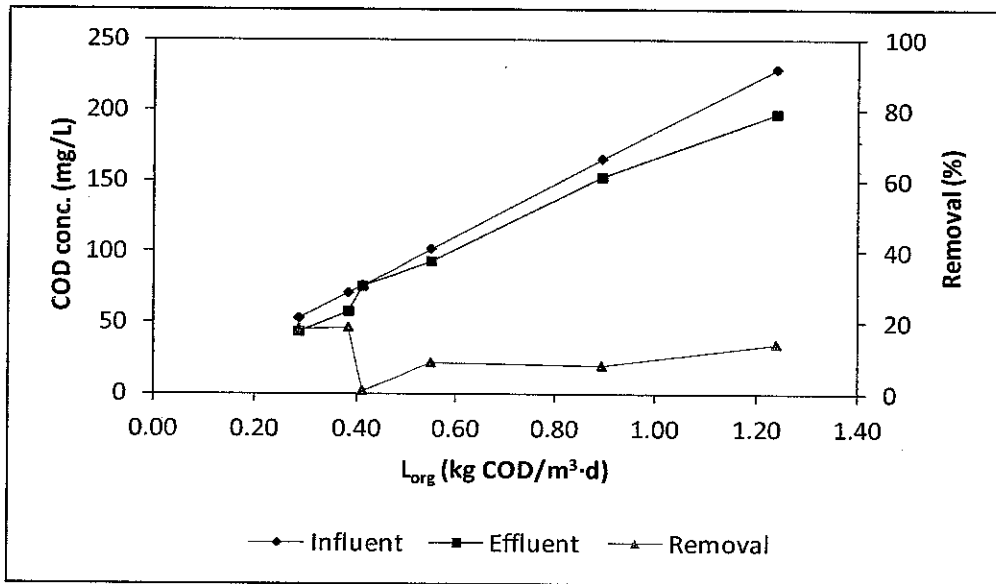
Figure 4.32: Average COD for influent, effluent and removal versus L_{org} for anoxic stages in reactor A and B.
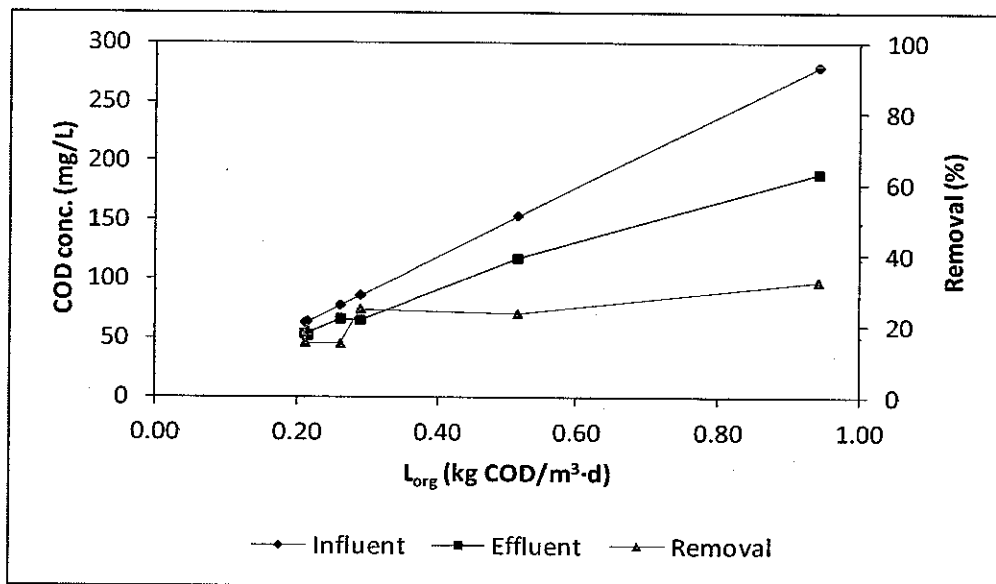
Figure 4.33: Average COD for influent, effluent and removal versus L_{org} for aerobic stages in reactor A and B.

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Figure 4.34 and Figure 4.35, show the specific substrate removal rate calculated for COD removed per MLVSS in the reactor and reactor volume and flowrate, plotted versus reactor effluent COD concentration for anoxic and aerobic stages. It can be observed that the correlation coefficient R^2 were 0.54 and 0.80 respectively.
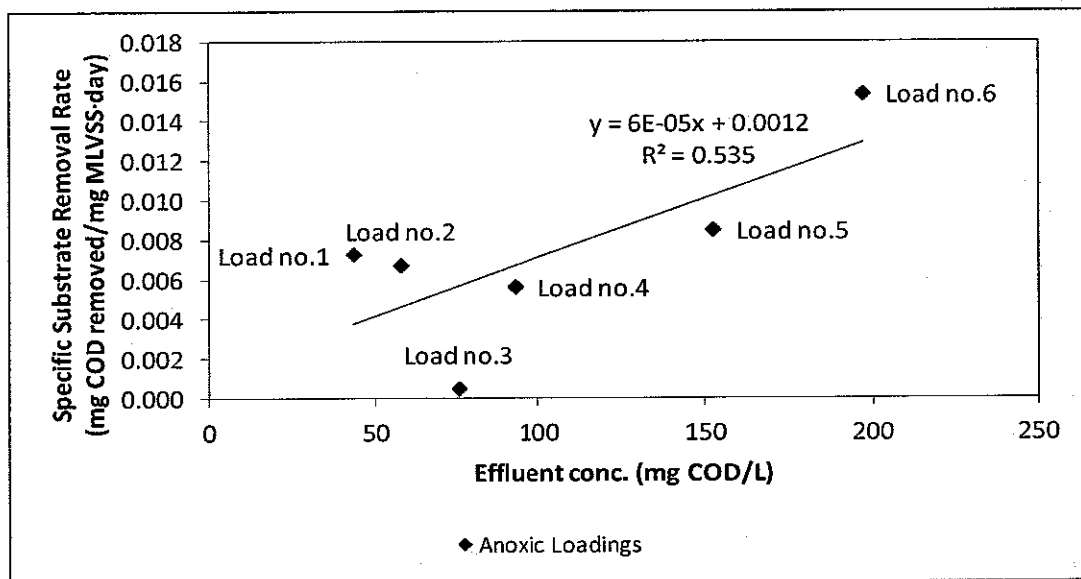
Figure 4.34: Specific total COD utilization rate versus effluent COD concentration for anoxic stages in reactor A and B.
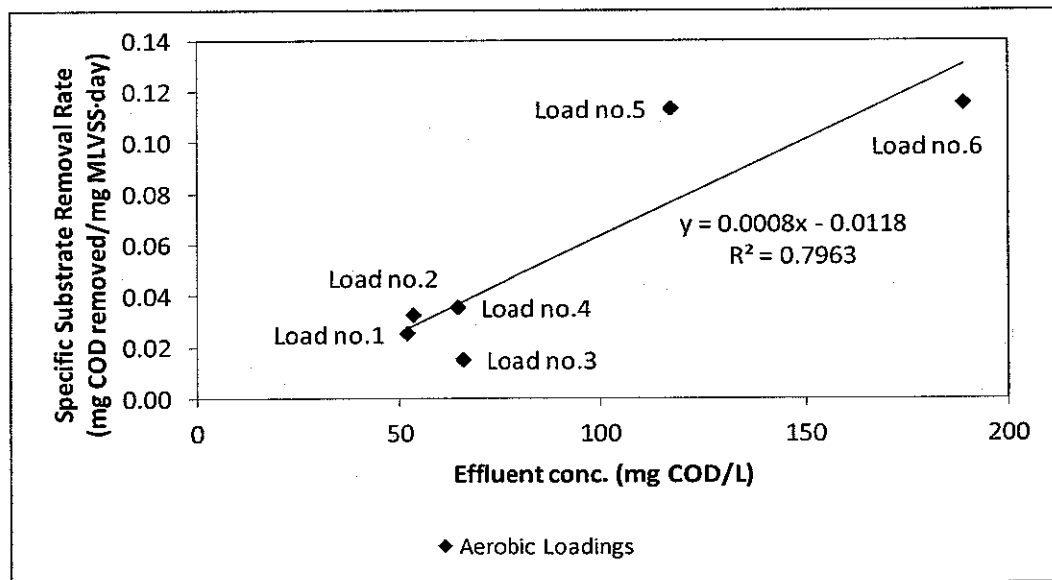
Figure 4.35: Specific total COD utilization rate versus effluent COD concentration for aerobic stages in reactor A and B.

Considering the anoxic and aerobic stages as one stage named anoxic-aerobic stage, Figure 4.36 presents the average influent and effluent total COD results for the anoxic-aerobic stage versus days of experiment. The two stages work with high recycle ratio, thus it will be considered as one stage.
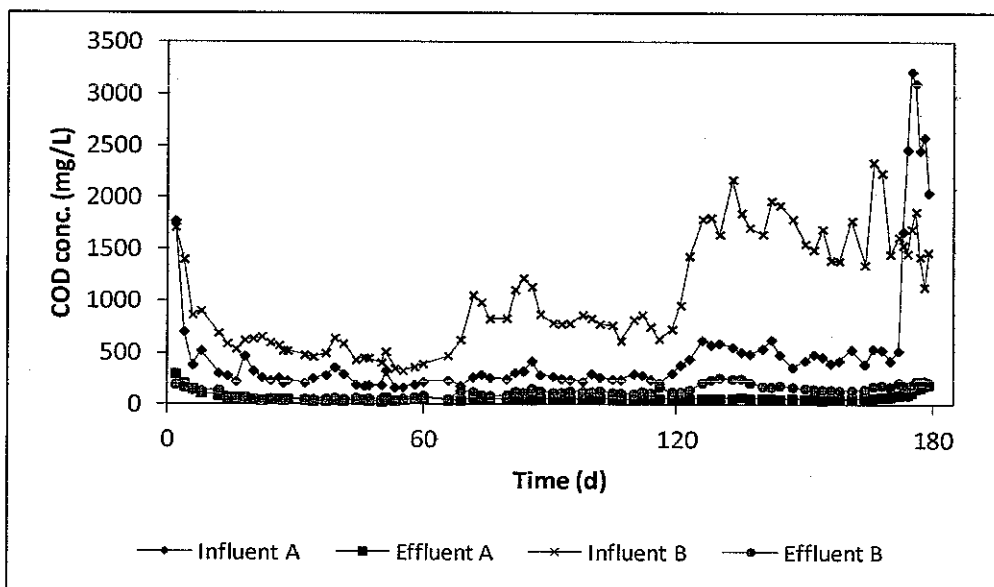
Figure 4.36: COD concentration versus time for anoxic-aerobic stages in reactor A and reactor B.

The average influent and effluent COD concentration when the reactor reached the steady state condition for each volumetric organic loading rate (L_{org}) was plotted in Figure 4.37 together with removal percentage versus volumetric organic load (calculated for the anoxic-aerobic stage) applied to reactor. It can be observed that as L_{org} increased the effluent concentration also increased. The removal percentage was initially 76% and continued to increase until the highest was 89% recorded in the last load. This indicates that the stage did not come to maximum capacity after which it decline in efficiency.
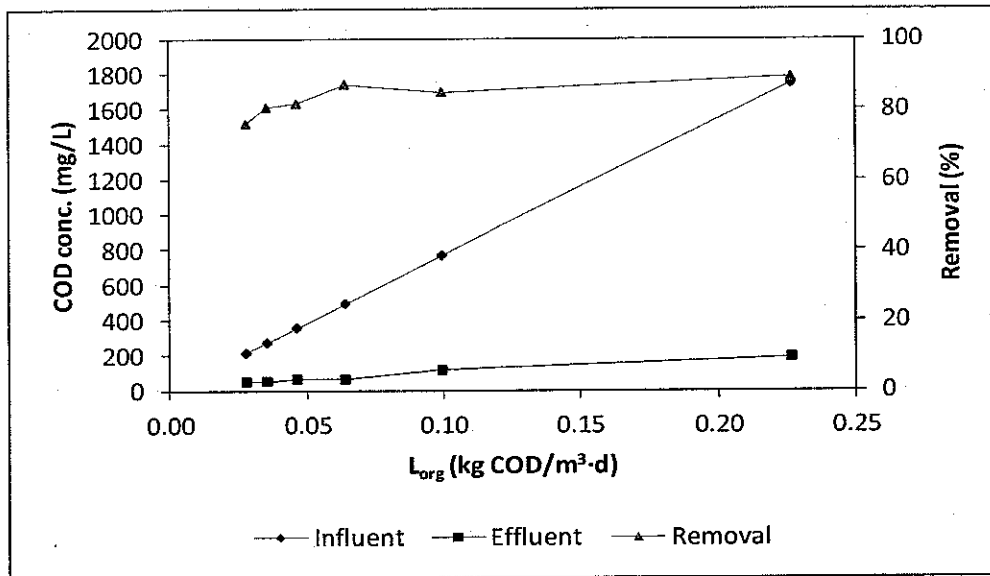
Figure 4.37: Average COD for influent, effluent and removal versus L_{org} for anoxic-aerobic stage in reactor A and B.

Figure 4.38, shows the specific substrate removal rate calculated for COD removed per MLVSS concentration in the reactor with respect to reactor volume and flowrate, plotted versus reactor effluent COD concentration for anoxic-aerobic stage. It can be observed that the correlation coefficient R^2 was 0.98.
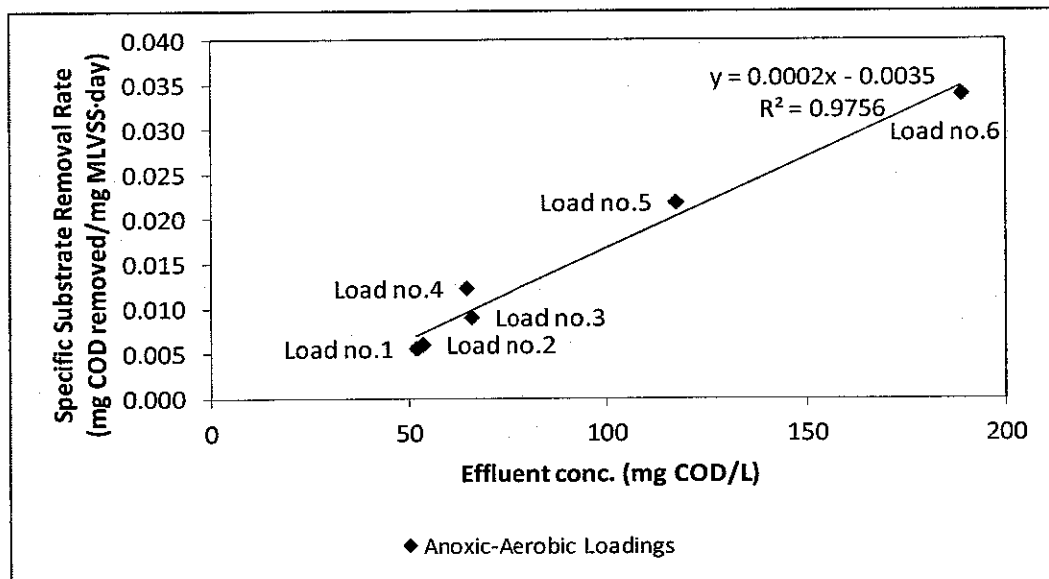
Figure 4.38: Specific total COD utilization rate versus effluent COD concentration for anoxic-aerobic stage in reactor A and B.

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The overall COD removal for the multi-stage biological reactor MSBR A and MSBR B was found to be in the range of 95% to 97%. Figure 4.39 presents the influent and effluent for all stages (anaerobic, anoxic and aerobic) in MSBR during the application of all six L_{org} and the full actual PRW load. Despite the high removal percentage, the final effluent COD concentration was below 100 mg/L for the first four loads and relatively high for the other two loads and also when actual PRW applied.
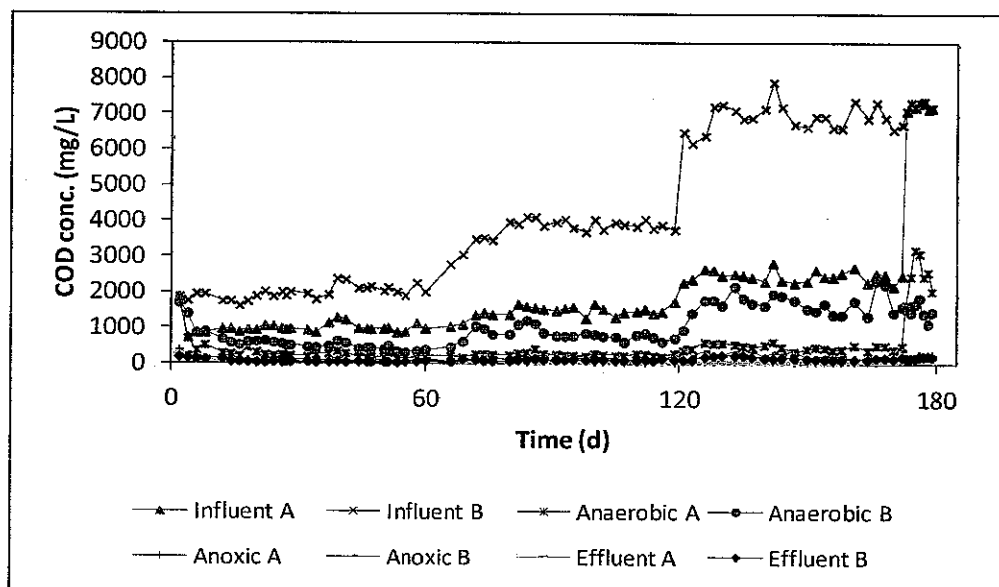
Figure 4.39: Influent and effluent COD concentration versus time for the three stages in MSBR A and B.

Each MSBR received three L_{org} before the full PRW applied. MSBR A effluent concentration was 65 mg COD/L and increased to 181 mg COD/L after full load was applied; while MSBR B effluent concentration was 168 mg COD/L and increased to 228 mg COD/L as shown in Figure 4.40.
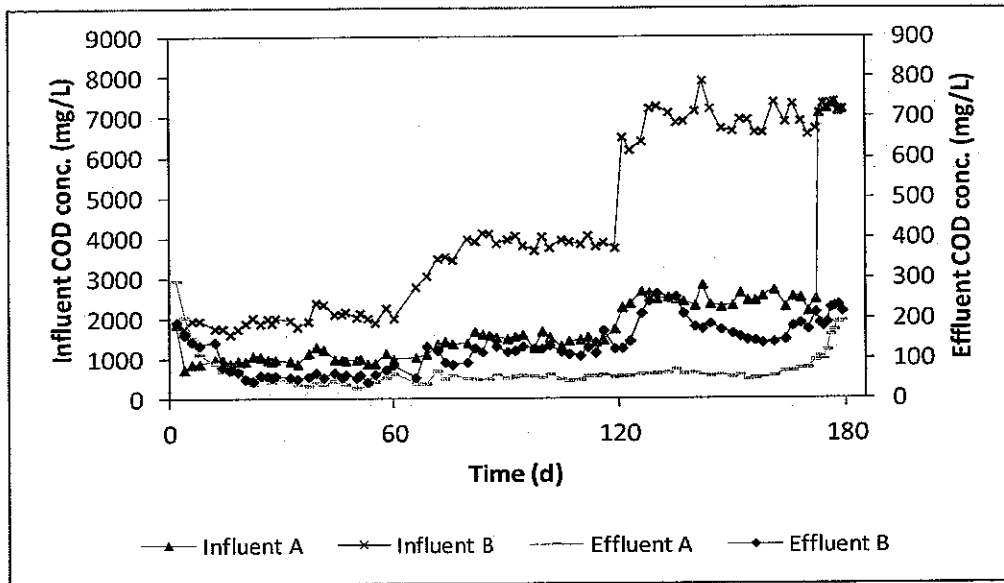
Figure 4.40: Influent and effluent COD concentration versus time for MSBR A and B.

The average influent and effluent COD concentration when the reactor reached the steady state condition for each volumetric organic loading rate (L_{org}) was plotted in Figure 4.41 together with removal percentage versus volumetric organic load (calculated for the MSBR) applied to reactor. It can be observed that as L_{org} increased the discharge effluent concentration also increased but was below 65 mg/L for the first four loads, and reached 117 and 189 mg/L for the other two loads respectively. The removal percentage was initially 95% and continued to increase until the highest was 97% recorded in the last load. This indicates that the reactor did not come to maximum capacity after which it decline in efficiency.
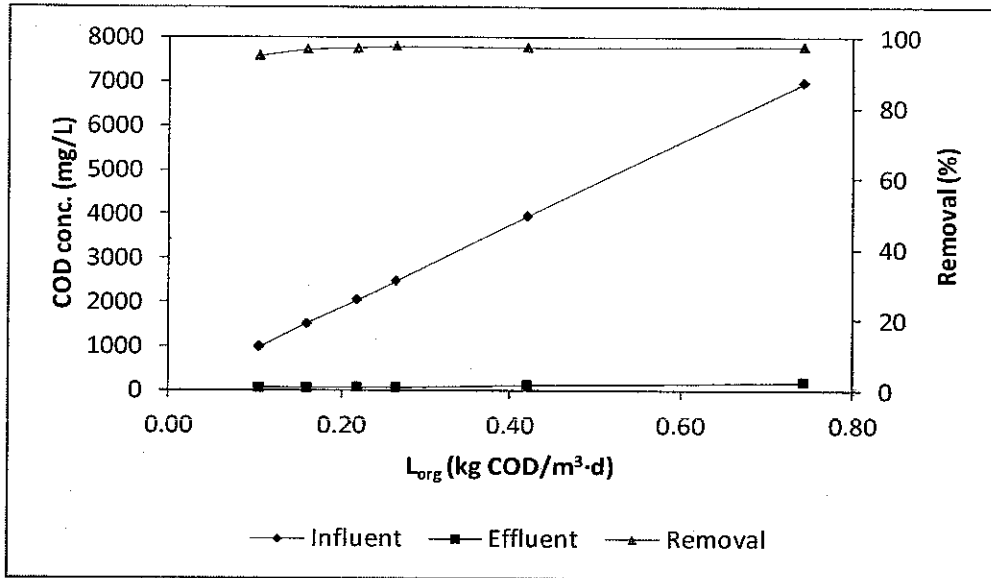
Figure 4.41: Average COD for influent, effluent and removal versus L_{org} for MSBR reactor A and B.

Figure 4.42, shows the specific substrate removal rate calculated for COD removed per MLVSS concentration in the reactor (calculated for all stages) with respect to MSBR reactor volume and flowrate, plotted versus reactor effluent COD concentration for MSBR. It can be observed that the correlation coefficient R^2 was 0.95.
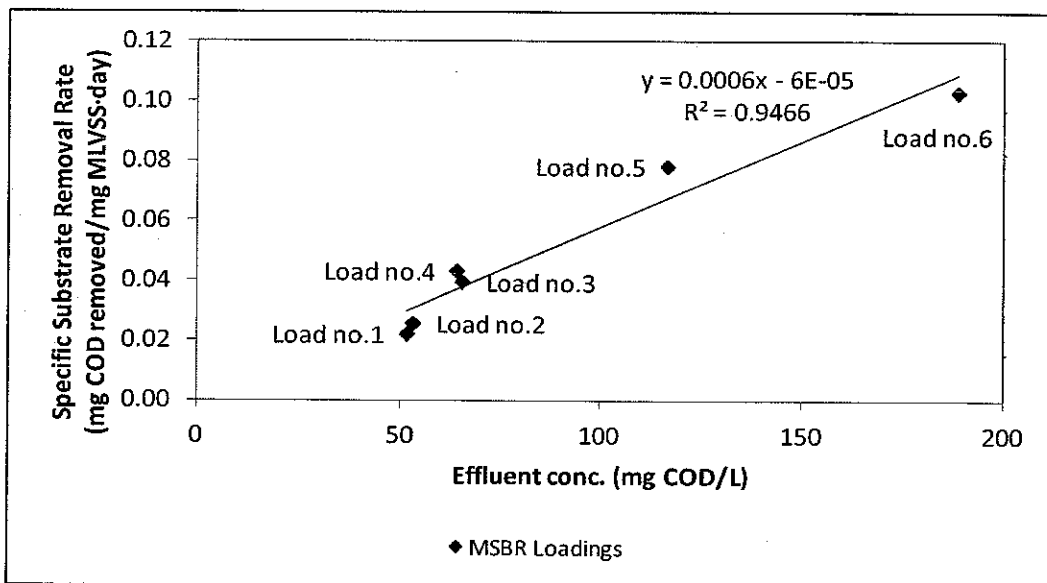
Figure 4.42: Specific total COD utilization rate versus effluent COD concentration for MSBR in reactor A and B.

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Summary for influent concentration applied to the MSBR reactors and after treatment effluent concentration in the three stages is shown in Table 4.10.

Table 4.10: MSBR performance under different influent COD concentration

Load	MSBR	Influent (mg/L)	Effluent (mg/L)		
			Anaerobic	Anoxic	Aerobic
1	A	982	214	43	52
2	A	1504	273	58	53
3	B	2048	357	75	66
4	A	2476	494	93	64
5	B	3944	768	152	117
6	B	6972	1746	197	189
PRW	A	7273	2552	268	181
PRW	B	7273	1479	276	228

4.4.1.3   Alkalinity

Alkalinity was increased for the influent to buffer the UASB reactors (anaerobic compartment in MSBRs) and prevent them from turning sour. To maintain buffering capacity for the reactors, alkalinity was added in the form of sodium bicarbonate to the influent of the anaerobic reactors. Alkalinity was not significantly produced as it might be consumed by carbon dioxide that dissolved in the reactors due to the partial pressure of gas in the reactor (Metcalf and Eddy, 2003). Figure 4.43 shows the alkalinity variation in the anaerobic stages in the MSBRs.
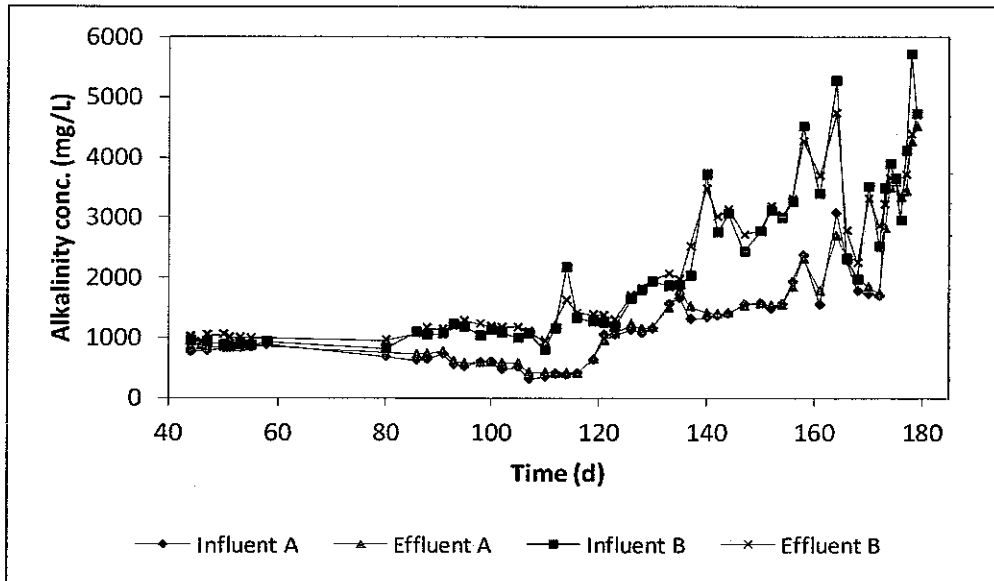
Figure 4.43: Alkalinity versus time for anaerobic stage in reactor A and reactor B.

It could be observed that the anaerobic effluent alkalinity was slightly higher than the influent as shown in Figure 4.44 with respect to the six volumetric organic loads (L_{org}) applied.
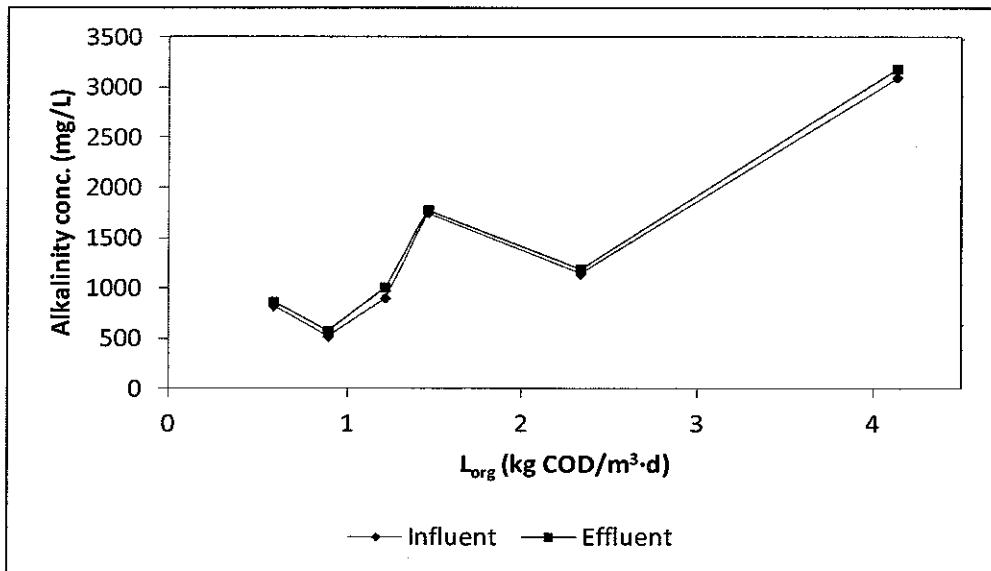
Figure 4.44: Average alkalinity versus L_{org} for anaerobic stage in reactor A and reactor B.

4.4.1.4 pH

pH for the influent and effluent of the anaerobic stages were left without adjustment. pH was adjusted once a day for the anoxic and aerobic reactors by decreasing it to neutral pH. Despite that, the pH was not stable and continued to increase. Influent pH during the experimental period was found to be on average slightly above neutral and increased more in the anaerobic effluent and subsequent stages as shown in Figure 4.45 and Figure 4.46.
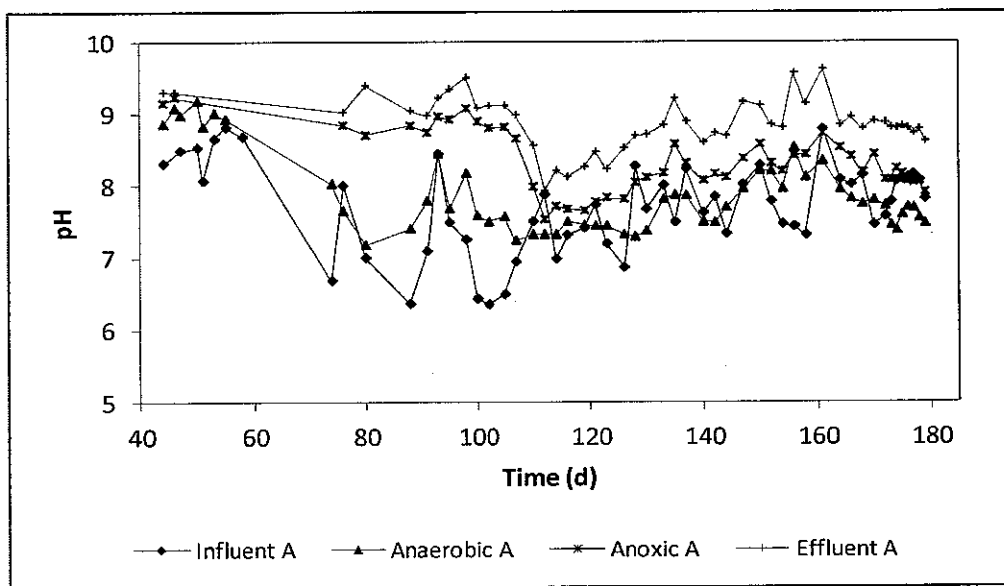
Figure 4.45: pH versus time for MSBR A.
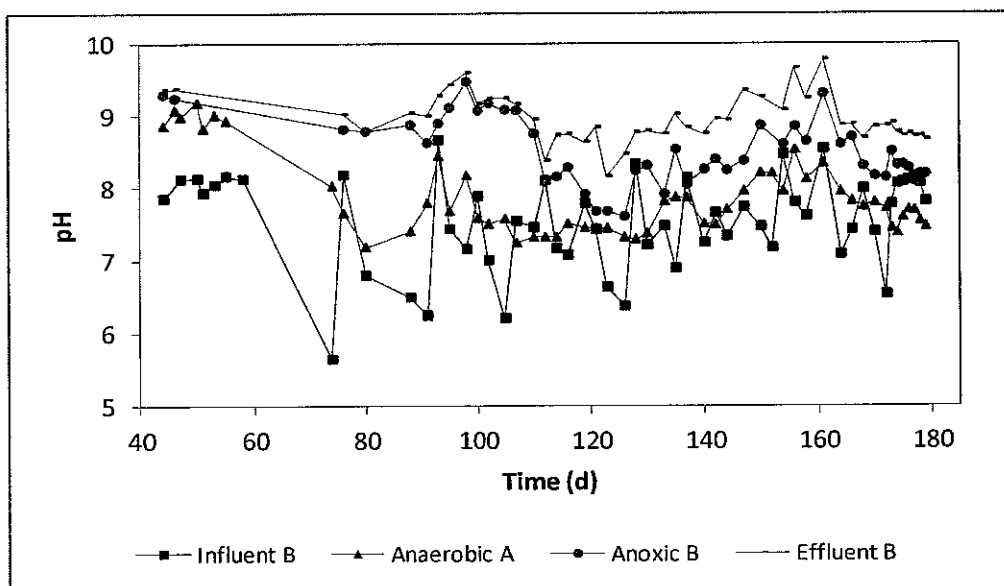
Figure 4.46: pH versus time for MSBR B.

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It can be observed that the pH increases throughout the stages which could be related to the alkalinity produced as shown in Figure 4.47 with respect to the six volumetric organic loads (L_{org}) applied. The optimal degradation performance occurs near a neutral pH, but pH in the range of 6.0 to 9.0 does not affect much the carbonaceous removal and is tolerable (Metcalf and Eddy, 2003).
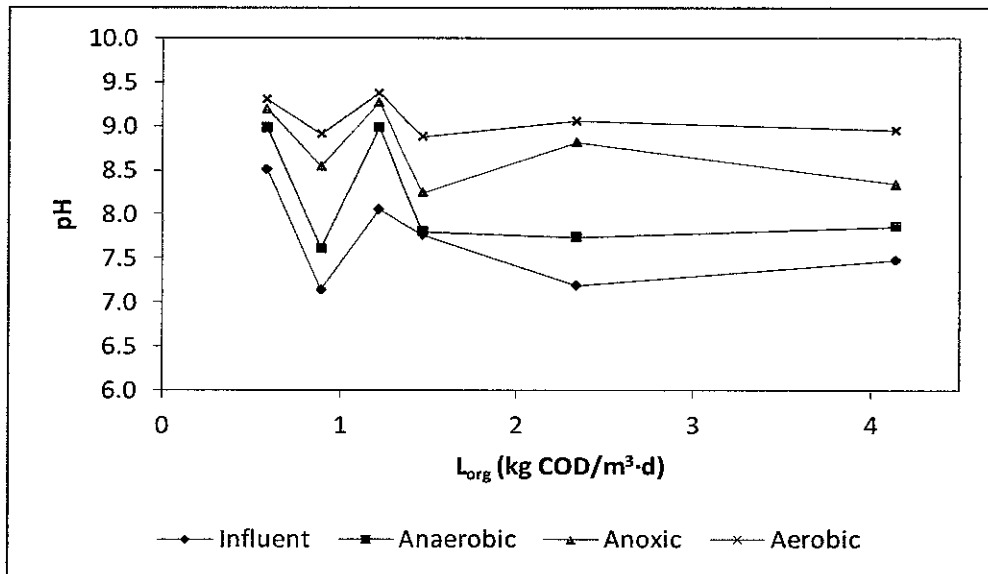
Figure 4.47: Average pH versus L_{org} for MSBR reactor A and reactor B.

4.4.1.5 Volatile Fatty Acid (VFA)

VFA was monitored in the two UASB reactors to ensure the VFA/alkalinity ratio was maintained less than 0.4 (Borja et al., 1998) and 0.5 (Zaher et al., 2008) by adjusting the reactors alkalinity. The average VFA concentration was plotted against time as shown in Figure 4.48 and Figure 4.49. The average VFA/alkalinity ratio was plotted against time as shown in Figure 4.50. The ratio was successfully maintained most of the time which was necessary (Behling et al., 1997) for the digester to be able to accommodate all potential fluctuations without major change in pH. The ratio was increased when the full load applied after which the reactor was recovered.

The process was stable at different concentrations for the anaerobic stages in MSBR reactor A and B because they were operated at different loads. As the load applied to the reactors was increased to a same load (raw undiluted PRW), the VFA in the reactors was also increased to similar concentrations.
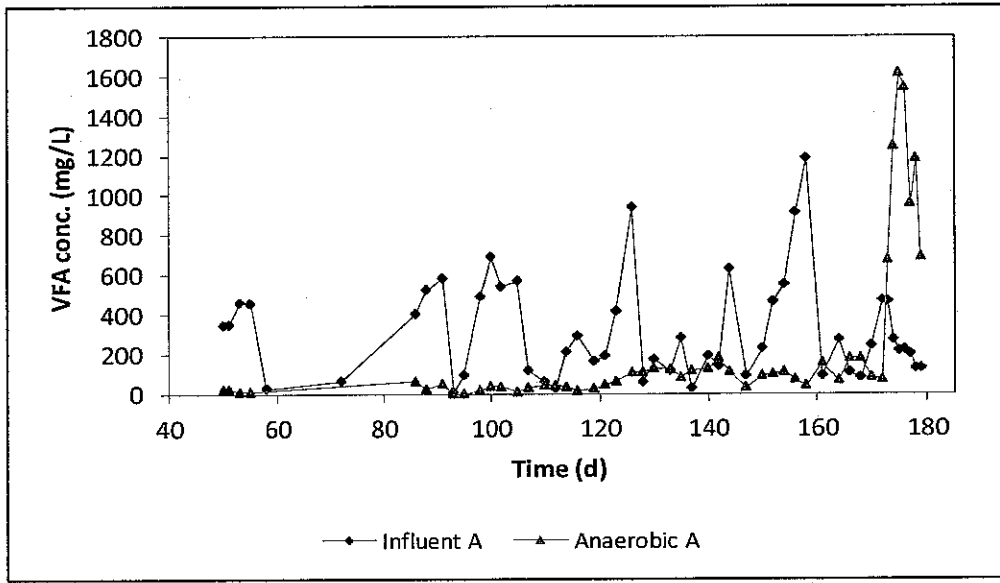
Figure 4.48: VFA versus time for anaerobic stage in reactor A.
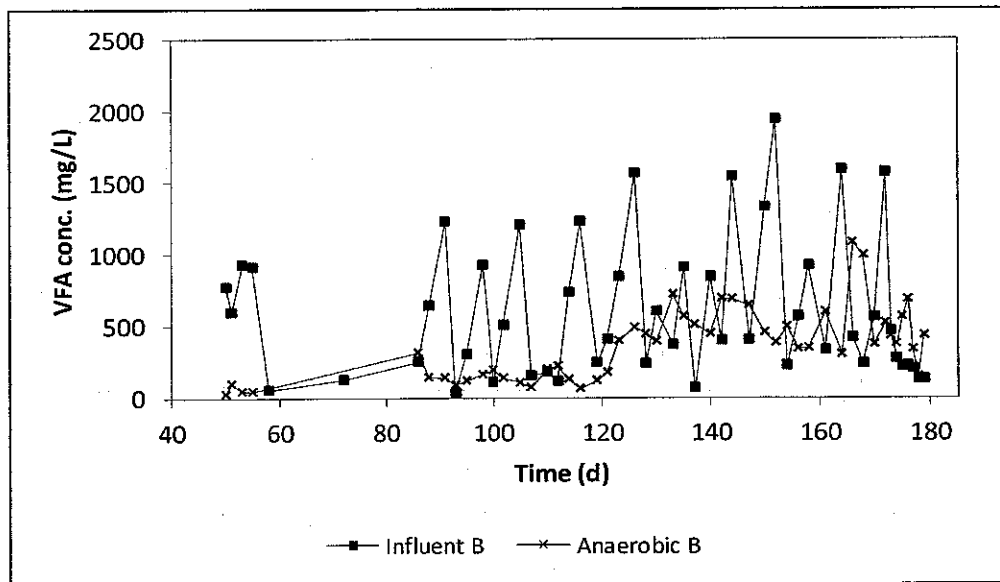
Figure 4.49: VFA versus time for anaerobic stage in reactor B.
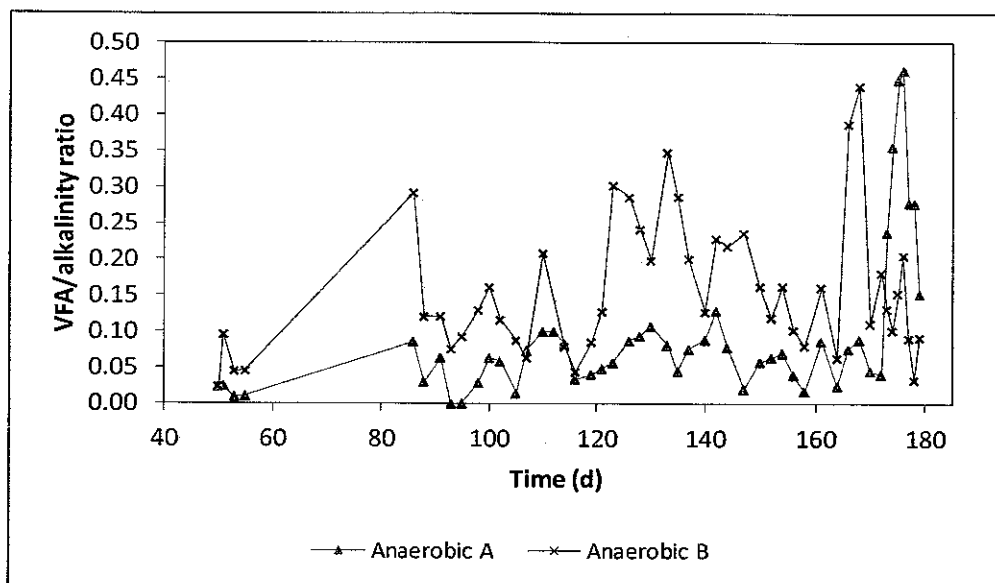
Figure 4.50: VFA/alkalinity ratio versus time for anaerobic stage in reactor A and B.

Figure 4.51 illustrates the average data for volatile fatty acid (VFA) concentration at steady state condition and the VFA/alkalinity ratio for the anaerobic reactors versus the six volumetric organic loads applied to the two reactors. The VFA concentration for the first five loads was found to be less than 150 mg/L indicating high methanogenic activity (Borja et al., 1998) and sufficient methanogenic population exists and sufficient time is available to minimize hydrogen and VFA concentrations (Metcalf and Eddy, 2003). That could keep the concentration low even when the load was constantly increased. But when the load was further increased to much higher than initial as represented by the sixth load (4.14 $kg/m^3 \cdot d$), the VFA suddenly increased to higher concentration (551 mg/L). The VFA/alkalinity ratio was targeted to be less than 0.4 which was necessary for the anaerobic reactor to be able to balance all potential fluctuations without major change in pH (Behling et al., 1997). The ratio was successfully maintained by adjusting the reactors alkalinity for all loads applied. When the first load was applied to the reactor, the VFA concentration was low, for that the alkalinity was also kept low. As the L_{org} applied to the reactors was increased, the steady state average VFA also increased and alkalinity was elevated to maintain the VFA/alkalinity ratio. Overall, the VFA/alkalinity ratio was found to be always much lower than the failure limit (0.3-0.4) value (Borja et al., 1998).

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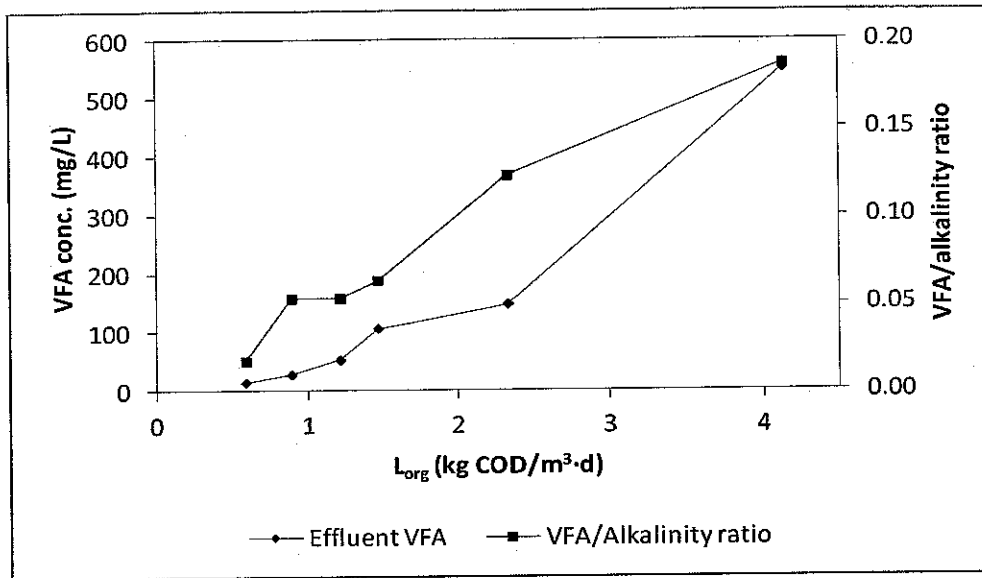
Figure 4.51: Average VFA and VFA/alkalinity ratio versus L$_{org}$ for anaerobic stage in reactor A and B.

4.4.1.6   Gas Production

Gas production was monitored for anaerobic stage in both MSBRs as shown in Figure 4.52 and Figure 4.53 which presents the actual measured gas and the theoretical methane and the theoretical gas calculated as shown in Section 3.5.2. Anaerobic stage in MSBR B which operated at higher load was producing amount of gas on average (2 L/d) closer to the theoretical (2.5 L/d) compared to in MSBR A which was producing amount of gas (0.7 L/d) half of the theoretical (1.4 L/d). Carbon dioxide is produced in the reactor and due to the pressure of gas in the reactor as well as in the gas collector, carbon dioxide solubilizes in the water (Metcalf and Eddy, 2003) resulted in less amount of gas and carbon dioxide. At higher gas production as in MSBR B, there was less time for carbon dioxide to dissolve into reactor water and gas collection system water.
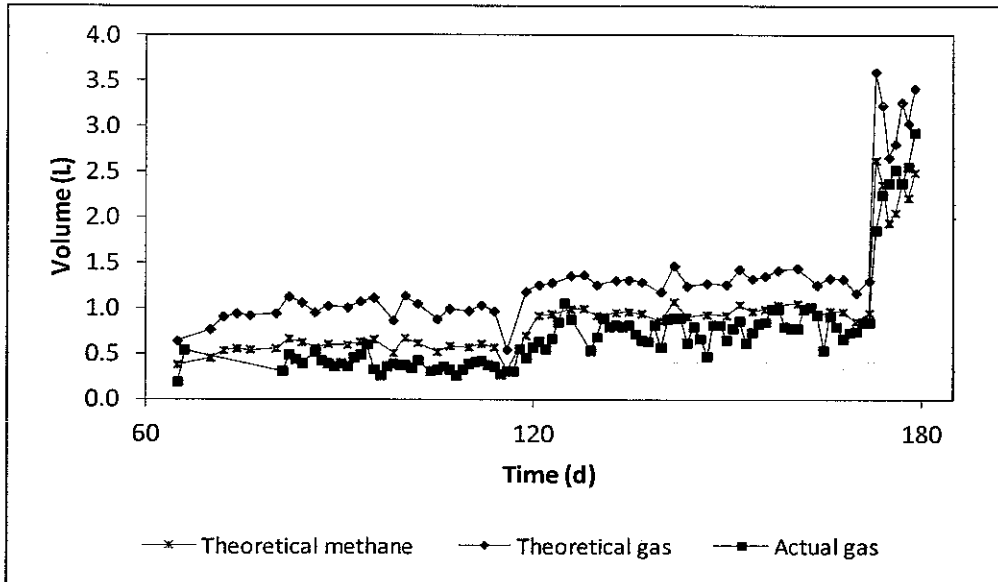
Figure 4.52: Gas production versus time for anaerobic stage in MSBR A.
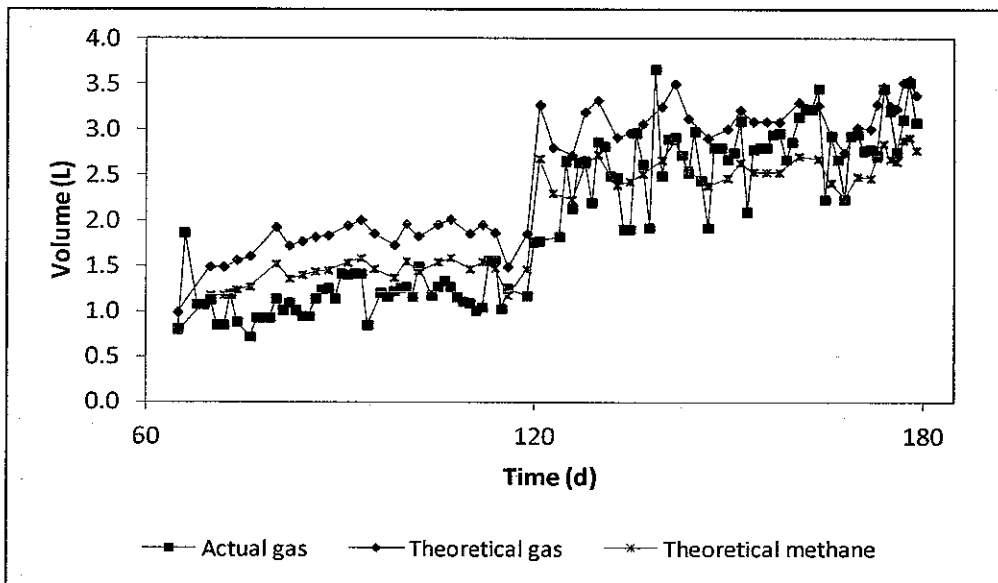
Figure 4.53: Gas production versus time for anaerobic stage in MSBR B.

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4.4.1.7 Ammonia-N

The average influent and effluent ammonia-nitrogen results for the anoxic-aerobic stage throughout the study period are shown in Figure 4.54. The average influent and effluent concentration was 3 and 1 mg/L, respectively. There was fluctuation during the study period for both influent and effluent concentrations. But when the reactors reached the steady state condition, there was removal in both reactors and found to be in the rage of 51-80%.
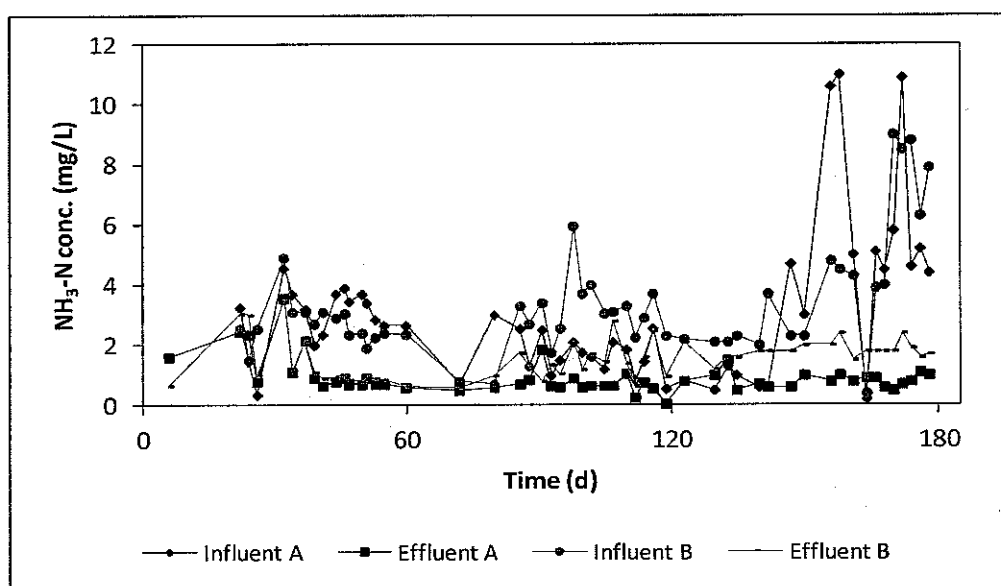
Figure 4.54: Ammonia-N versus time for anoxic-aerobic stage in reactor A and B.

Figure 4.55 presents the influent, effluent and removal percentage for ammonia-nitrogen versus six L_{org} applied on the anoxic-aerobic stage in MSBR A and B. The average influent and effluent concentrations continued to increase as the L_{org} increased, while the average removal was 63%. The nitrification was mainly affected by the pH value which increased most of the time beyond the optimum level of 7.5 to 8, and also inhibited by the presence of petroleum refinery refractory compounds such as phenol and benzene (Metcalf and Eddy, 2003).
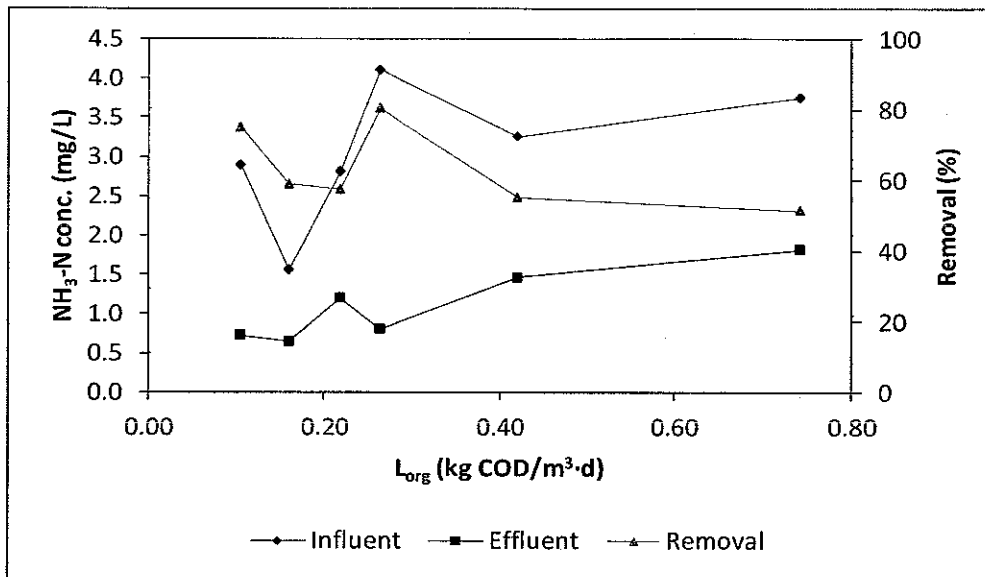
Figure 4.55: Average ammonia-N influent, effluent and removal versus L_{org} for anoxic-aerobic stage in reactor A and B.

4.4.1.8   Nitrate-N

Average influent and effluent nitrate-nitrogen concentration results for the anoxic-aerobic stage throughout the study period are shown in Figure 4.56. The average influent was 3.7 mg/L while the average effluent was 1.6 mg/L. There was fluctuation during the study period for both influent and effluent. But during the reactors' steady state condition, there was removal in both reactors and found to be in the range of 15-82%. The nitrate nitrogen content was low and the need for anoxic stage might be not necessary, but this stage was important and designed to increase the removal of BTEX and phenol which are recalcitrant compounds and provide room for them to be degraded before being volatized during the aeration and agitation in the aerobic stage.
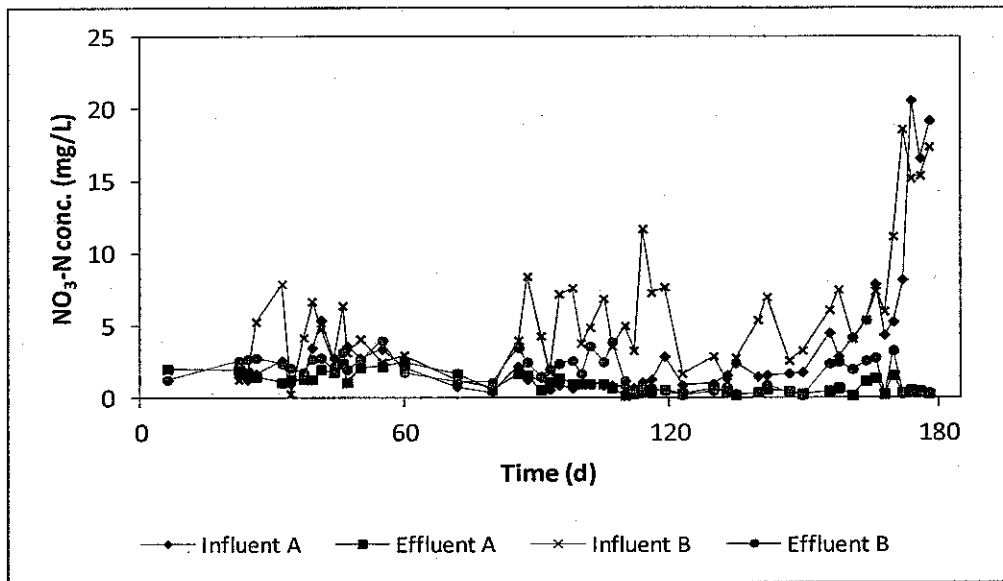
Figure 4.56: Nitrate-N concentration versus time for anoxic-aerobic stage in reactor A and reactor B.

Figure 4.57 presents the influent, effluent and removal percentage for nitrate-nitrogen versus six L_{org} applied on the anoxic-aerobic stage in MSBR A and B. The average influent and effluent concentrations continued to increase as the L_{org} increased, while the average removal was 49%.
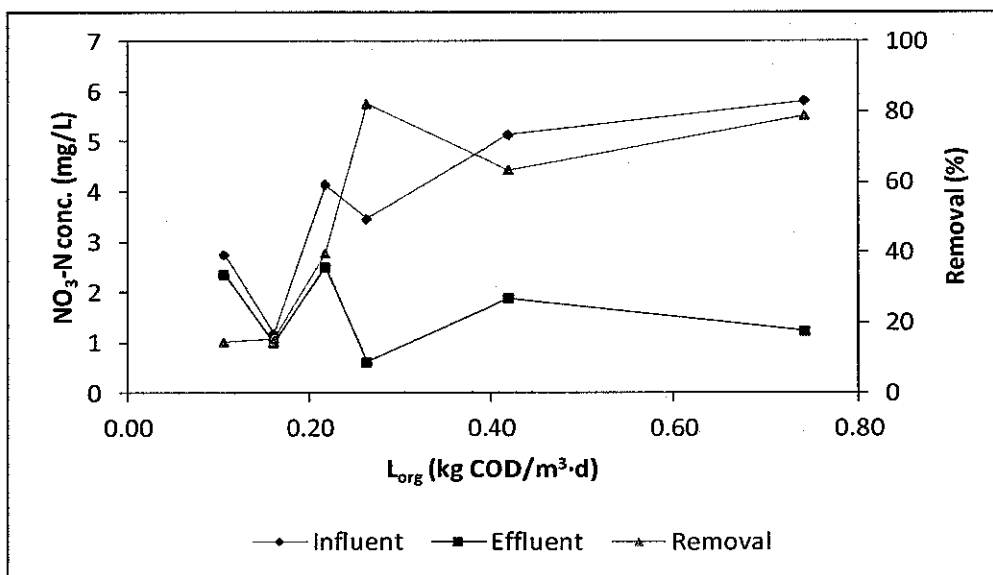
Figure 4.57: Average nitrate-N concentration for influent, effluent and removal versus L_{org} for anoxic-aerobic stage in reactor A and B.

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4.4.1.9   Phenol

Phenol was monitored and the average effluent concentration was noted when the reactor reached the steady state condition during the application of the six L_{org} as shown in Figure 4.58. The anaerobic stage removed on average 29% of phenol, while the average MSBR removal efficiency was 79% similar to what was reported by Sarfaraz et al. (2004). The effluent of three loads out of the six loads applied were within the required effluent limit of 1.0 mg/L (Environment, 2009).
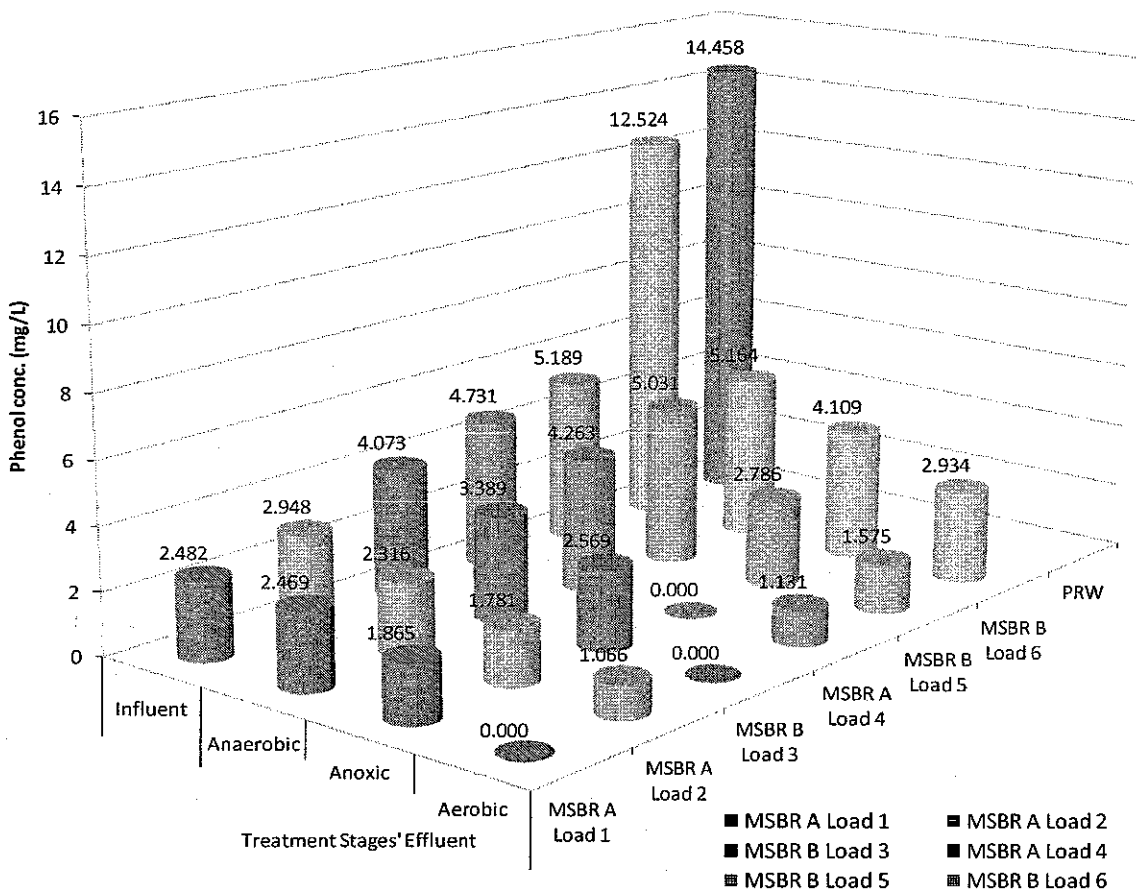
Figure 4.58: Phenol concentration throughout the anaerobic, anoxic and aerobic stages in the multi-stage biological reactor treating PRW.

4.4.1.10 BTEX

BTEX components (Benzene, Toluene, Ethyl benzene, m-p-Xylene and o-Xylene) were monitored and the average effluent concentration was noted when the reactor finished the acclimatization period and comes to steady state condition for all six L_{org} as shown in Figure 4.59. Benzene was removed on average by 99% during the anaerobic stage treatment, and the average final discharge of the MSBR reactor (0.006 mg/L) was approximately showing complete removal. Although the BTEX concentration during the application of all loads was approximately more than 18 mg/L, but there was no adverse effect as reported in the literature for concentration of 18 mg/L (Wong and Gerhardt, 2002), and the MSBR reactor managed to perform according to the discharge limit of 0.05 mg/L (IFC, 2007). Three stages of anaerobic followed by anoxic and aerobic configuration was effective in treating the BTEX.
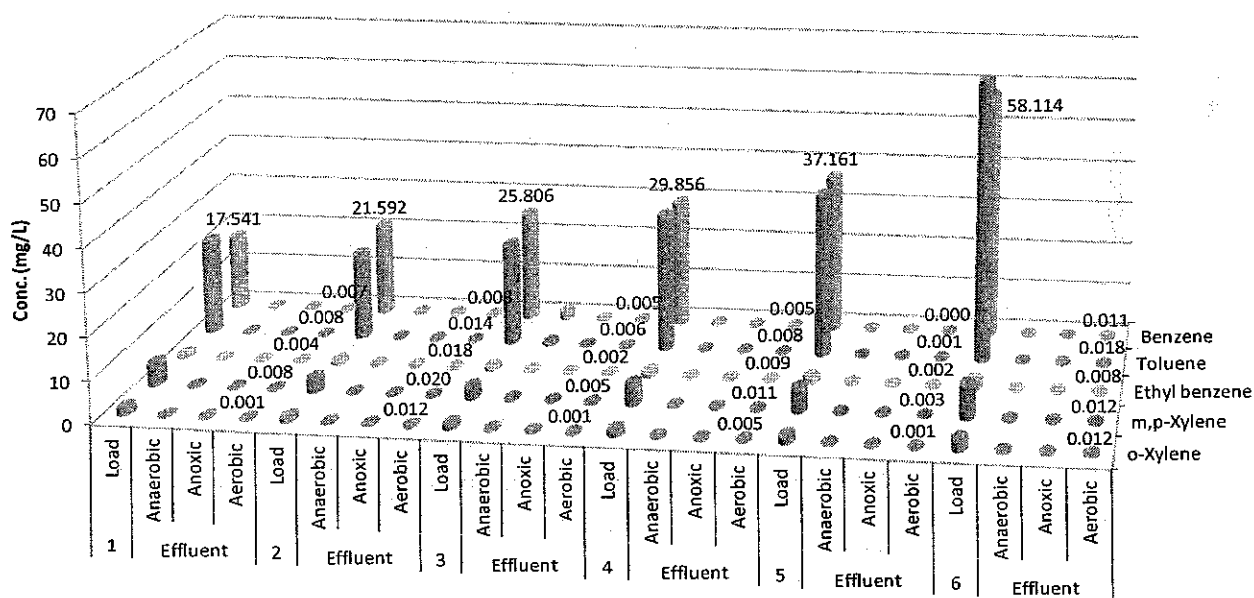
Figure 4.59: BTEX concentration for volumetric organic loading rates applied to two multi-stage biological reactors operating in parallel throughout the anaerobic, anoxic and aerobic stages treating PRW.

4.4.1.11 Summary of Results for MSBR Performance

MSBR showed effective treatment performance under different loads in wide range of influent COD (1000-7000 mg/L), and all effluent concentration were below 200 mg/L discharge limit Standard B as in the Environmental Quality (Industrial Effluents) Regulations set by Environment (2009). Phenol and BTEX were also effectively removed throughout the three stages in the MSBR. Summary of the results are presented in Table 4.11.

Table 4.11: Summary of results for MSBR performance

MSBR		Load	COD		BOD$_{5\ d,\ 20°C}$		MLSS	MLVSS	Ammonia		Nitrate		Flowrate	
			in	out	in	out	-	-	in	out	in	out	in	out
					mg/L						L/d			
A	Anaerobic	1	982	214	433	117	10348	7808	1.33	2.89	2.85	2.75	1.4	1.4
		2	1504	273	662	75	16668	12049	3.23	1.56	2.24	1.17	1.4	1.4
		4	2476	494	1080	103	17884	12419	3.45	4.10	4.24	3.46	1.4	1.4
B		3	2048	357	751	130	15526	10677	4.08	2.81	2.92	4.15	1.4	1.4
		5	3944	768	1888	320	15993	11377	5.84	3.25	3.05	5.14	1.4	1.4
		6	6972	1746	2853	1571	16591	11831	9.57	3.75	3.14	5.82	1.4	1.4
A	Anoxic	1	53	43	40	46	10263	7215	0.86	0.98	2.38	2.15	22.4	22.4
		2	71	58	63	16	14906	10653	0.70	0.90	1.01	0.98	22.4	22.4
		4	102	93	54	18	15283	8567	1.01	1.58	0.79	0.69	22.4	22.4
B		3	76	75	57	57	9206	6738	1.30	1.45	2.60	2.66	22.4	22.4
		5	165	152	80	49	11388	8340	1.57	1.67	2.09	2.04	22.4	22.4
		6	229	197	147	36	13911	11267	1.94	2.13	1.51	1.93	22.4	22.4
A	Aerobic	1	64	52	46	45	2295	1599	0.98	0.73	2.15	2.35	22.4	1.4
		2	63	53	16	62	1399	992	0.90	0.64	0.98	0.99	22.4	1.4
		4	86	64	18	51	3101	2012	1.01	0.81	0.69	0.61	22.4	1.4
B		3	77	66	57	51	3600	2581	1.45	1.20	2.66	2.50	22.4	1.4
		5	153	117	49	63	1583	1068	1.67	1.46	2.04	1.88	22.4	1.4
		6	279	189	36	52	4041	2648	2.13	1.82	1.93	1.23	22.4	1.4

4.4.2 Multi-stage Biological Reactor Modeling and Simulation

Artificial neural networks tool in MATLAB (R2009a) software was used to model the multi-stage biological reactor data for influent and effluent concentration for all the three stages (anaerobic, anoxic and aerobic). The network type was feed-forward backpropagation (FFBP), and the training function was Levenberg–Marquardt algorithms (Trainlm), and the adaption learning function was gradient descent momentum algorithms (Learngdm). Two transfer functions were tested, log sigmoid transfer function (Logsig) at hidden layer and a linear transfer function (Purelin) at output layer, and tangent sigmoid transfer function (Tansig) at hidden layer and a linear transfer function (Purelin) at output layer, were used and compared to define the optimum model.

Optimum number of neuron was selected based on:

- Minimum root mean square error (RMSE)

- Maximum variance accounted for (VAF)

- Maximum correlation coefficient (R^2)

- Minimum mean absolute percentage error (MAPE)

The selected model was then used to predict the reactor performance. The simulation data were then used to find the optimum performance of the reactor.

4.4.2.1 Anaerobic Stage Modeling

The anaerobic stage in the Multi-stage Biological Reactor was modeled using artificial neural networks software. Logsig-Purelin transfer function was compared to Tansig-Purelin transfer function to define the optimum model. The selected best model was then used to predict the reactor performance.

During testing and validation of data, different number of neurons was tested ranging from 5 to 35. Table 4.12 below shows part of the number of neurons tested

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(5-15) and the score registered for RMSE, VAF, R^2 and MAPE during evaluation of Logsig-Purelin, and Tansig-Purelin transfer functions.

Table 4.12: Number of neurons tested and the score for evaluation parameters for anaerobic stage

Neurons	Logsig-Purelin				Tansig-Purelin			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.076	85.952	0.859	16.878	0.076	86.027	0.860	17.035
6	0.076	86.134	0.860	17.340	0.076	86.104	0.860	16.552
7	0.075	86.249	0.862	17.255	0.075	86.229	0.862	17.279
8	0.076	85.956	0.859	16.884	0.075	86.147	0.861	16.622
9	0.075	86.250	0.862	16.694	0.075	86.170	0.861	*15.971*
10	0.075	86.500	0.864	16.810	0.075	86.154	0.861	16.576
11	0.075	86.516	0.864	16.977	0.075	86.388	0.864	16.750
12	0.074	*86.741*	0.867	17.585	*0.074*	*86.638*	*0.866*	16.827
13	0.074	86.608	0.866	16.426	0.075	86.424	0.864	16.023
14	0.075	86.133	0.861	*16.204*	0.076	86.111	0.860	16.907
15	*0.074*	86.724	*0.867*	16.205	0.075	86.412	0.864	16.427

Although the number of neurons are in the range of 5-35, but from Figure 4.60 and Figure 4.61 it was noted that after neuron 15 and from plotted line representing the R^2 from the training set is losing similarity with R^2 from validation set, indicating over fitting and the model will not be able to generalize the pattern of the data that used as training set during validation (Jeon and University, 2007).
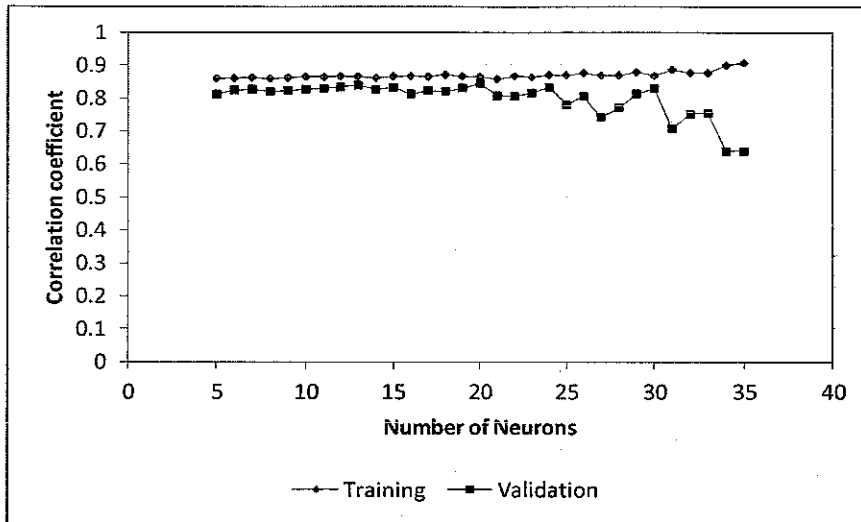
Figure 4.60: R^2 scores versus number of neurons tested for Logsig-Purelin transfer function for anaerobic stage.
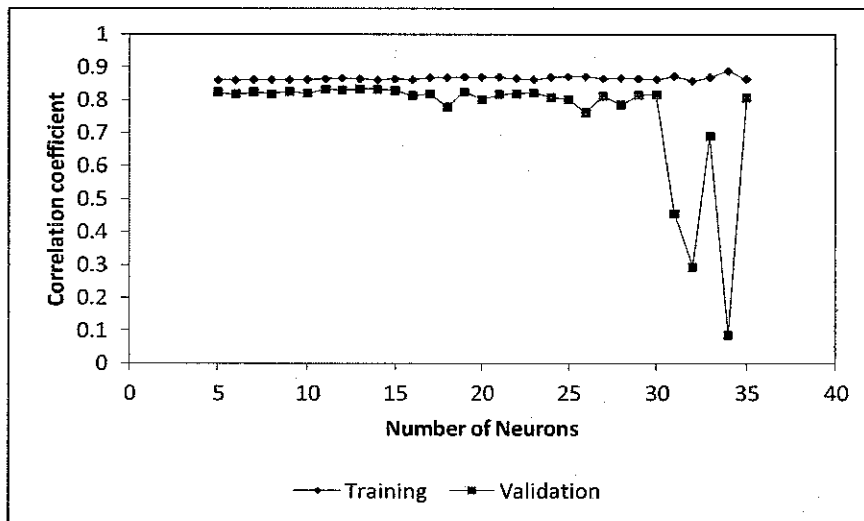
Figure 4.61: R^2 scores versus number of neurons tested for Tansig-Purelin transfer function for anaerobic stage.

Thus, the number of neurons was limited to the range between 5-15 neurons, and the optimum neuron was selected as shown in Table 4.12 based on minimum RMSE, maximum VAF, maximum R^2 and minimum MAPE.

Logsig-Purelin transfer function indicated 15 neurons is the optimum, while Tansig-Purelin transfer function suggested 12 neurons. It is usually preferable to use

of simpler models, with fewer number of parameters than more complicated ones with more parameters, whenever feasible (Hamed et al., 2004). Thus, tangent sigmoid transfer function (Tansig) at hidden layer and a linear transfer function (Purelin) at output layer with 12 neurons is the optimum transfer function.

Figure 4.62 showed the measured experimental data and the predicted using ANN for eighty entries of data that were used for training. Figure 4.63 showed the measured experimental data and the predicted using ANN for eighty entries of data that were used for validation. The best selected model shows significant prediction of actual experiment based on minimum RMSE, maximum VAF, maximum R^2 and minimum MAPE; hence, it was then used for simulation.
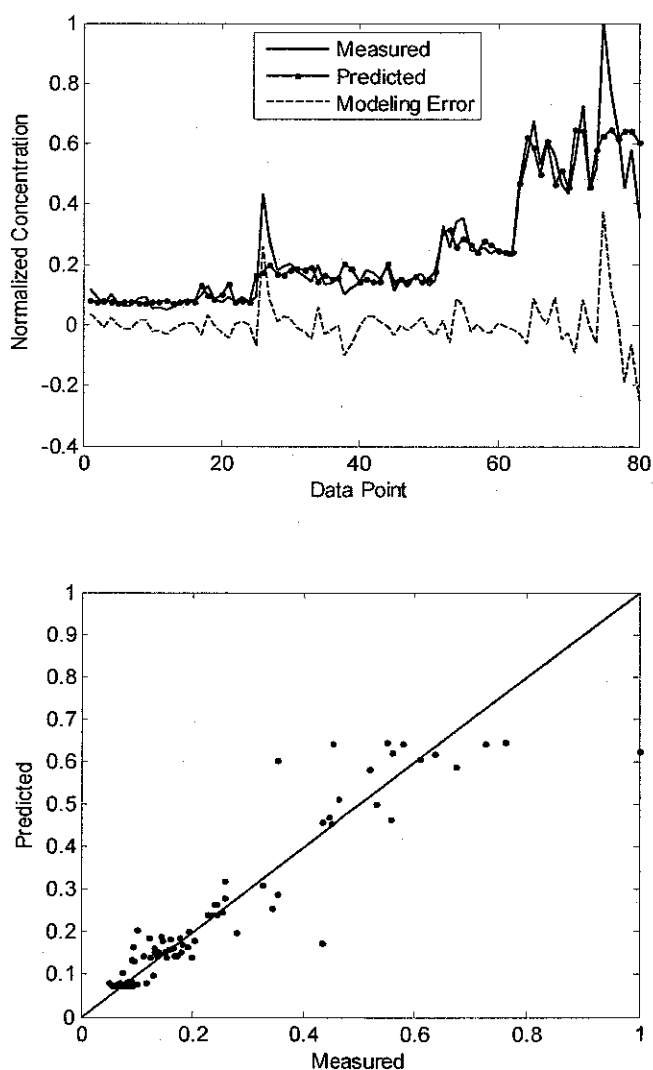
Figure 4.62: Anaerobic stage measured and predicted normalized data for training set
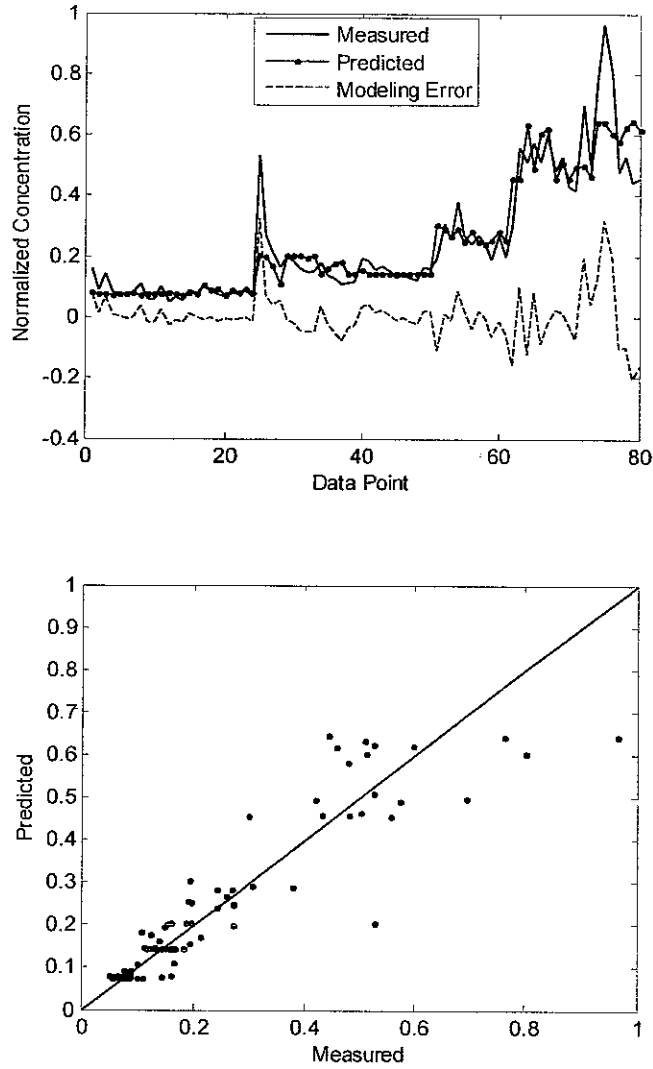
Figure 4.63: Anaerobic stage measured and predicted normalized data for validation set

4.4.2.2 Anaerobic Stage Simulation

The best model with Tansig-Purelin transfer function and 12 neurons was used to simulate random data to find out the optimum efficiency. Figure 4.64 shows all the hundred and sixty data set that was used for both the training and validation, used here for simulation.
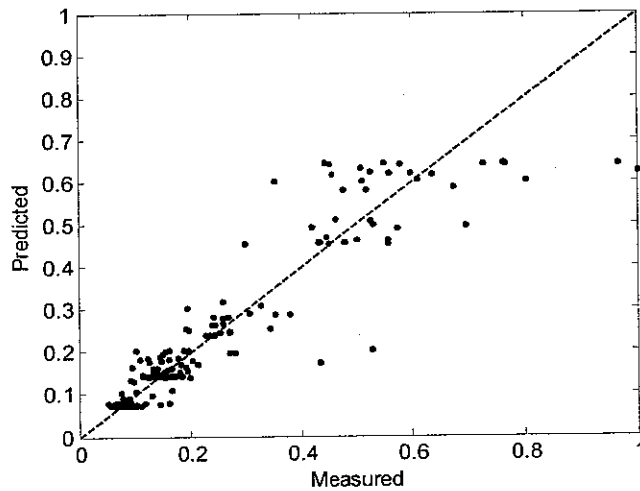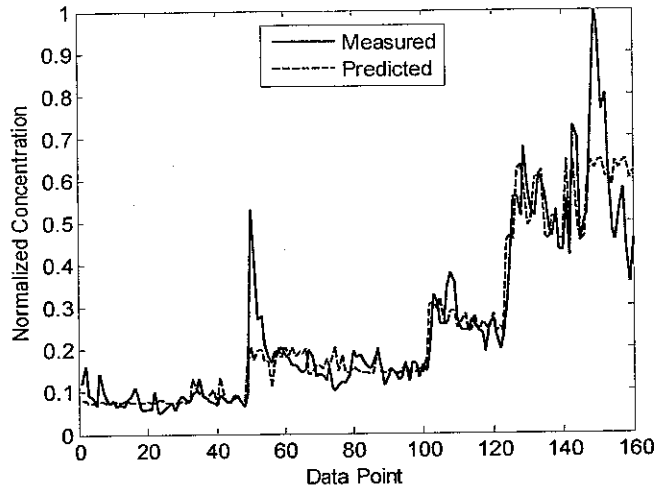
Figure 4.64: Anaerobic stage measured and predicted normalized data for actual data simulation

Random data entries ranged from 500 to 10000 mg/L was used as influent to simulate the reactor performance; Figure 4.65 shows the simulated influent and effluent concentrations in addition to removal efficiency.

Highest removal efficiency observed was 82% recorded at range of influent COD concentration between 1300 to 1400 mg/L and of influent concentration in the COD range between 2500 to 2600 mg/L.
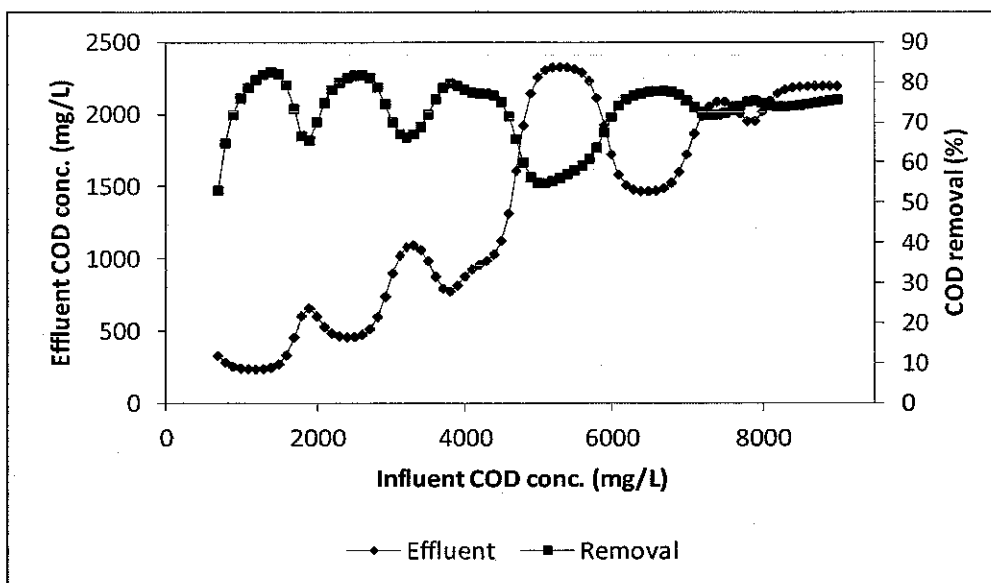
Figure 4.65: Anaerobic stage effluent concentration and removal efficiency versus influent concentration using best selected model for Tansig-Purelin transfer function.

Modeling the data obtained from the anaerobic stage in the multi-stage biological reactor under various loads, resulted in a model that used tangent sigmoid transfer function (Tansig) at hidden layer and a linear transfer function (Purelin) at output layer with 12 neurons as the optimum transfer function.

Simulation using the optimum model with random data entries ranged between 500 to 9000 mg/L as influent, resulted in a pattern that simulate the reactor performance for data that were never really experimentally tested in the lab. Lab experiment was showing highest removal of 82% which confirmed by using the best selected model that developed using mathematical model.

4.4.2.3   Anoxic-Aerobic Stage Modeling

The anoxic-aerobic stage in the Multi-stage Biological Reactor was modeled using artificial neural networks software. Logsig-Purelin transfer function was compared to Tansig-Purelin transfer function to define the optimum model. The selected model was then used to predict the reactor performance.

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During testing and validation of data, number of neurons was tested ranging from 5 to 35. Table 4.13 below shows some of the number of neurons tested (5-10) and the score registered for RMSE, VAF, R^2 and MAPE during evaluation of Logsig-Purelin, and Tansig-Purelin transfer functions.

Table 4.13: Number of neurons tested and the score for evaluation parameters for Anoxic-Aerobic stage

Neurons	Logsig-Purelin				Tansig-Purelin			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.089	82.935	0.828	16.001	0.088	83.277	0.832	15.248
6	0.088	83.363	0.833	*14.624*	0.084	84.853	0.848	15.460
7	0.086	83.941	0.839	15.420	0.087	83.826	0.838	15.541
8	0.086	84.241	0.842	15.720	0.084	84.851	0.848	15.164
9	*0.083*	*85.610*	*0.852*	15.107	*0.083*	*85.270*	*0.853*	15.540
10	0.084	84.904	0.849	15.197	0.083	85.064	0.850	*15.076*

Although the number of neurons are in the range of 5-35, but from Figure 4.66 and Figure 4.67 it was noted that after neuron 10 and from plotted line representing the R^2 from the training set is losing similarity with R^2 from validation set, indicating over fitting and the model will not be able to generalize the pattern of the data that used as training set during validation (Jeon and University, 2007).
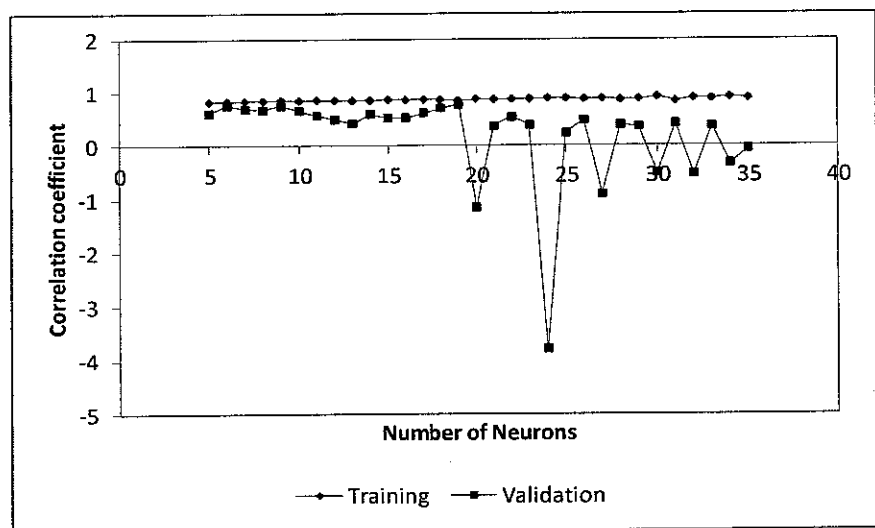
Figure 4.66: R^2 scores versus number of neurons tested for Logsig-Purelin transfer function for anoxic-aerobic stage.
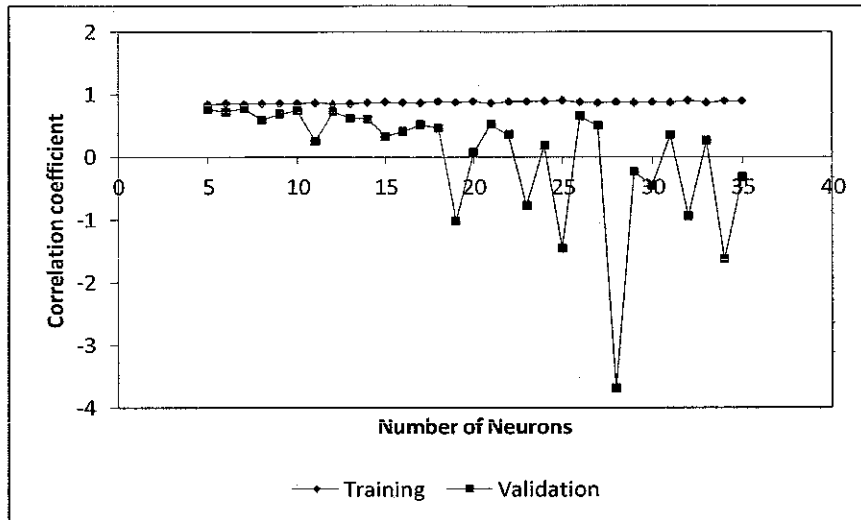
Figure 4.67: R^2 scores versus number of neurons tested for Tansig-Purelin transfer function for anoxic-aerobic stage.

Thus, the number of neurons was limited to the range between 5-10 neurons, and the optimum neuron was selected as shown in Table 4.13 based on minimum RMSE, maximum VAF, maximum R^2 and minimum MAPE.

Both Logsig-Purelin and Tansig-Purelin transfer function indicated 9 neurons is the optimum. R^2 in Tansig-Purelin was slightly higher and all four parameters were closer. Thus, tangent sigmoid transfer function (Tansig) at hidden layer and a linear transfer function (Purelin) at output layer with 9 neurons is the optimum transfer function.

Figure 4.68 showed the measured experimental data and the predicted using ANN for eighty entries of data that were used for training. Figure 4.69 showed the measured experimental data and the predicted using ANN for eighty entries of data that were used for validation. The best selected model shows significant prediction of actual experiment based on minimum RMSE, maximum VAF, maximum R^2 and minimum MAPE; hence, it was then used for simulation.
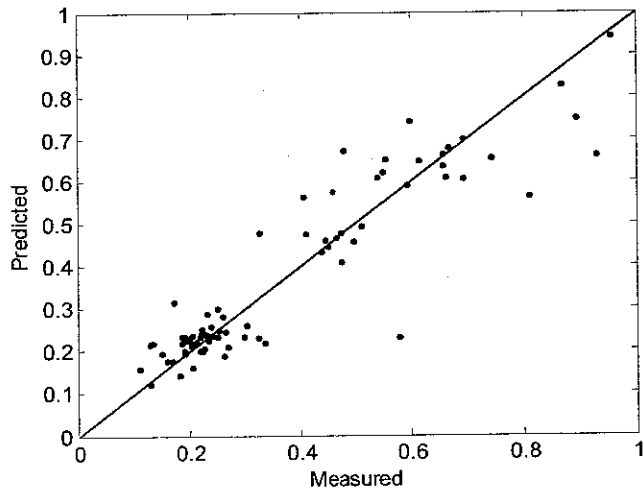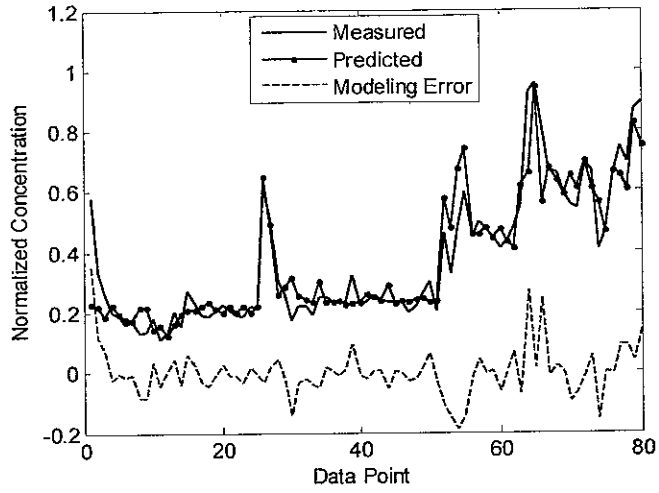
Figure 4.68: Anoxic-aerobic stage measured and predicted normalized data for training set
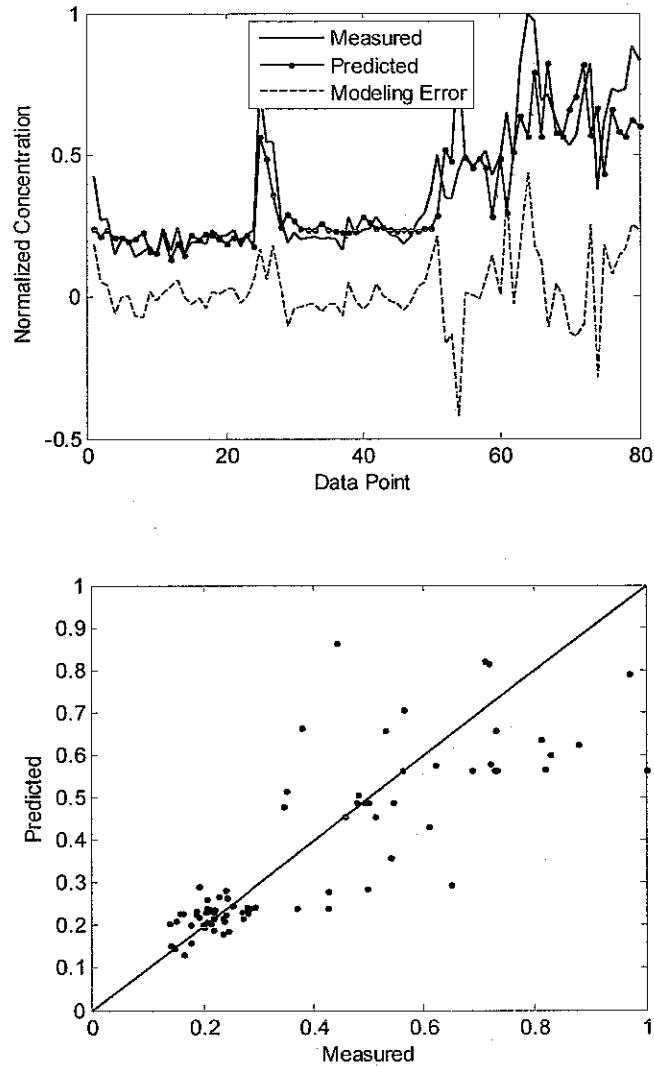
Figure 4.69: Anoxic-aerobic stage measured and predicted normalized data for
validation set

4.4.2.4 Anoxic-Aerobic Stage Simulation

The best model with Tansig-Purelin transfer function and 9 neurons was used to
simulate random data to find out the optimum efficiency. Figure 4.70 shows all the
hundred and sixty data set that was used for both the training and validation, used here
for simulation.
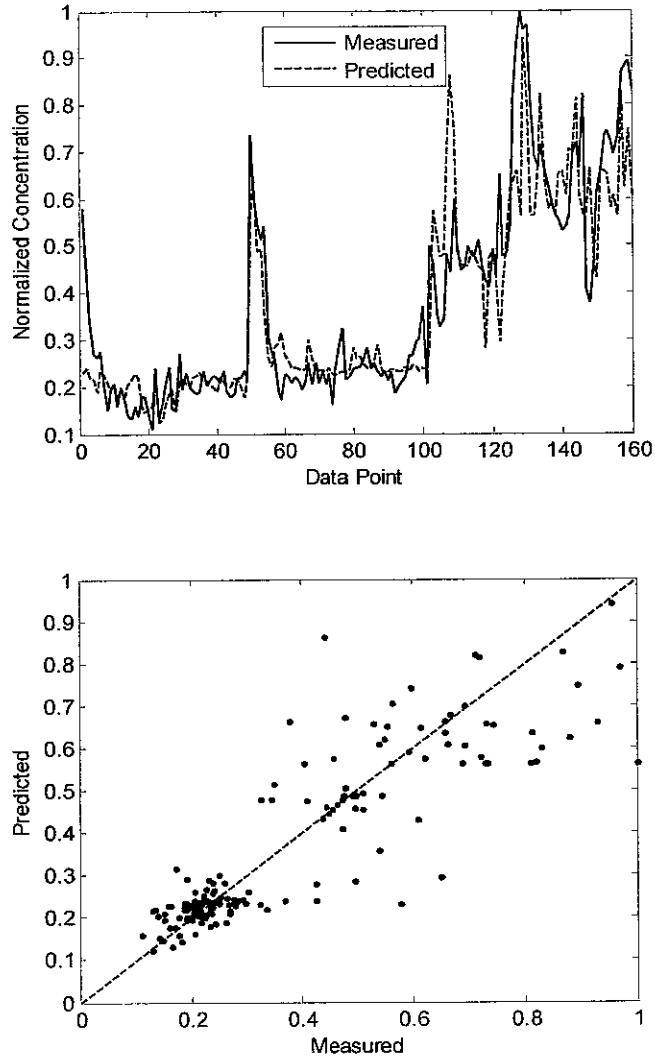
Figure 4.70: Anoxic-aerobic stage measured and predicted normalized data for actual data simulation

Random data entries ranged from 150 to 4800 mg/L was used as influent to simulate the reactor performance; Figure 4.71 shows the simulated influent and effluent concentrations in addition to removal efficiency.

Highest removal efficiency observed was 96% recorded and was recorded at influent COD of 3150 mg/L, while the corresponded effluent COD concentration was 115 mg/L.

Effluent COD concentration below 100 mg/L was recorded for influent COD range between 150 to 700 mg/L corresponding to removal efficiency in the range of 78-88%.
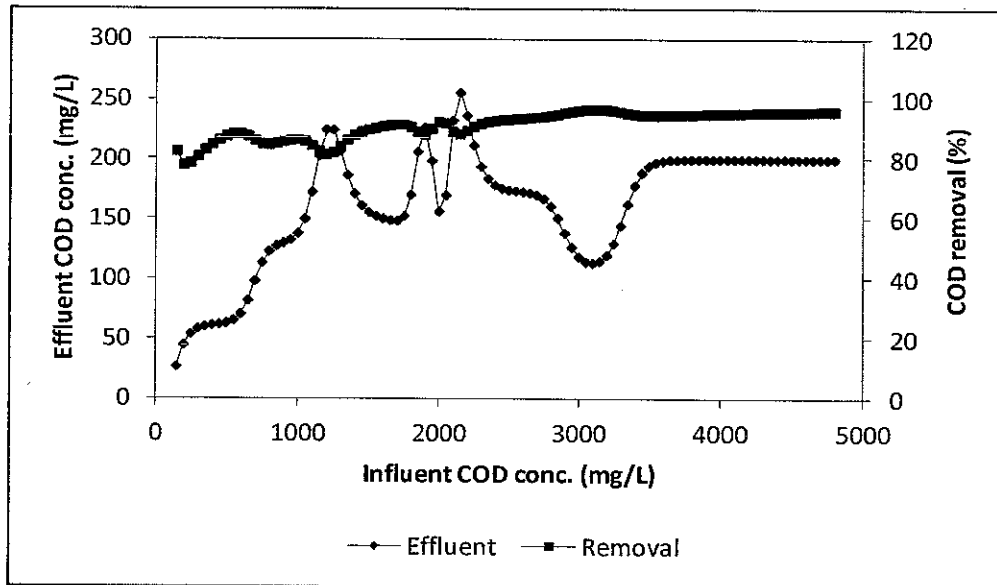
Figure 4.71: Anoxic-aerobic effluent concentration and removal efficiency versus influent concentration using best selected model for Tansig-Purelin transfer function.

Modeling the data obtained from the anoxic-aerobic stage in the multi-stage biological reactor under various loads, resulted in a model that used tangent sigmoid transfer function (Tansig) at hidden layer and a linear transfer function (Purelin) at output layer with 9 neurons as the optimum transfer function.

Simulation using the optimum model with random data entries range between 150 to 4800 mg/L as influent, resulted in a pattern that simulate the reactor performance for data that were never really experimentally tested in the lab. Lab experiment was showing highest removal of 89% and could not define the exact load that can give effluent concentration below 100 mg/L; but from the simulation model, 96% removal efficiency was recorded for 3150 mg/L, and loads that can give COD concentration below 100 mg/L were defined.

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4.4.2.5 MSBR Modeling

The Multi-stage Biological Reactor was modeled using artificial neural networks software. Logsig-Purelin transfer function was compared to Tansig-Purelin transfer function to define the optimum model. The selected model was then used to predict the reactor performance.

During testing and validation of data, number of neurons was tested ranging from 5 to 35. Table 4.14 below shows some of the number of neurons tested (5-14) and the score registered for RMSE, VAF, R^2 and MAPE during evaluation of Logsig-Purelin, and Tansig-Purelin transfer functions.

Table 4.14: Number of neurons tested and the score for evaluation parameters for MSBR

Neurons	Logsig-Purelin				Tansig-Purelin			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.103	77.177	0.770	16.645	0.104	76.897	0.767	16.870
6	0.101	77.850	0.778	16.508	*0.100*	*78.465*	*0.784*	17.547
7	0.100	78.453	0.784	16.303	0.101	78.283	0.781	*16.562*
8	0.101	78.161	0.782	*15.858*	0.102	77.752	0.777	16.908
9	0.100	78.569	0.785	16.446	0.100	78.205	0.782	15.906
10	0.100	78.371	0.784	16.413	0.101	78.322	0.782	16.296
11	0.100	78.580	0.785	16.658	0.100	78.295	0.783	17.028
12	0.100	78.313	0.783	16.599	0.101	78.326	0.781	16.570
13	*0.098*	*79.081*	*0.791*	16.133	0.101	78.161	0.782	16.618
14	0.099	78.662	0.786	15.972	0.101	78.315	0.779	15.821

Although the number of neurons are in the range of 5-35, but from Figure 4.72 and Figure 4.73 it was noted that after neuron 14 and from plotted line representing the R^2 from the training set is losing similarity with R^2 from validation set, indicating over fitting and the model will not be able to generalize the pattern of the data that used as training set during validation (Jeon and University, 2007).

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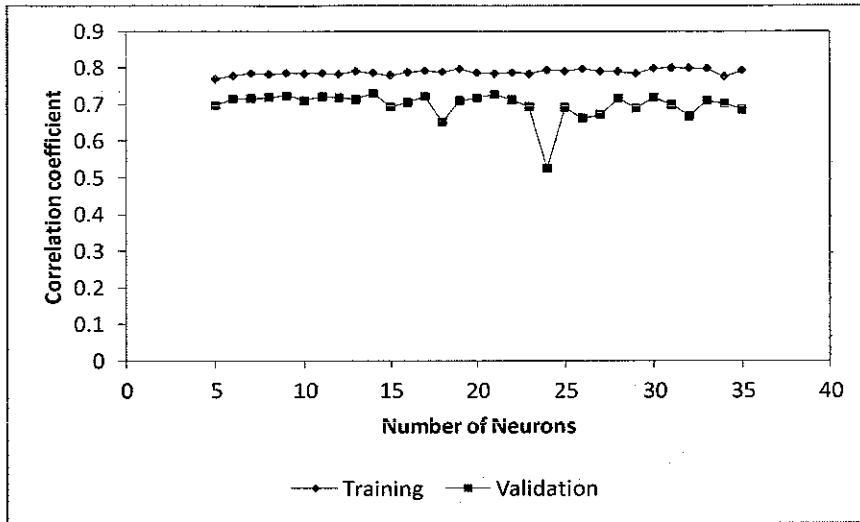
Figure 4.72: R^2 scores versus number of neurons tested for Logsig-Purelin transfer function for MSBR.
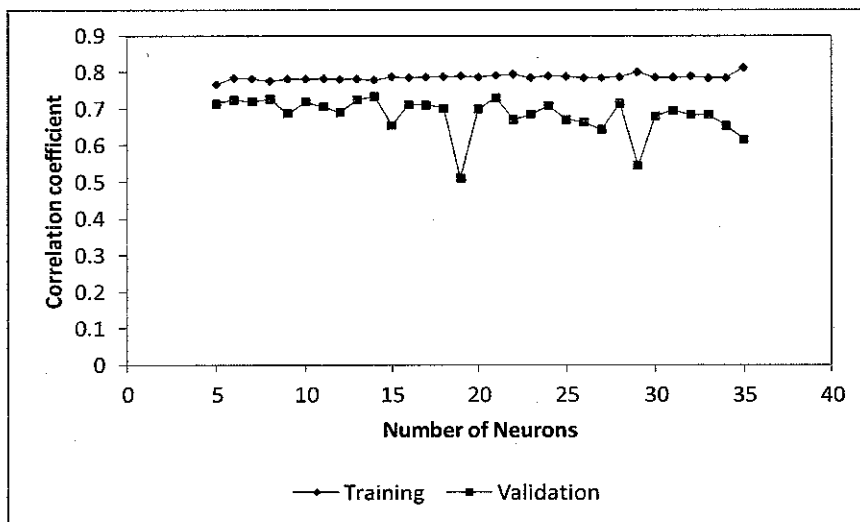
Figure 4.73: R^2 scores versus number of neurons tested for Tansig-Purelin transfer function for MSBR.

Thus, the number of neurons was limited to the range between 5-14 neurons, and the optimum neuron was selected as shown in Table 4.14 based on minimum RMSE, maximum VAF, maximum R^2 and minimum MAPE.

Logsig-Purelin transfer function indicated 13 neurons is the optimum, while Tansig-Purelin transfer function suggested 6 neurons. It is usually preferable to use of

simpler models, with fewer number of parameters than more complicated ones with more parameters, whenever feasible (Hamed et al., 2004). Thus, tangent sigmoid transfer function (Tansig) at hidden layer and a linear transfer function (Purelin) at output layer with 6 neurons is the optimum transfer function.

Figure 4.74 showed the measured experimental data and the predicted using ANN for eighty entries of data that were used for training. Figure 4.75 showed the measured experimental data and the predicted using ANN for eighty entries of data that were used for validation. The best selected model shows significant prediction of actual experiment based on minimum RMSE, maximum VAF, maximum R^2 and minimum MAPE; hence, it was then used for simulation.
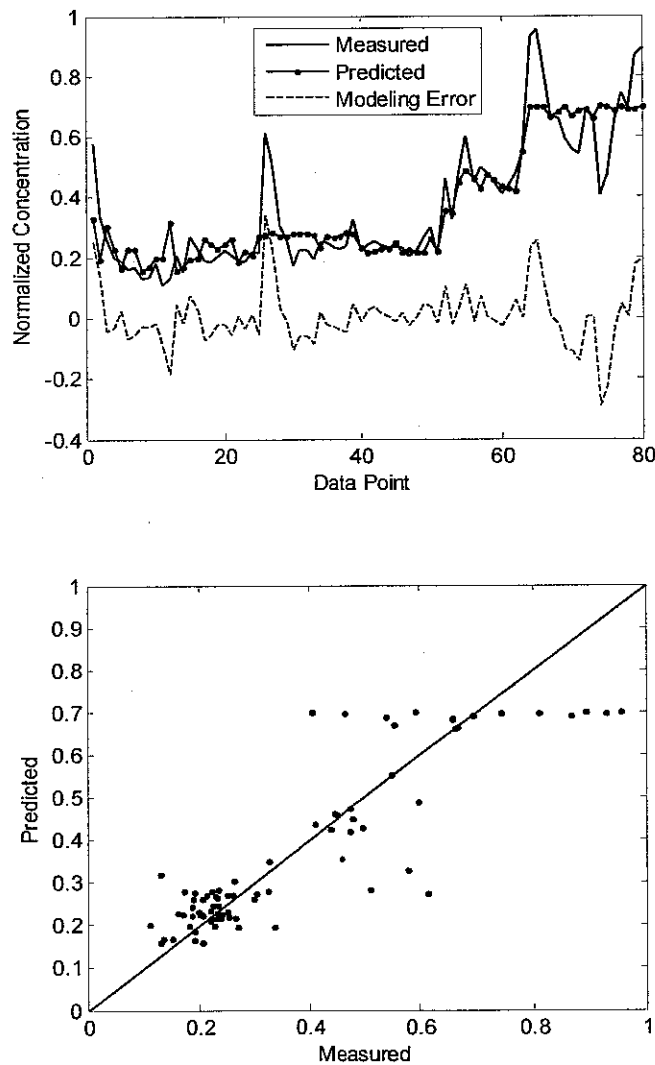
Figure 4.74: MSBR measured and predicted normalized data for training set

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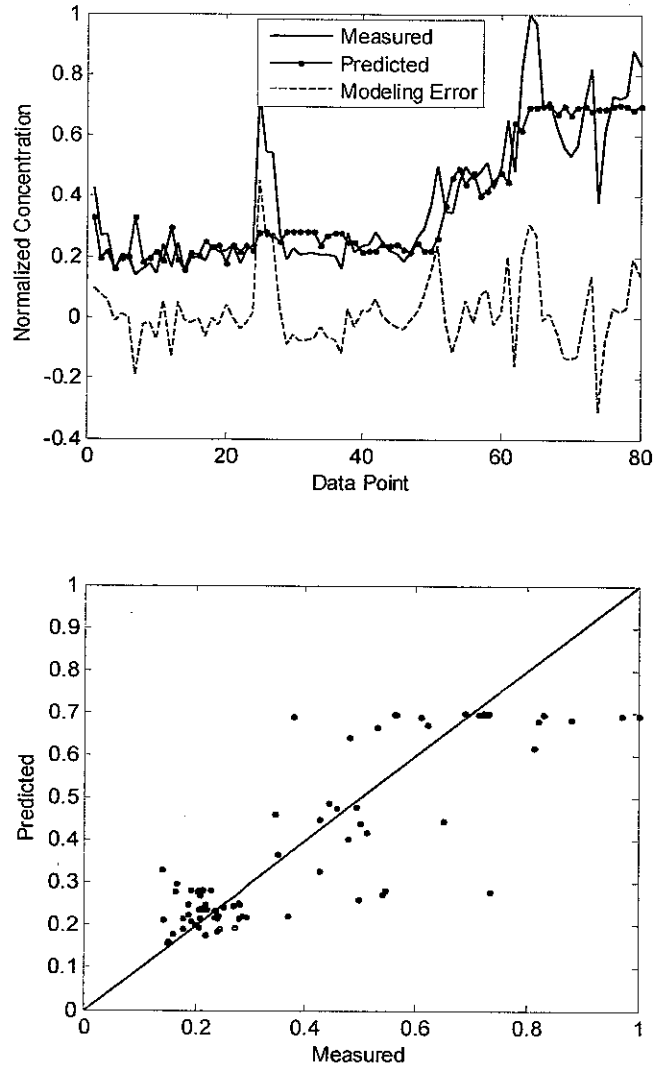
Figure 4.75: MSBR measured and predicted normalized data for validation set

4.4.2.6 MSBR Simulation

The best model with Tansig-Purelin transfer function and 6 neurons was used to simulate random data to find out the optimum efficiency. Figure 4.76 shows all the hundred and sixty data set that was used for both the training and validation, used here for simulation.
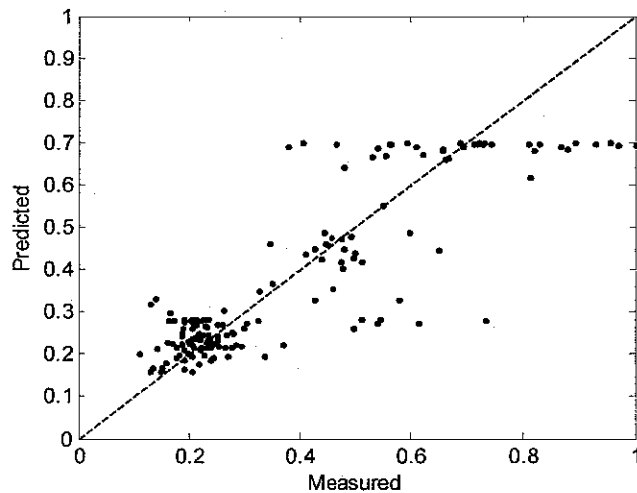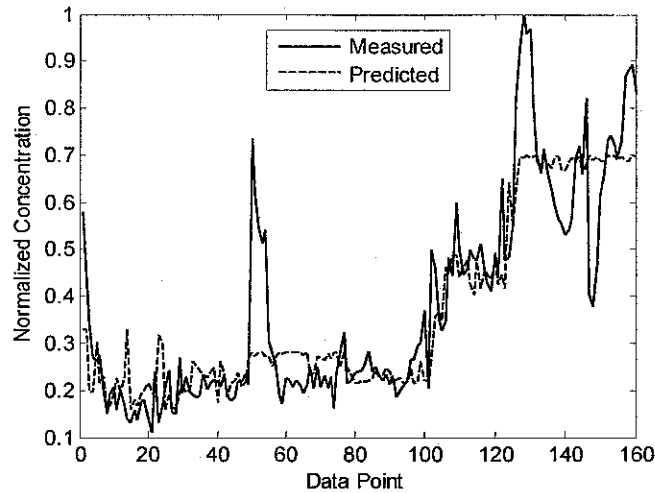
Figure 4.76: MSBR measured and predicted normalized data for actual data
simulation

Random data entries in the range from 500 to 10000 mg/L were used as influent
to simulate the reactor performance. Figure 4.77 shows the simulated influent and
effluent concentrations in addition to removal efficiency.

Highest removal efficiency predicted was 98% recorded at range of influent COD
concentration between 255 to 3200 mg/L and of influent COD in the range between
5200 to 6300 mg/L and of COD influent from 7300 mg/L up to the last value tested.

Effluent COD concentration below 100 mg/L was predicted for influent COD
concentration in the range between 900 to 3600 mg/L.
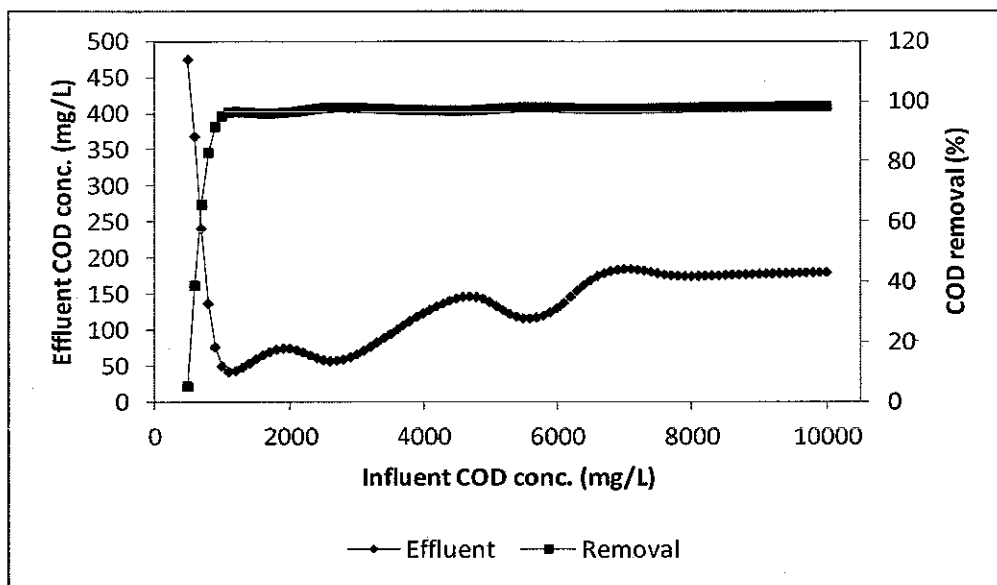
Figure 4.77: MSBR effluent concentration and removal efficiency versus influent concentration using best selected model for Tansig-Purelin transfer function.

Modeling the data obtained from the multi-stage biological reactor under various loads, resulted in a model that used tangent sigmoid transfer function (Tansig) at hidden layer and a linear transfer function (Purelin) at output layer with 6 neurons as the optimum transfer function.

Simulation using the optimum model with random data entries in the range between 500 to 10000 mg/L as influent, resulted in a pattern that simulate the reactor performance for data that were never experimentally tested in the lab. Lab experiment was showing highest removal of 97% and could not define the exact load that can give effluent concentration below 100 mg/L; but from the simulation model, 98% removal efficiency was repeatedly predicted for various loads, and loads that can give COD concentration below 100 mg/L were defined.

4.5 Summary of Results

Biodegradability batch study was conducted to determine the degradation rate which showed PRW to be ultimately biodegradable. From the biodegradability study results, it was shown that the petroleum refinery wastewater collected from final equalization tank at a local petroleum refinery facility is ultimately biodegradable using both aerobically as well as anaerobically, with more than 90% COD removals. It can be observed that sCOD in test suspension in aerobic treatment of PRW can achieve below 50 mg/L after one day of treatment. However, anaerobic treatment of the same source of wastewater resulted in sCOD concentration in test suspension below 50 mg/L after 9 days of treatment. However, it was also found that the petroleum refinery wastewater achieved better COD removals when treated aerobically.

SBR treatability study on aerobic reactor, coupled anaerobic-aerobic reactor, and mixed domestic refinery influent aerobic reactor were tested. From the sequencing batch reactor results, it was shown that the desired treatment level for PRW wastewater can be achieved. Aerobic SBR reactors reported effluent COD concentration below 100 mg/L. Highest percentage COD removals were reported in the aerobic system and also in the combined anaerobic-aerobic system. The total cycle for aerobic reactor and the combined system was 24 hr and 48 hr, respectively. Lowest effluent COD concentration was recorded in the aerobic reactor when the wastewater was treated together with domestic wastewater. Nutrients provided by the domestic wastewater further enhance the treatment, but it caused dilution to the original strength. However, further study need to be conducted on the nutritional requirements for the biological study. Overall, Anaerobic-aerobic reactor was relatively better.

SBR monitoring study for different parameters on a single operation cycle was carried out. Monitoring for 24 hr cycle with 8 hr sampling intervals showed that all three aerobic reactors achieved sCOD removal in the first 8 hr of aeration. This indicated that further refinement should be conducted with shorter aeration cycle which was carried with 1.5 hr sampling intervals. All the three SBR showed high and similar removal efficiency. Anaerobic-aerobic SBR configuration gave biological

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path for effective biodegradation; it may require longer cycle but it gave overall highest removal efficiency with low effluent concentration for COD, Ammonia-nitrogen, TSS and VSS. This investigation was needed with minimum sampling intervals as it indicate that the optimum operation condition required shorter SBR cycle for aerobic reactors and longer for anaerobic reactor. At the end of this study, the aerobic degradation of PRW results indicates that most of the degradation was taken place in the first 6 hr from the beginning of the cycle. From the anaerobic degradation of PRW results, 24 hr cycle was not sufficient to achieve the desired removal and longer cycle was needed. It can be observed also from the aerobic degradation of the anaerobic effluent results that on average 6 hr duration was sufficient for effective degradation and removal of substrate; which applies also to the aerobic degradation of PRW mixed with domestic wastewater.

Anaerobic-anoxic-aerobic train SBR study, investigated on the configuration capacity to achieve efficient treatment. Anaerobic stage was designed to break down major compounds. Anoxic stage was designed for denitrification which removes recalcitrant compounds. Aerobic stage was designed for nitrification and polishing the final effluent. The operation of anaerobic and anoxic SBR was improved with gas collection and recycling set-up and achieved average 77% COD removal efficiency. The volatile organic compound BTEX was treated and monitored under the three stages of treatment process. The anaerobic degradation of BTEX reached on average 78% removals. Anoxic received the anaerobic effluent and recycled effluent from aerobic reactor, the average removal was 74% from the concentration received which corresponded to 19% from the overall system performance. Aerobic received the anoxic effluent and removed on average 83% from the concentration received which corresponded to 3% from the overall system performance. There was complete degradation throughout the process. Although the nitrate nitrogen content was low and the need for anoxic stage might be not necessary, but this stage was important and designed to remove recalcitrant compounds and provide room for volatile compounds to be degraded before being volatized during the aeration and agitation in the aerobic stage. The multi stage process with different biological conditions degraded effectively the complex and volatile pollutant.

Utilizing different biological treatment steps in single reactor can treat complex petroleum refinery wastewater. Anaerobic-Anoxic-Aerobic reactor configuration set-up with continuous flow was the outcome of all lab studies. The reactor accommodates the three stages to give the best compact biological system. The reactor was fabricated and acclimatized for the optimum operation and performance. Each reactor received the influent in the anaerobic compartment, to break down major compounds but not to the discharge limit. Anaerobic compartment utilized the anaerobic microorganisms in the absence of oxygen to biodegrade the wastewater and generation of gaseous products occurred. The anoxic compartment received the anaerobic stage effluent combined with recycled wastewater from the aerobic compartment. Anoxic compartment worked at low oxygen level environment as the microorganisms used chemically combined oxygen such as that found in nitrate. Although the nitrate nitrogen content was low, but this stage was important and designed to remove recalcitrant compounds and provide room for compounds to be degraded before being volatized during the aeration in the aerobic stage. The aerobic compartment received the anoxic stage effluent for polishing. Aerobic stage utilized aerobic microorganisms in oxygen-rich environment to biodegrade the wastewater. Aeration was provided to increase the dissolved oxygen and provide the mixing. The COD removal efficiency was always above 95% and effluent concentration was below 65 mg/L for four loads out of six. When L_{org} of 0.42 and 0.74 kg COD/m^3·d were applied, corresponded to influent concentration of 3944 and 6972 mg/L, effluent concentration increased to 117 and 189 mg/L respectively. The two multi-stage biological reactors (MSBR) were in steady state operation at 0.26 kg COD/m^3·d and 0.74 kg COD/m^3·d prior to receiving the full wastewater load at 0.77 kg COD/m^3·d. High COD removal was recorded even when the full load of raw petroleum refinery wastewater was introduced. MSBR A -which was operated at lower load-, took 7 days to stabilize to similar effluent characteristics of MSBR B. High COD removal was recorded even when the load of raw petroleum refinery wastewater suddenly increased to three times the steady state load. MSBR took seven days to stabilize from shock loading to similar effluent characteristics of gradual load increase. Satisfactory results below 100 mg/L could be achieved while operating the multi-stage biological reactor at 0.26 kg COD/m^3·d with influent COD concentration of

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2468 mg/L and effluent COD concentration of 64 mg/L. All effluents for the six loads applied were below the COD standard discharge limit of 200 mg/L, and the gradual increase of the full actual PRW resulted in effluent below the standard limit, while the sudden increase and shock load of PRW resulted in average effluent COD concentration of 228 mg/L in seven days.

Modeling the data obtained from the multi-stage biological reactor under various loads, resulted in a model that used feed-forward backpropagation (FFBP) as network type, the training function was Levenberg–Marquardt algorithms (Trainlm), and the adaption learning function was gradient descent momentum algorithms (Learngdm), tangent sigmoid transfer function (Tansig) was used at hidden layer and a linear transfer function (Purelin) at output layer with 6 neurons as the optimum best model.

Simulation using the optimum model with random data entries in the range of 500-10000 mg/L as influent, resulted in a pattern that simulate the reactor performance for data that were never experimentally tested in the lab. Lab experiment was showing highest removal of 97% and could not define the exact load that can give effluent concentration below 100 mg/L; but from the simulation model, 98% removal efficiency was repeatedly predicted for various loads, and loads that can give concentration below 100 mg/L were defined. Highest removal efficiency observed was 98% recorded at range of influent 255-3200 mg/L and of influent concentration in the range 5200-6300 mg/L and of influent from 7300 mg/L up to the last value tested. Effluent concentration below 100 mg/L was recorded for influent concentration range 900-3600 mg/L.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This research aimed at developing an integrated biological treatment system for petroleum refinery wastewater (PRW).

- The first objective of this research was to determine the biodegradability of the petroleum refinery wastewater and to determine its degradation percentage. From the results it was found that the PRW that was collected from final equalization tank at a local petroleum refinery facility was ultimately biodegradable using both aerobic and anaerobic treatment, with more than 90% COD removal. sCOD in test suspension reached below 50 mg/L after one day of aerobic treatment and nine days of anaerobic treatment.

- The second objective was to investigate the treatability of the PRW in different configuration of sequencing batch reactor. From the results of the aerobic reactor, coupled anaerobic-aerobic reactor, and mixed domestic and refinery influent aerobic reactor, the aerobic reactors produced effluent COD concentration below 100 mg/L. Highest percentage COD removals were observed in the aerobic reactor and also in the coupled anaerobic-aerobic reactor. SBR monitoring study for different parameters on a single operation cycle was carried out and showed that all three aerobic reactors achieved sCOD removal in the first 8 hr of aeration. Anaerobic-aerobic SBR configuration showed overall highest removal efficiency with low effluent concentration for COD, ammonia-nitrogen, TSS and VSS. From the anaerobic degradation of PRW results, 24 hr cycle was not sufficient to achieve the desired removal and longer cycle was needed. Anaerobic-anoxic-aerobic SBR achieved average 77% COD removal efficiency. The volatile organic compound such as BTEX was monitored under the three stages of treatment and achieved complete degradation in the process. The multi stage

process with different biological conditions resulted in effective degradation of the complex volatile pollutant.

- The third objective was to develop an integrated multi-stage biological reactor (MSBR) that incorporates different biological conditions in a single compact reactor for effective treatment. Anaerobic-anoxic-aerobic reactor configuration set-up with continuous flow was the outcome of the lab studies. The reactor accommodates the three stages to give the best compact biological system. The COD removal efficiency was always above 95% and effluent concentration was below 65 mg/L for four loads out of six. High COD removal was recorded even when the full load of raw petroleum refinery wastewater was introduced and even when the load of raw PRW suddenly was increased to three times the steady state load. The MSBR took seven days to stabilize from shock loading to similar effluent characteristics of gradual load increase.

- The fourth objective was to develop a simulation performance mathematical model for the MSBR. A model was developed using a network type of feed-forward backpropagation, and the training function was Levenberg–Marquardt algorithms, and the adaption learning function was gradient descent momentum algorithms, tangent sigmoid transfer function at hidden layer and a linear transfer function at output layer with 6 neurons as the optimum best model. From the simulation using the optimum model, 98% removal efficiency was repeatedly predicted for various loads. Effluent COD below 100 mg/L was predicted for influent COD in the range of 900-3600 mg/L.

It is recommended for future work to investigate the process details with regard to volume, flowrate and retention time in addition to process optimization. This unique reactor with its configuration could be used for treatment of different sources of industrial and domestic wastewaters. More advantages could be detailed when operating this reactor in parallel with other type of processes with the same load and source of wastewater. More investigation is needed on the degradation pathway for phenol and BTEX, and removal of heavy metals. Further, additional nutrient

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requirement for enhanced degradation may be investigated. Modeling could be optimized with advanced modeling software.

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PUBLICATIONS AND AWARDS

The developed multi-stage biological reactor during this study was filed for patent, in addition to two funded projects, while several journal papers, conference papers, awards and achievements were derived from this study.

The followings are the papers:

1. Gasim, H.A., Kutty, S.R.M. & Isa, M.H., Biodegradability of petroleum refinery wastewater in batch reactor. Proceeding of International Conference on Sustainable Building and Infrastructure (ICSBI), 2010 Kuala Lumpur.

2. Kutty, S.R.M., Gasim, H.A., Khamaruddin, P.F. & Malakahmad, A., 2011. Biological treatability study for refinery wastewater using bench scale sequencing batch reactor systems. Water Resources Management VI. Southampton: WIT Transactions on Ecology and the Environment.

3. Gasim, H.A., Kutty, S.R.M., & Isa, M.H., 2011. Petroleum refinery effluent biodegradation in sequencing batch reactor. *International Journal of Applied Science and Technology*, Vol. 1 No. 6; November 2011, Pages 179-183, ISSN 2221-1004.

4. Gasim, H.A., Kutty, S.R.M., Isa, M.H. & Isa, M.P.M., 2012. Treatment of petroleum refinery wastewater by using UASB reactors. *International Journal of Chemical and Biological Engineering*, 6, 174-177.

5. Gasim, H.A., Kutty, S.R.M. & Isa, M.H. Treatment of petroleum refinery wastewater using multi-stage biological reactor. Proceeding of International Conference on Civil, Offshore & Environmental Engineering (ICCOEE), 2012 Kuala Lumpur.

6. Gasim, H.A., Kutty, S.R.M. & Isa, M.H., Anaerobic treatment of petroleum refinery wastewater. International Conference on Waste Management and Environmental Engineering (ICWMEE), 2012 Kuala Lumpur.

7. Gasim, H.A., Kutty, S.R.M., Alemu, L.T., & Isa M.H., Optimization of anaerobic treatment of petroleum refinery wastewater using artificial neural networks. (communicated).

8. Gasim, H.A., Kutty, S.R.M., & Isa M.H., Optimization of treatment of petroleum refinery wastewater using artificial neural networks. (communicated).

9. Gasim, H.A., Kutty, S.R.M., & Isa M.H., Modelling of Anoxic-Aerobic Biological Reactor. (communicated).

The followings are the awards:

1. Overall Champion and Gold Medal Winner and Chief Minister of Perak Special Award (Aman Jaya Trophy) in Academic Research Exhibition (ACADREX 2012) Citrawarna Inovasi Malaysia.

2. Gold Medal Winner in recognition of Innovative Excellence in the category of Industrial Equipment at the twenty seventh edition of the Invention & New Product Exposition (INPEX 2012) USA.

3. Gold Medal Winner in the twenty third edition of the International Invention, Innovation and Technology Exhibition (ITEX 2012) Malaysia.

4. Bronze Medal Winner in the eleventh edition of the Malaysia Technology Expo (MTE 2012).

5. Gold Medal Winner in the twenty seventh edition of Engineering Design Exhibition (EDX 2011) Malaysia.

The following is the patent:

1. Patenting "Multi-Stage Biological Reactor for Maximum Treatment of Wastewater". (Patent filed).

The followings are the funded research projects:

1. Contract research project (Biological Treatability Study of KR-2 Effluent Treatment Plant) for PETRONAS Penapisan Terengganu Sdn. Bhd.

2. STIRF funded project (68/90.10) (Treatment of Petroleum Refinery Effluent Wastewater and Modified Biological Treatment).

APPENDIX (A)

Table A.1: Wastewater characteristics for HSEQ and FEQ

Parameter	Unit	High strength Tank (HSEQ)		Final Tank (FEQ)	
		1st 12 hr*	2nd 12 hr*	1st 12 hr*	2nd 12 hr*
pH	-	4.7	4.7	6.5	6.7
$BOD_{5\ d,\ 20°C}$	mg/L	13967	13233	1482	1303
COD	mg/L	27733	25967	2781	2933
Suspended solids	mg/L	104	136	32	30
Mercury (Hg)	mg/L	<0.001	<0.001	<0.001	<0.001
Cadmium (Cd)	mg/L	<0.001	<0.001	<0.001	<0.001
Chromium, Hexavalent (Cr^{6+})	mg/L	<0.05	<0.05	<0.05	0.08
Copper (Cu)	mg/L	<0.01	<0.01	<0.01	<0.01
Arsenic (As)	mg/L	<0.05	<0.05	<0.05	<0.05
Cyanide (Cn)	mg/L	0.055	0.05	<0.05	<0.05
Lead (Pb)	mg/L	<0.05	<0.05	<0.05	<0.05
Chromium, Trivalent (Cr^{3+})	mg/L	<0.05	<0.05	<0.05	<0.05
Manganese (Mn)	mg/L	5.19	5.26	0.33	0.32
Nickel (Ni)	mg/L	0.23	0.23	0.01	<0.01
Tin (Sn)	mg/L	<0.1	<0.1	<0.1	<0.1
Zinc (Zn)	mg/L	4.32	4.53	0.21	0.18
Boron (B)	mg/L	1.9	1.8	<0.2	<0.2
Iron (Fe)	mg/L	144	148.3	11.9	8.8
Phenol	mg/L	19.3	18.6	22	28.2
Free Chlorine (Cl)	mg/L	<0.1	<0.1	<0.1	<0.1
Sulphide	mg/L	0.027	0.037	0.047	0.027
Oil and Grease	mg/L	1.5	1.7	40	23.3
Total Dissolved Solid	mg/L	126.7	123	1516.7	1343.3
Chloride	mg/L	9010	8306.7	482.7	458
Alkalinity	mg/L	930.3	1086.7	159.7	181.7
Benzene	mg/L	5.2	5.3	29.5	31.4
Toluene	mg/L	1.9	1.8	16.5	18.2
Ethyl benzene	mg/L	37.3	42.3	35.8	41.0
Xylene	mg/L	17.5	19.4	18.6	17.8

* Average concentrations. Adopted from a local petroleum refinery (PPTSB) unpublished data.
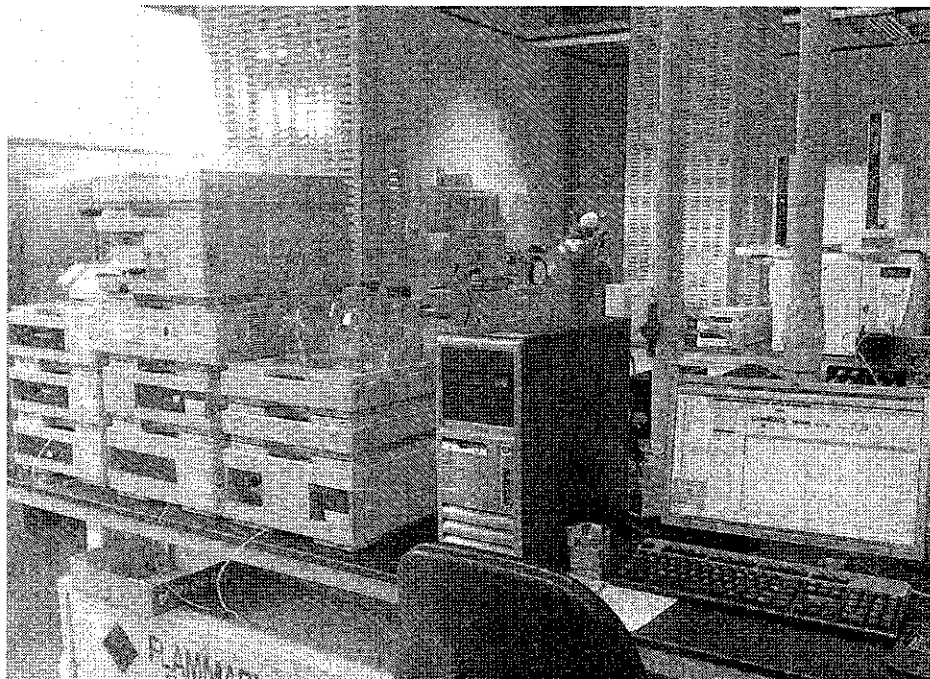
Figure B.1: High performance liquid chromatography (HPLC)
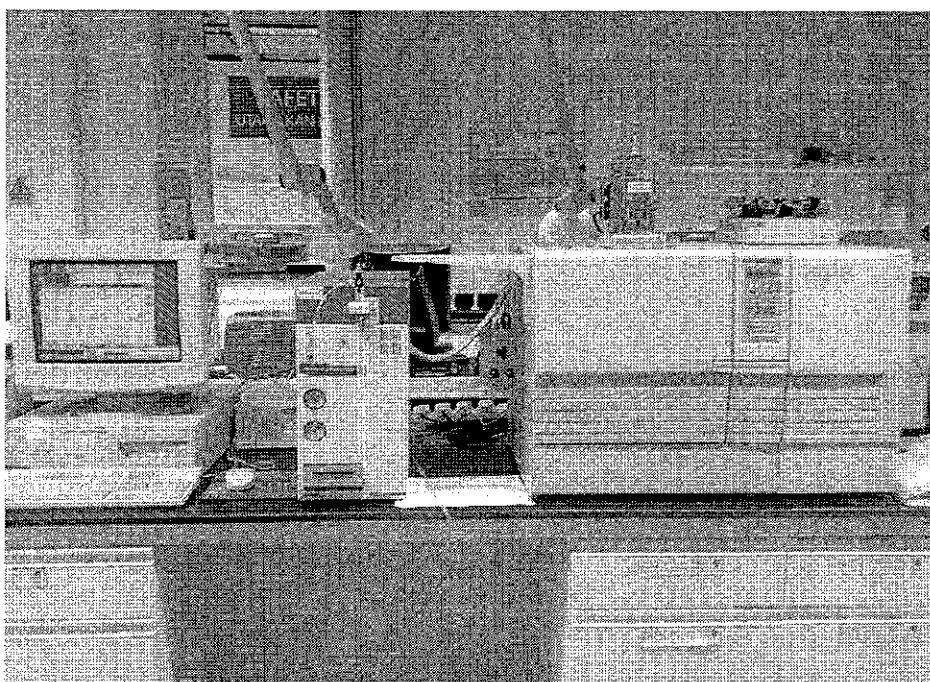
Figure B.2: Gas chromatography mass spectrometry (GC-MS)

APPENDIX (C)

Table C.1: Biodegradability conc. (mg/L) and degradation (%) for the FEQ and HSEQ

Influent	FEQ				Blank	HSEQ			
	Concentration		Degradation		Conc.	Concentration		Degradation	
Date	Aerobic	Anaerobic	Aerobic	Anaerobic	mg/L	Aerobic	Anaerobic	Aerobic	Anaerobic
0									
0.125	159	273			29	2325	2463		
1	22	207	99	24	21	1828	2230	21	9
2	23	161	98	42	20	1730	2143	26	13
3	29	151	99	50	28	1398	1940	40	21
4	31	123	99	62	30	1300	1743	45	30
7	29	72	89	69	28	628	1263	65	42
8	36	44	100	97	36	438	1075	82	57
9	32	42	100	96	32	173	853	94	66
10	34	39	96	95	28	119	621	96	76
11	33	36	94	96	26	119	449	96	83
14	31	38	100	97	31	105	189	97	94
15	32	34	99	98	30	99	148	97	95
16	30	33	99	98	29	109	130	97	96
17	28	33	95	95	22	74	118	98	96
18	34	45	96	93	29	75	128	98	96
28	40	46	99	97	39	85	104	98	97

APPENDIX (D)

Table D.1: Treatability conc. (mg/L) for the FEQ in SBR

Date	Aerobic	Anaerobic	Aerobic 4 Anaerobic	Aerobic 4 Mixed WW
1	61	330	100	74
2	60	438	97	55
3	55	470	63	42
5	68	380	42	39
6	54	444	53	34
7	53	447	73	38
8	75	461	62	51
9	46	450	36	34
10	60	486	51	45
11	85	474	63	39
12	78	459	80	42
13	58	458	64	37

Table D.2: Monitoring parameters conc. (mg/L) for 24 hr in SBR

Time (hr)	Aerobic	Anaerobic	Aerobic 4 Anaerobic	Aerobic 4 Mixed WW
sCOD				
1.0	645	1008	167	257
8.0	58	591	58	49
15.0				
21.5	65	350	52	46
Ammonia-N				
1.0	8.23	9.10	5.60	5.30
8.0	0.87	9.67	1.30	0.13
15.0	3.90	10.67	1.43	0.00
21.5	5.50	14.27	0.67	0.13
Nitrate-N				
1.0	0.75	1.50	0.00	0.67
8.0	0.30	1.03	0.33	0.53
15.0	0.73	1.60	1.80	0.73
21.5	1.57	1.23	2.50	1.53
MLSS				
1.0	4058	1467	758	2425
8.0	3458	1367	1767	2400

Table D.2 (continued)

Time (hr)	Aerobic	Anaerobic	Aerobic 4 Anaerobic	Aerobic 4 Mixed WW
MLSS				
15.0	2942	1433	1858	2350
21.5	2308	2750	1925	3242
MLVSS				
1.0	3350	1067	667	2325
8.0	2867	1025	1142	2108
15.0	2425	1192	1475	1917
21.5	1942	1308	1417	2275

Table D.3: Monitoring parameters conc. (mg/L) for 7 hr in SBR

Time (hr)	Aerobic	Anaerobic	Aerobic 4 Anaerobic	Aerobic 4 Mixed WW
sCOD				
1.0	740	920	145	337
2.5	148	799	65	80
4.0	65	722	54	48
5.5	58	650	42	34
7.0	35	563	35	27
8.0	51	574	48	37
Ammonia-N				
1.0	4.30	10.10	5.90	4.70
2.5	5.63	12.37	9.23	6.10
4.0	0.47	10.70	3.90	3.77
5.5	0.00	9.53	2.27	2.20
7.0	0.07	10.53	1.30	2.43
8.0	0.27	10.27	0.40	2.20
Nitrate-N				
1.0	1.07	1.03	3.30	5.27
2.5	1.10	1.73	4.13	2.10
4.0	1.60	0.73	6.17	1.80
5.5	0.30	0.00	8.93	1.83
7.0	1.57	0.83	11.37	3.23
8.0	0.07	1.63	9.70	2.93
MLSS				
1.0	3992	675	2417	3367
2.5	3817	1275	1808	3900
4.0	4633	2217	2183	3508
5.5	5250	2000	2458	2625
7.0	4042	792	2767	3217
8.0	4817	1192	2242	3425

Table D.3 (continued)

Time (hr)	Aerobic	Anaerobic	Aerobic 4 Anaerobic	Aerobic 4 Mixed WW
	MLVSS			
1.0	2792	450	1850	2642
2.5	3208	758	1267	3333
4.0	3825	1417	1192	2517
5.5	3242	1317	1525	2450
7.0	3125	542	2375	2800
8.0	3942	1008	1650	2117

APPENDIX (E)

Table E.1: Influent and effluent conc. (mg/L) for the Three-Stage SBR

Date	Influent	Effluent		
	PRW	Anaerobic	Anoxic	Aerobic
1	1257	1047	477	378
2	1074	1069	572	500
3	896	1039	623	398
4	899	689	610	369
5	1515	1005	475	315
6	1479	1112	512	294
7	1453	1146	553	289
8	1430	1146	633	275
19	1139	1039	834	302
21	1350	892	617	331
22	1368	823	539	332
26	1310	1169	719	356
27	1297	1130	647	339
28	1229	1069	648	291
29	1379	1056	628	282
30	1347	1034	599	261
33	1225	1104	703	304
35	1236	1039	644	313
36	1202	1067	634	319
37	1191	1087	668	274
40	1368	1149	721	278
41	1290	1140	818	300
44	1478	1169	684	286

Table E.2: Influent and effluent BTEX conc. (mg/L) for the Three-Stage SBR

Date	Influent	Effluent		
	PRW	Anaerobic	Anoxic	Aerobic
Benzene	17.919	6.564	1.153	0.118
Toluene	1.983	0.366	0.052	0.011
Ethyl benzene	0.024	0.003	0.000	0.000
m-Xylene	0.383	0.076	0.009	0.002
p-Xylene	0.370	0.074	0.008	0.002
o-Xylene	0.273	0.059	0.007	0.001

Table E.3: Theoretical and actual methane gas (L) for anaerobic reactor in the Three-Stage SBR

Date	Theoretical Methane (L)	Actual Methane (L)
1	0.160	0.085
2	0.004	0.072
3		0.097
4	0.159	0.060
5	0.388	0.091
6	0.279	0.121
7	0.234	0.085
8	0.216	0.085
9		0.078
10		0.078
11		0.078
12		0.056
13		0.056
14		0.056
15		0.056
16		0.056
17		0.080
18		0.080
19	0.076	0.080
20		0.097
21	0.349	0.121
22	0.415	0.115
23		0.121
24		0.121
25		0.121
26	0.107	0.145
27	0.127	0.133
28	0.122	0.145
29	0.246	0.151
30	0.238	0.145
33	0.092	0.121
35	0.150	0.103

Table F.1: MLSS and MLVSS conc. (mg/L) for the stages in the MSBR

Date	MLSS						MLVSS					
	Anaerobic		Anoxic		Aerobic		Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B	A	B	A	B
5	12998	22501	18890	20713	13900	10199	9990	16107	11580	15820	10540	7972
22	11900	12300	20460	25293	6753	7260	10000	9040	14780	19420	5080	5460
24	8580	13373	30010	26420	6633	7580	6187	7300	20340	17907	4640	5100
26	9047	10747	23550	12173	6073	5973	6790	7560	15140	7380	4140	4247
32	8980	26060	11840	10500	4433	6227	7524	17793	5660	6060	3240	4493
34	13653	7660	6527	10227	4653	5160	9713	5650	4564	6960	3413	3827
41	11787	22293	10433	6727	2720	4313	8527	15567	6560	4513	2107	3167
50	9247	19367	10720	9865	2553	3747	6500	13393	6913	6715	1840	2700
51					2247	3780					1572	2651
53					2695	3848					1890	2848
55	9589	12406	13504	10898	2480	3618	7222	9111	7822	7264	1655	2625
58			10130	9333	1877	2923			6910	6235	1360	2067
60					1917	3683					1273	2597
66	14967	17707	11453	14450	2074	3785	10653	12480	7793	9561	1396	2589
69	17073	14793	12460	11220	1877	3033	11907	11100	8580	7800	1337	2013
72					1997	3340					1337	2290
74					1820	2833					1190	1940
76	12380	22873	11973	12520	1773	2097	8787	15800	8120	8600	1157	1417
80					2190	1687					1420	1227
82					1757	1493					1197	1127
84	14953	10500	13693	11833	1857	1193	10587	8060	9440	7773	1290	883
86					1620	833					1040	529
88					1627	651					1073	449
91	22767	14880	16860	9400	1920	940	14860	10153	10653	6473	1203	623
93					1933	1411					1160	858
95					1791	1382					1082	833
98	17867	15207	17087	11967	1456	1360	15500	10667	10020	7953	891	831
100					1156	598					722	393
102					1160	951					793	649
105			17360	13633	1451	1051			11287	8727	884	664
107					1644	1482					1284	1011
110					1251	1320					900	871
112			13833	15527	1249	1947			9027	10787	900	1322
116					1233	1693					891	1120

Table F.1 (continued)

Date	MLSS						MLVSS					
	Anaerobic		Anoxic		Aerobic		Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B	A	B	A	B
119			8367	6933	8137	5920			5567	4760	5477	4040
121					3987	3070					2637	2073
123					3283	2360					2310	1637
126			17060	14787	3244	2858			10827	10060	2284	1922
128					2962	2273					2002	1542
130					2580	1691					1778	1164
133	20193	18640	16347	12273	2227	1440	13920	13580	11200	8680	1529	991
135					2167	2771					1482	1782
140	14107	16493	19040	11633	3071	4371	9727	11373	12220	7793	1873	2678
142					3164	4891					1907	3004
144					3896	5513					2296	3371
147	23013	17467	18733	14007	3531	7180	16220	12427	12367	9720	2273	4518
150					3493	5280					2253	3511
152					2564	3722					1713	2478
154	17240	17413	15160	14867	3309	4064	12180	12313	10067	10007	2153	2656
156					3171	3787					2096	2591
158					3149	4104					2029	2722
161	13220	14333	7980	13453	2960	4062	9467	10293	5353	9047	1876	2698
164					2771	5473					1771	3551
166					2629	4540					1716	3031
168	19533	15200	12660	16360	2816	5096	13000	11000	8567	11267	1782	3418
170					3740	5276					2329	3562
172					3500	5082					2176	3347
174					3400	4936					2147	3389
176	24960	17067	16060	16167	2913	5518	17373	12647	9693	11053	1889	3631
178	19033	13473	14900	15127	3107	6942	12827	9627	6300	10253	2071	4398
179					2047	5824					1344	3731

Table F.2: SVI (mL/g) in the aerobic stage in the MSBR A & B

Date	MSBR A		MSBR B	
	Reading	SVI	Reading	SVI
65	75	30	162.5	45
66	70	37	160	55
69	100	53	185	61
74	85	47	115	41
76	80	45	125	60
80	100	46	90	53
82	90	51	85	57
84	90	48	80	67

Table F.2 (continued)

Date	MSBR A		MSBR B	
	Reading	SVI	Reading	SVI
86	90	56	50	60
88	100	61	40	61
91	100	52	30	32
93	80	41	50	35
95	90	50	70	51
98	80	55	50	37
100	90	78	40	67
102	80	69	30	32
105	60	41	20	19
107	80	49	40	27
110	90	72	40	30
112	60	48	90	46
126	120	37	110	38
128	120	41	110	48
130	110	62	90	77
133	90	40	40	28
135	95	44	100	36
137	130	60	90	32
140	130	42	140	32
142	140	44	160	33
144	160	41	190	34
147	150	42	190	26
150	150	43	180	34
152	120	47	140	38
154	150	45	160	39
156	140	44	150	40
158	140	44	160	39
161	140	47	150	37
164	120	43	150	27
166	135	51	160	35
168	130	46	190	37
170	160	43	230	44
172	150	43	240	47
174	150	44	190	38
176	120	41	240	43
178	120	39	270	39
179	100	49	270	46

Table F.3: pH value for PRW and the effluent in the MSBR stages

Date	Influent		Effluent					
	PRW		Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B
44	8.31	7.85	8.86	8.98	9.15	9.29	9.30	9.36
46			9.08	8.99	9.23	9.24	9.30	9.38
47	8.49	8.12	8.98	8.87				
50	8.53	8.13	9.18	9.20				
51	8.07	7.93	8.82	8.87				
53	8.65	8.04	9.01	9.06				
55	8.81	8.16	8.93	8.91				
58	8.68	8.12						
74	6.68	5.64	8.03	7.62				
76	8.00	8.18	7.65	7.34	8.84	8.81	9.02	9.02
80	7.00	6.79	7.18	7.15	8.70	8.78	9.39	8.78
88	6.36	6.49	7.40	7.21	8.83	8.87	9.04	9.04
91	7.09	6.24	7.79	7.84	8.74	8.62	8.97	9.00
93	8.44	8.66	8.44	8.52	8.96	8.89	9.22	9.28
95	7.49	7.43	7.68	7.96	8.92	9.11	9.34	9.43
98	7.25	7.15	8.17	8.34	9.07	9.47	9.50	9.60
100	6.43	7.88	7.58	7.63	8.89	9.07	9.08	9.17
102	6.35	7.00	7.50	7.68	8.80	9.17	9.11	9.24
105	6.49	6.20	7.57	7.79	8.81	9.08	9.11	9.24
107	6.94	7.54	7.24	7.64	8.65	9.07	8.98	9.16
110	7.50	7.45	7.32	7.59	7.98	8.75	8.56	8.95
112	7.87	8.10	7.32	7.59	7.53	8.08	7.93	8.38
114	6.98	7.16	7.32	7.87	7.71	8.15	8.21	8.73
116	7.31	7.07	7.50	8.05	7.67	8.28	8.12	8.75
119	7.41	7.78	7.45	7.83	7.65	7.91	8.26	8.64
121	7.73	7.42	7.44	7.53	7.77	7.67	8.47	8.84
123	7.19	6.63	7.44	7.52	7.83	7.67	8.23	8.16
126	6.86	6.37	7.32	7.37	7.81	7.60	8.52	8.47
128	8.27	8.33	7.29	7.41	8.04	8.23	8.69	8.77
130	7.67	7.21	7.37	7.55	8.11	8.31	8.71	8.79
133	8.00	7.47	7.81	7.59	8.17	7.91	8.84	8.75
135	7.49	6.89	7.87	7.74	8.57	8.53	9.21	9.02
137	8.23	8.14	7.86	7.76	8.31	8.04	8.89	8.84
140	7.62	7.24	7.50	7.66	8.07	8.25	8.60	8.75
142	7.84	7.65	7.49	7.70	8.16	8.39	8.73	8.96
144	7.33	7.33	7.70	7.92	8.11	8.24	8.69	8.94
147	8.01	7.73	7.96	7.96	8.37	8.37	9.16	9.35
150	8.28	7.46	8.21	8.21	8.57	8.86	9.11	9.26
152	7.78	7.17	8.20	8.49	8.31		8.84	
154	7.46	8.46	7.96	8.16	8.20	8.60	8.80	9.08

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Table F.3 (continued)

Date	Influent		Effluent					
	PRW		Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B
156	7.43	7.80	8.53	8.52	8.41	8.85	9.56	9.66
158	7.31	7.61	8.12	8.08	8.43	8.64	9.14	9.24
161	8.78	8.54	8.34	8.63	8.72	9.30	9.61	9.78
164	8.08	7.08	7.95	8.08	8.52	8.60	8.84	8.87
166	8.01	7.42	7.82	7.68	8.40	8.70	8.95	8.88
168	8.14	7.99	7.74	7.59	8.18	8.30	8.79	8.69
170	7.45	7.39	7.80	7.76	8.43	8.16	8.89	8.85
172	7.57	6.53	7.72	7.81	8.08	8.14	8.87	8.86
173	7.77	7.77	7.45	7.80	8.07	8.50	8.80	8.90
174	8.06	8.06	7.38	7.73	8.23	8.31	8.79	8.77
175	8.08	8.08	7.60	7.80	8.16	8.32	8.82	8.72
176	8.11	8.11	7.70	7.78	8.06	8.27	8.79	8.75
177	8.15	8.15	7.69	7.86	8.04	8.09	8.72	8.71
178	8.07	8.07	7.55	7.85	8.05	8.19	8.78	8.72
179	7.81	7.81	7.47	7.84	7.90	8.19	8.61	8.67

Table F.4: COD conc. (mg/L) for PRW and the effluent in the MSBR stages

Date	Influent		Effluent					
	PRW		Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B
2	1877	1877	1773	1710	403	231	296	193
4	746	1767	703	1402	219	286	205	162
6	877	1957	382	868	151	208	153	144
8	877	1957	520	903	130	187	112	135
12	987	1761	302	690	89	167	89	143
14	987	1761	279	587	88	120	71	80
16	891	1623	223	536	71	106	69	73
18	962	1749	467	621	73	97	73	68
20	946	1894	323	633	51	92	52	50
22	1074	2025	262	655	46	87	40	45
24	1057	1883	232	601	56	109	50	60
26	991	2001	258	571	50	89	54	58
27	949	1901	209	519	47	80	42	54
28	981	2015	231	519	51	101	53	58
32	950	1961	208	478	51	96	45	55
34	876	1805	254	461	45	83	37	51
37	1143	1929	283	495	46	99	34	56
39	1297	2391	358	641	42	176	42	66
41	1231	2357	294	587	48	73	36	54

Table F.4 (continued)

Date	Influent		Effluent					
	PRW		Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B
44	992	2107	191	429	65	83	47	66
46	984	2117	179	451	38	111	48	55
47	963	2168	186	448	54	159	37	61
50	982	2039	189	406	37	74	29	54
51	1005	2138	327	509	46	73	63	60
53	882	2013	164	347	47	79	34	43
55	895	1907	168	328	43	83	44	62
58	1137	2264	193	361	75	124	54	74
60	994	2008	218	393	107	164	64	85
66	1047	2781	234	471	43	72	40	54
69	1111	3060	181	626	81	123	39	131
72	1369	3485	266	1055	78	161	71	121
74	1436	3539	290	988	60	220	51	92
76	1377	3453	259	829	61	191	60	86
80	1391	3977	248	833	58	98	52	91
82	1677	3917	308	1108	59	162	50	127
84	1615	4116	323	1221	48	201	49	117
86	1580	4108	421	1139	76	220	49	157
88	1536	3871	287	873	67	188	62	132
91	1501	3964	273	788	58	329	53	118
93	1557	4052	251	779	98	232	56	120
95	1600	3812	243	786	69	183	59	131
98	1274	3695	223	867	75	138	57	126
100	1684	4037	299	834	62	129	54	125
102	1539	3764	264	779	65	134	62	135
105	1319	3960	246	768	75	183	50	119
107	1453	3905	243	618	50	118	47	112
110	1481	3851	298	820	67	161	49	108
112	1547	4060	286	866	57	150	57	130
114	1423	3800	246	754	59	166	58	115
116	1466	3898	211	636	59	167	62	171
119	1747	3761	303	731	56	211	56	126
121	2279	6503	383	962	67	499	57	127
123	2377	6190	442	1437	82	255	58	145
126	2671	6403	623	1795	89	387	63	214
128	2641	7220	581	1806	91	253	63	244
130	2491	7277	594	1647	101	256	64	263
133	2531	7117	557	2175	92	358	67	252
135	2492	6877	509	1853	90	279	75	255
137	2437	6907	491	1713	82	392	63	213

Table F.4 (continued)

Date	Influent PRW		Effluent Anaerobic		Effluent Anoxic		Effluent Aerobic	
	A	B	A	B	A	B	A	B
140	2321	7160	543	1649	84	227	66	181
142	2841	7910	629	1971	87	349	61	175
144	2363	7217	487	1927	85	303	58	188
147	2284	6723	362	1796	79	392	62	173
150	2329	6653	428	1557	69	190	56	164
152	2645	6947	490	1499	67	214	61	156
154	2461	6937	463	1699	76	238	49	148
156	2448	6633	403	1397	83	218	53	146
158	2565	6620	426	1391	81	237	55	140
161	2715	7373	536	1779	86	155	58	142
164	2293	6890	396	1353	83	199	70	149
166	2553	7337	543	2345	93	217	70	182
168	2524	6903	531	2243	86	208	77	189
170	2191	6583	426	1455	100	373	79	175
172	2488	6717	523	1621	116	423	98	216
173	7103	7103	1674	1545	153	228	107	190
174	7343	7343	2469	1461	149	229	100	183
175	7230	7230	3221	1700	201	229	123	192
176	7343	7343	3108	1868	298	322	161	228
177	7387	7387	2461	1431	175	285	173	231
178	7160	7160	2587	1141	299	248	192	235
179	7203	7203	2052	1474	299	251	196	218

Table F.5: Alkalinity and VFA conc. (mg/L) for PRW & the effluent in MSBR stages

Date	Alkalinity Influent PRW		Alkalinity Effluent Anaerobic		Alkalinity Effluent Anoxic		Alkalinity Effluent Aerobic		VFA Influent PRW		VFA Effluent Anaerobic	
	A	B	A	B	A	B	A	B	A	B	A	B
44	766	957	860	1023								
46			880	930								
47	783	933	850	1050								
50	830	878	851	1051					344	771	20	25
51	840	840	900	1000					347	595	22	96
53	830	890	840	1000					458	927	8	45
55	840	870	860	990					454	909	9	45
58	880	930							25	54		
72									63	125		
80	680	820	740	960								

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Table F.5 (continued)

Date	Alkalinity						VFA					
	Influent				Effluent		Influent				Effluent	
	PRW		Anaerobic		Anoxic		Aerobic		PRW		Anaerobic	
	A	B	A	B	A	B	A	B	A	B	A	B
86	620	1090	720	1070	800	980	820	1070	402	250	62	312
88	640	1040	730	1160	880	1120	900	1130	523	641	22	140
91	730	1070	770	1140	680	960	640	860	580	1228	49	138
93	550	1220	610	1190	700	1010	680	1000	6	32	0	90
95	520	1180	570	1280	730	1100	700	1110	92	301	0	119
98	590	1030	590	1230	620	1080	620	1100	488	925	17	160
100	600	1130	600	1190	650	1130	620	1160	689	108	38	192
102	470	1080	580	1170	640	1200	680	1210	538	504	34	136
105	510	990	570	1170	620	1190	630	1170	568	1205	8	103
107	310	1070	420	1100	590	1160	570	1160	116	152	31	70
110	350	790	420	940	250	690	230	660	59	176	42	196
112	400	1150	410		960	260	210	230	28	114	41	219
114	380	2170	410	1620	170	460	130	390	209	730	34	128
116	410	1330	410	1410	110	380	80	350	289	1229	14	62
119	630	1270	640	1380	140	460	130	340	162	241	26	118
121	1050	1250	950	1370					189	405	46	175
123	1050	1180	1070	1300					414	841	61	393
126	1130	1650	1230	1700					939	1565	107	486
128	1080	1790	1150	1820					56	234	108	440
130	1150	1930	1170	1950					171	599	126	388
133	1560	1860	1500	2060					114	364	122	717
135	1660	1880	1790	1970					279	907	81	565
137	1310	2030	1520	2510					26	65	115	504
140	1340	3710	1410	3470					189	839	125	442
142	1370	2750	1400	3010					138	395	180	688
144	1400	3060	1420	3130					627	1542	111	683
147	1550	2430	1530	2710					89	399	31	641
150	1570	2770	1570	2780					226	1328	91	452
152	1480	3110	1540	3180					462	1940	98	379
154	1560	2990	1550	3030					549	220	109	492
156	1930	3250	1840	3300	525	870	445	835	912	562	73	337
158	2370	4510	2310	4260	680	1200	580	890	1186	917	40	342
161	1550	3390	1780	3690	490	820	460	840	88	329	154	595
164	3070	5270	2700	4730	1020	1000	720	860	269	1589	67	299
166	2290	2310	2330	2780	760	850	635	835	106	416	177	1077
168	1780	1970	2000	2250	530	510	480	485	79	233	178	990
170	1730	3510	1850	3310	660	1100	580	800	240	559	84	368
172	1700	2520	1740	2860	900	1480	570	860	469	1570	71	519
173	3480	3480	2830	3220					463	463	674	424

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Table F.5 (continued)

Date	Alkalinity						VFA					
	Influent				Effluent		Influent				Effluent	
	PRW		Anaerobic		Anoxic		Aerobic		PRW		Anaerobic	
	A	B	A	B	A	B	A	B	A	B	A	B
174	3890	3890	3500	3650	640	790	550	630	270	270	1248	372
175	3650	3650	3600	3660					214	214	1616	561
176	2950	2950	3340	3320	760	790	580	630	220	220	1543	682
177	4110	4110	3440	3710					198	198	958	336
178	5710	5710	4260	4380	790	650	590	500	125	125	1184	144
179	4720	4720	4520	4700					126	126	689	432

Table F.6: Gas production (mL) in the anaerobic stage in the MSBR A & B

Date	MSBR A	MSBR B
65	187	806
66	537	1865
68		1075
69		1075
70		1124
71		847
72		847
73		1189
74		879
76		717
77		928
78		928
79		928
80		1140
81	309	1010
82	489	1091
83	440	1010
84	391	945
85		945
86	521	1140
87	423	1238
88	391	1254
89	358	1140
90	391	1417
91	358	1401
92	456	1417
93	489	1417
94	603	847
95	326	

Table F.6 (continued)

Date	MSBR A	MSBR B
96	261	1205
97	358	1156
98	391	1221
99	375	1254
100	375	1270
101	342	1156
102	423	1498
103		
104	309	1173
105	326	1270
106	358	1335
107	326	1270
108	261	1156
109	326	1107
110	391	1091
111	407	1010
112	423	1042
113	375	1563
114	358	1563
115	277	1026
116	309	1254
117	309	
118	554	
119	456	1173
120	570	1759
121	635	1775
122	554	
123	668	
124	847	1824
125	1059	2655
126	879	2133
127		2638
128		2655
129	537	2199
130	684	2866
131	896	2817
132	798	2492
133	814	2475
134	798	1905
135	814	1905
136	717	2964
137	651	2622

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Table F.6 (continued)

Date	MSBR A	MSBR B
138	635	1922
139	814	3664
140	570	2492
141	879	2899
142	896	2915
143	896	2720
144	619	2524
145	798	2980
146	668	2443
147	472	1922
148	814	2801
149	814	2801
150	651	2671
151	782	2752
152	863	3094
153	619	2101
154	733	2785
155	831	2801
156	847	2801
157	993	2948
158	993	2964
159	798	2671
160	782	2866
161	782	3143
162	993	3225
163	1010	3225
164	928	3453
165	537	2231
166	912	2931
167	798	2671
168	668	2231
169	733	2931
170	749	2948
171	847	2769
172	847	2785
173	1857	2720
174	2247	3453
175	2378	3208
176	2524	2752
177	2378	3111
178	2557	3518
179	2931	3078

Table F.7: Ammonia-N conc. (mg/L) for PRW and the effluent in the MSBR stages

| Date | Influent | | Effluent | | | | | |
| | PRW | | Anaerobic | | Anoxic | | Aerobic | |
	A	B	A	B	A	B	A	B
4	3.53	3.85						
6							1.60	0.67
22	1.10	6.05	3.25	2.55	2.40	2.50	2.45	3.05
24	0.90	3.85	1.45	1.50	1.50	1.60	2.35	3.00
26	0.95	3.40	0.35	2.55	0.50	0.65	0.80	1.00
32	2.15	3.15	4.55	4.90	3.55	3.95	3.55	3.50
34	4.10	6.40	3.70	3.10	1.30	1.60	1.10	1.05
37	2.80	3.15	3.20	3.10	1.90	2.10	2.15	2.15
39	3.80	4.40	2.00	2.70	1.05	1.45	0.90	1.10
41	3.40	5.35	2.35	3.10	0.75	1.20	0.65	0.90
44	3.00	5.00	3.70	2.90	1.60	1.95	0.80	0.95
46	3.00	5.00	3.90	3.05	1.30	1.15	0.90	0.95
47	2.50	3.20	3.45	2.35	1.00	1.25	0.70	0.85
50	3.30	4.15	3.70	2.40	1.30	0.95	0.70	0.80
51	1.00	5.55	3.40	1.90	1.00	1.00	0.90	0.95
53	1.40	3.15	2.85	2.25	1.00	1.00	0.70	0.90
55	1.20	2.75	2.65	2.40	0.80	1.00	0.70	0.85
60	1.70	1.85	2.65	2.35	1.10	0.20	0.60	0.65
72	0.60	1.20	0.70	0.80	2.70	1.20	0.50	0.60
80	0.50	1.00	3.00	0.70	1.00	0.90	0.60	1.00
86	4.73	6.25	2.55	3.30	0.75	1.60	0.70	1.75
88	4.45	6.28	1.30	2.70	1.50	1.30	0.85	1.30
91	3.15	5.25	2.50	3.40	1.75	2.55	1.85	0.80
93	1.60	5.00	1.00	1.75	0.90	1.60	0.65	1.35
95	6.10	6.30	1.50	2.55	0.85	1.80	0.60	1.05
98	2.80	6.27	2.10	5.95	1.75	1.95	0.90	2.10
100	3.40	6.85	1.75	3.70	0.45	1.60	0.60	1.20
102	3.65	6.26	1.60	4.00	1.30	1.90	0.65	1.70
105	2.95	6.06	1.20	3.05	0.40	1.50	0.65	1.45
107	3.70	5.60	2.10	3.10	1.30	1.35	0.65	2.80
110	4.10	3.85	1.85	3.30	1.15	1.60	1.05	1.40
112	1.60	6.05	0.85	2.25	0.80	1.25	0.25	0.65
114	1.60	6.05	1.45	2.90	0.35	1.35	0.75	1.60
116	1.30	3.90	2.55	3.70	0.85	2.30	0.55	2.50
119	5.55	6.60	0.55	2.30	0.30	1.05	0.05	0.95
123	0.90	3.80	0.80	2.20	0.90	1.30	0.80	2.10
130	11.60	5.20	0.50	2.10	0.70	1.90	1.00	1.20
133	1.60	2.70	1.30	2.10	1.20	1.70	1.50	1.60
135	0.50	3.60	1.00	2.30	1.40	1.80	0.50	1.60
140	0.60	3.70	0.60	2.00	0.90	2.10	0.70	1.80

Table F.7 (continued)

Date	Influent PRW		Effluent Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B
142	1.20	6.70	0.60	3.70	1.00	1.80	0.60	1.80
147	1.80	3.50	4.70	2.30	1.10	1.80	0.60	1.80
150	1.80	2.70	3.00	2.30	1.50	2.20	1.00	2.00
156	3.00	19.20	10.60	4.80	2.30	2.40	0.80	2.00
158	3.50	19.10	11.00	4.50	2.20	0.80	1.00	2.40
161	5.10	18.20	5.00	4.30	1.60	2.00	0.80	1.50
164	4.30	11.40	0.20	0.40	2.30	2.00	0.90	1.80
166	3.70	11.80	5.10	3.90	1.60	1.80	0.90	1.80
168	6.00	13.10	4.50	4.00	1.10	1.70	0.60	1.80
170	4.30	15.50	5.80	9.00	1.60	3.20	0.50	1.80
172	5.30	7.10	10.90	8.50	3.90	4.80	0.70	2.40
174	12.30	12.30	4.60	8.80	1.40	2.20	0.80	1.90
176	13.20	13.20	5.20	6.30	1.40	1.90	1.10	1.60
178	13.20	13.20	4.40	7.90	1.80	2.20	1.00	1.70

Table F.8: Nitrate-N conc. (mg/L) for PRW and the effluent in the MSBR stages

Date	Influent PRW		Effluent Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B
4	4.50	3.75						
6							2.07	1.30
22	0.90	1.40	1.50	1.30	1.40	0.80	2.00	2.60
24	1.10	3.60	1.30	1.90	1.20	2.70	1.80	2.70
26	1.80	4.80	1.70	5.30	2.40	2.80	1.50	2.80
32	6.70	3.60	2.60	7.90	2.30	1.80	1.10	2.40
34	1.50	3.20	1.00	0.30	1.30	2.60	1.30	2.10
37	2.00	3.40	1.40	4.20	1.60	1.80	1.30	1.80
39	3.10	3.70	3.50	6.70	1.60	3.30	1.30	2.70
41	3.00	1.60	5.40	4.80	1.90	3.20	2.00	2.80
44	2.30	4.80	2.80	2.50	1.80	3.70	1.80	2.00
46	2.20	4.70	3.20	6.40	2.30	2.80	2.40	3.20
47	0.90	1.80	3.60	3.20	1.70	2.20	1.10	2.00
50	0.90	1.60	2.80	4.10	1.70	3.00	2.10	2.70
55	4.50	1.20	3.40	2.50	2.50	3.10	2.20	4.00
60	1.20	2.50	2.10	3.00	1.80	1.80	2.50	1.80
72	2.60	1.80	0.80	1.20	0.80	1.50	1.70	1.10
80	1.60	0.60	0.40	0.80	0.80	1.10	0.60	1.10
86	2.40	3.10	2.20	4.00	1.50	2.80	1.70	3.50
88	1.70	3.00	1.30	8.40	1.50	3.00	1.60	2.50

Table F.8 (continued)

Date	Influent PRW		Effluent Anaerobic		Anoxic		Aerobic	
	A	B	A	B	A	B	A	B
91	1.10	3.40	1.40	4.30	0.90	3.30	0.60	1.50
93	1.20	3.20	0.60	1.80	1.20	2.30	1.10	2.00
95	1.40	4.00	0.90	7.20	1.20	2.40	1.40	2.40
98	1.71	3.32	0.70	7.60	1.40	2.40	1.00	2.60
100	1.80	3.40	1.10	3.80	1.00	1.90	1.00	1.70
102	1.75	3.50	1.00	4.90	1.10	2.60	1.00	3.60
105	2.00	2.60	0.90	6.90	1.00	2.70	1.00	2.50
107	2.60	3.40	0.90	3.60	1.10	2.30	0.70	3.90
110	3.10	3.20	0.80	5.00	0.40	1.80	0.20	1.20
112	2.60	3.00	0.70	3.30	0.40	1.20	0.30	0.60
114	2.60	4.20	1.10	11.70	0.60	1.20	0.40	0.70
116	3.80	4.50	1.30	7.30	0.60	1.50	0.50	0.70
119	5.20	2.20	2.90	7.70	0.40	1.00	0.60	0.50
123	0.10	1.20	0.90	1.70	0.20	0.30	0.30	0.20
130	1.80	1.00	1.00	2.90	0.60	0.40	0.70	0.50
133	1.50	1.20	1.60	1.10	0.30	0.60	0.50	0.50
135	1.00	0.90	2.40	2.80	0.30	0.40	0.20	0.30
140	1.10	2.10	1.50	5.40	0.40	0.50	0.40	0.40
142	1.10	1.40	1.60	7.00	0.50	1.30	0.60	0.90
147	2.50	2.00	1.70	2.60	0.10	0.60	0.50	0.40
150	1.50	1.20	1.80	3.30	0.40	0.50	0.30	0.20
156	14.20	7.50	4.50	6.10	0.40	1.80	0.50	2.40
158	23.50	3.10	2.90	7.50	1.40	5.20	0.70	2.50
161	3.40	4.30	4.20	4.10	0.20	2.00	0.20	2.00
164	1.90	3.80	5.40	5.40	1.70	2.60	1.20	2.60
166	3.80	2.60	7.90	7.40	1.70	2.70	1.40	2.80
168	4.20	4.80	4.40	6.00	1.10	1.20	0.30	0.30
170	3.40	7.80	5.30	11.20	1.20	6.60	1.60	3.30
172	2.80	5.40	8.20	18.60	0.50	4.20	0.40	0.30
174	5.30	5.30	20.60	15.20	1.00	1.10	0.60	0.40
176	5.90	5.90	16.60	15.40	0.70	0.60	0.50	0.40
178	9.30	9.30	19.20	17.40	1.70	0.90	0.30	0.40

Table F.9: Phenol conc. (mg/L) for PRW and the effluent MSBR stages

Loads	Influent	Effluent		
		Anaerobic	Anoxic	Aerobic
PRW	14.458			
1	2.482	2.469	1.865	0.000
2	2.948	2.316	1.781	1.066
3	4.073	3.389	2.569	0.000
4	4.731	4.263	0.000	1.131
5	5.189	5.031	2.786	1.575
6	12.524	5.164	4.109	2.934

Table F.10: BTEX conc. (mg/L) for PRW and the effluent in the MSBR stages

Loads	Compound	Raw	Treatment Stages		
		PRW	Anaerobic	Anoxic	Aerobic
Load 1	Benzene	17.541	0.018	0.004	0.007
	Toluene	22.532	0.021	0.004	0.008
	Ethyl benzene	0.761	0.010	0.002	0.004
	m, p-Xylene	5.181	0.024	0.005	0.008
	o-Xylene	1.591	0.009	0.001	0.001
Load 2	Benzene	21.592	0.002	0.004	0.008
	Toluene	20.509	0.004	0.006	0.014
	Ethyl benzene	0.605	0.003	0.007	0.018
	m, p-Xylene	3.109	0.003	0.008	0.020
	o-Xylene	0.868	0.005	0.005	0.012
Load 3	Benzene	25.806	1.563	0.003	0.005
	Toluene	23.929	0.375	0.002	0.006
	Ethyl benzene	0.744	0.000	0.001	0.002
	m, p-Xylene	2.645	0.181	0.003	0.005
	o-Xylene	0.999	0.105	0.001	0.001
Load 4	Benzene	29.856	0.003	0.003	0.005
	Toluene	32.337	0.003	0.004	0.008
	Ethyl benzene	1.069	0.003	0.005	0.009
	m, p-Xylene	4.899	0.005	0.004	0.011
	o-Xylene	1.277	0.004	0.005	0.005
Load 5	Benzene	37.161	0.001	0.001	0.000
	Toluene	38.394	0.000	0.001	0.001
	Ethyl benzene	1.289	0.000	0.000	0.002
	m, p-Xylene	5.396	0.000	0.000	0.003
	o-Xylene	1.469	0.002	0.001	0.001

Table F.10 (continued)

Loads	Compound	Raw	Treatment Stages		
		PRW	Anaerobic	Anoxic	Aerobic
Load 6	Benzene	58.114	0.005	0.000	0.011
	Toluene	66.391	0.006	0.000	0.018
	Ethyl benzene	2.062	0.000	0.001	0.008
	m, p-Xylene	7.683	0.005	0.000	0.012
	o-Xylene	2.442	0.003	0.000	0.012

APPENDIX (G)

Table G.1: Logsig-Purelin number of neurons tested and the score for evaluation parameters for the anaerobic stage in the MSBR

Neurons	Training				Validation			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.076	85.952	0.859	16.878	0.087	81.259	0.811	20.284
6	0.076	86.134	0.860	17.340	0.084	82.484	0.824	18.357
7	0.075	86.249	0.862	17.255	0.084	82.681	0.826	18.963
8	0.076	85.956	0.859	16.884	0.085	82.046	0.820	20.437
9	0.075	86.250	0.862	16.694	0.084	82.307	0.823	19.280
10	0.075	86.500	0.864	16.810	0.084	82.833	0.827	19.741
11	0.075	86.516	0.864	16.977	0.083	82.892	0.828	19.312
12	0.074	86.741	0.867	17.585	0.082	83.381	0.834	19.240
13	0.074	86.608	0.866	16.426	0.080	83.077	0.839	18.749
14	0.075	86.133	0.861	16.204	0.084	83.673	0.826	16.692
15	0.074	86.724	0.867	16.205	0.082	83.243	0.832	19.318
16	0.074	86.796	0.867	16.516	0.087	81.333	0.813	17.179
17	0.074	86.589	0.865	16.585	0.084	82.502	0.823	19.558
18	0.073	87.119	0.871	15.706	0.085	82.038	0.820	19.229
19	0.074	86.716	0.867	17.047	0.083	83.187	0.831	17.725
20	0.074	86.492	0.865	16.317	0.079	84.521	0.845	18.300
21	0.076	85.834	0.858	17.072	0.088	80.756	0.807	20.642
22	0.074	86.680	0.867	16.713	0.089	80.843	0.805	17.760
23	0.075	86.480	0.864	15.911	0.086	81.644	0.816	18.804
24	0.073	86.999	0.870	16.576	0.082	83.273	0.833	20.436
25	0.073	87.008	0.870	15.617	0.094	78.069	0.779	22.914
26	0.071	87.577	0.876	16.561	0.089	80.585	0.806	20.406
27	0.073	86.956	0.869	15.467	0.102	74.924	0.743	18.735
28	0.073	86.983	0.870	16.659	0.096	77.165	0.771	20.704
29	0.071	87.825	0.878	15.832	0.087	81.314	0.813	19.442
30	0.074	86.751	0.867	16.916	0.083	82.944	0.829	19.862
31	0.068	88.734	0.887	16.171	0.109	70.841	0.708	19.909
32	0.071	87.777	0.876	16.889	0.100	75.579	0.751	21.351
33	0.071	87.756	0.877	15.273	0.099	75.503	0.755	20.904
34	0.064	89.933	0.899	15.950	0.121	63.874	0.638	22.798
35	0.062	90.687	0.907	14.955	0.121	64.026	0.639	18.894

Table G.2: Tansig-Purelin number of neurons tested and the score for evaluation parameters for the anaerobic stage in the MSBR

Neurons	Training				Validation			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.076	86.027	0.860	17.035	0.084	82.424	0.824	19.747
6	0.076	86.104	0.860	16.552	0.086	82.504	0.818	18.971
7	0.075	86.229	0.862	17.279	0.084	82.433	0.824	19.388
8	0.075	86.147	0.861	16.622	0.086	81.863	0.818	19.280
9	0.075	86.170	0.861	15.971	0.084	82.794	0.826	18.817
10	0.075	86.154	0.861	16.576	0.085	82.147	0.821	19.472
11	0.075	86.388	0.864	16.750	0.082	83.227	0.832	18.891
12	0.074	86.638	0.866	16.827	0.083	83.110	0.831	19.259
13	0.075	86.424	0.864	16.023	0.082	83.469	0.834	18.132
14	0.076	86.111	0.860	16.907	0.082	83.286	0.832	20.390
15	0.075	86.412	0.864	16.427	0.083	82.967	0.829	17.489
16	0.075	86.136	0.861	16.832	0.087	81.468	0.814	19.557
17	0.074	86.756	0.868	17.353	0.085	81.915	0.819	19.552
18	0.074	86.778	0.868	15.532	0.095	78.024	0.778	17.634
19	0.073	86.949	0.869	17.307	0.084	82.515	0.825	23.750
20	0.073	86.949	0.869	16.809	0.090	80.139	0.801	20.956
21	0.073	86.981	0.870	16.355	0.086	81.961	0.817	21.051
22	0.074	86.478	0.865	16.020	0.086	81.858	0.818	20.858
23	0.075	86.242	0.862	16.362	0.085	82.196	0.822	20.002
24	0.073	86.993	0.869	16.514	0.088	80.791	0.808	20.230
25	0.073	87.067	0.871	17.009	0.089	80.248	0.802	20.523
26	0.073	87.119	0.871	17.088	0.098	76.328	0.762	20.516
27	0.074	86.674	0.865	16.072	0.087	81.297	0.813	21.387
28	0.074	86.711	0.867	16.339	0.093	78.566	0.785	21.137
29	0.074	86.468	0.865	16.621	0.086	81.571	0.816	20.604
30	0.075	86.330	0.863	16.449	0.086	81.800	0.817	21.472
31	0.072	87.368	0.873	15.808	0.148	45.684	0.456	28.773
32	0.076	85.953	0.859	15.702	0.228	27.542	0.294	24.581
33	0.073	87.088	0.869	15.789	0.112	69.166	0.691	21.304
34	0.068	89.544	0.889	13.591	0.209	5.499	0.086	38.267
35	0.075	86.372	0.863	15.382	0.088	80.672	0.807	25.735

Table G.3: Logsig-Purelin number of neurons tested and the score for evaluation parameters for the anoxic-aerobic stage in the MSBR

Neurons	Training				Validation			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.089	82.935	0.828	16.001	0.141	64.549	0.616	20.189
6	0.088	83.363	0.833	14.624	0.112	75.974	0.755	19.213
7	0.086	83.941	0.839	15.420	0.126	70.214	0.693	18.202
8	0.086	84.241	0.842	15.720	0.130	69.075	0.672	18.168
9	0.083	85.610	0.852	15.107	0.113	75.439	0.753	19.477
10	0.084	84.904	0.849	15.197	0.131	68.450	0.664	18.425
11	0.081	85.790	0.858	14.753	0.149	57.490	0.569	18.864
12	0.082	85.679	0.856	15.171	0.161	54.036	0.494	19.274
13	0.083	85.294	0.850	14.698	0.173	48.940	0.420	22.192
14	0.082	85.376	0.854	14.794	0.144	60.376	0.597	19.378
15	0.079	87.028	0.865	14.139	0.156	72.018	0.524	21.269
16	0.080	86.078	0.861	14.665	0.155	53.271	0.530	20.114
17	0.079	86.930	0.866	14.127	0.139	65.939	0.622	20.273
18	0.080	86.414	0.863	14.209	0.123	72.929	0.708	21.053
19	0.083	85.305	0.849	15.002	0.108	77.399	0.774	20.178
20	0.076	87.683	0.876	13.607	0.332	-104.74	-1.151	29.621
21	0.079	86.616	0.865	13.822	0.181	41.757	0.365	19.364
22	0.077	87.526	0.872	14.433	0.154	56.726	0.537	24.533
23	0.076	87.647	0.876	13.528	0.178	41.629	0.385	26.905
24	0.072	88.929	0.889	14.152	0.496	-366.84	-3.787	24.716
25	0.071	89.198	0.891	12.987	0.198	33.521	0.236	37.016
26	0.075	87.790	0.877	13.225	0.164	49.732	0.478	27.160
27	0.073	88.399	0.883	13.748	0.313	-82.470	-0.910	23.223
28	0.080	86.082	0.861	13.720	0.176	39.525	0.394	23.904
29	0.075	87.888	0.879	13.988	0.181	37.879	0.360	24.553
30	0.063	91.325	0.913	12.709	0.278	-46.927	-0.503	21.400
31	0.086	84.467	0.839	12.883	0.173	45.700	0.418	25.939
32	0.070	89.522	0.895	13.007	0.280	-48.727	-0.531	26.067
33	0.073	88.638	0.885	12.788	0.180	39.011	0.366	27.280
34	0.065	90.992	0.910	13.540	0.261	-27.527	-0.329	24.501
35	0.072	89.095	0.888	13.341	0.233	-0.776	-0.057	25.933

Table G.4: Tansig-Purelin number of neurons tested and the score for evaluation parameters for the anoxic-aerobic stage in the MSBR

Neurons	Training				Validation			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.088	83.277	0.832	15.248	0.111	77.242	0.761	17.290
6	0.084	84.853	0.848	15.460	0.121	72.496	0.715	18.695
7	0.087	83.826	0.838	15.541	0.109	77.863	0.770	18.829
8	0.084	84.851	0.848	15.164	0.146	60.674	0.588	25.643
9	0.083	85.270	0.853	15.540	0.127	70.044	0.688	20.443
10	0.083	85.064	0.850	15.076	0.114	74.797	0.745	19.547
11	0.081	85.831	0.858	15.138	0.196	24.894	0.249	22.631
12	0.086	83.958	0.839	15.001	0.119	74.291	0.722	19.920
13	0.083	84.988	0.849	14.691	0.140	64.069	0.620	18.455
14	0.079	86.397	0.864	14.871	0.144	61.944	0.598	19.880
15	0.077	87.399	0.873	14.318	0.186	33.456	0.329	19.348
16	0.078	86.830	0.867	14.865	0.174	40.954	0.409	18.570
17	0.081	85.992	0.858	14.144	0.158	55.339	0.517	21.565
18	0.073	88.432	0.884	13.903	0.166	47.552	0.460	23.755
19	0.077	87.281	0.871	13.938	0.322	-101.94	-1.022	25.166
20	0.074	88.185	0.881	13.376	0.218	7.786	0.075	22.826
21	0.082	85.991	0.856	13.826	0.157	53.294	0.521	20.133
22	0.075	88.106	0.879	13.244	0.182	37.689	0.356	23.363
23	0.074	88.077	0.881	13.716	0.302	-71.451	-0.776	22.089
24	0.073	88.579	0.886	13.923	0.204	21.234	0.187	25.863
25	0.069	89.727	0.897	12.793	0.355	-135.41	-1.454	21.689
26	0.077	87.210	0.872	13.926	0.134	66.073	0.650	32.813
27	0.080	86.196	0.860	14.929	0.160	50.033	0.500	27.689
28	0.077	87.523	0.873	12.540	0.491	-368.54	-3.686	34.318
29	0.078	87.229	0.869	13.559	0.252	-307.54	-0.237	23.193
30	0.077	87.120	0.870	13.523	0.273	-35.426	-0.454	28.228
31	0.079	86.782	0.864	14.915	0.182	35.311	0.353	25.671
32	0.069	89.994	0.896	13.804	0.316	-92.500	-0.944	47.545
33	0.080	86.204	0.862	13.966	0.195	27.821	0.259	26.025
34	0.070	89.416	0.893	13.280	0.367	-161.62	-1.626	33.532
35	0.072	88.721	0.887	13.384	0.260	-31.202	-0.320	27.850

Table G.5: Logsig-Purelin number of neurons tested and the score for evaluation parameters for the MSBR

Neurons	Training				Validation			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.103	77.177	0.770	16.645	0.125	70.609	0.698	18.117
6	0.101	77.850	0.778	16.508	0.121	71.705	0.715	18.547
7	0.100	78.453	0.784	16.303	0.121	71.764	0.716	18.159
8	0.101	78.161	0.782	15.858	0.120	72.052	0.719	18.661
9	0.100	78.569	0.785	16.446	0.119	72.781	0.724	19.617
10	0.100	78.371	0.784	16.413	0.122	71.291	0.711	18.438
11	0.100	78.580	0.785	16.658	0.120	72.182	0.721	19.404
12	0.100	78.313	0.783	16.599	0.120	72.490	0.719	19.601
13	0.098	79.081	0.791	16.133	0.121	71.529	0.714	19.503
14	0.099	78.662	0.786	15.972	0.118	73.341	0.730	18.749
15	0.101	78.363	0.780	16.172	0.125	72.278	0.694	20.644
16	0.099	78.946	0.788	16.283	0.123	70.652	0.706	20.257
17	0.098	79.181	0.792	16.415	0.120	72.275	0.721	20.678
18	0.099	78.938	0.789	16.034	0.134	65.595	0.652	19.721
19	0.097	79.715	0.797	16.386	0.122	71.258	0.710	18.129
20	0.099	78.758	0.786	15.855	0.120	72.215	0.718	20.748
21	0.100	78.719	0.785	16.150	0.118	72.688	0.727	20.505
22	0.099	78.794	0.787	16.660	0.121	72.303	0.713	20.520
23	0.100	78.422	0.784	15.210	0.125	69.551	0.694	20.056
24	0.098	79.820	0.794	16.069	0.156	52.587	0.526	20.738
25	0.098	79.079	0.791	15.532	0.126	69.396	0.692	20.034
26	0.097	79.946	0.797	15.742	0.132	66.672	0.663	20.124
27	0.098	79.074	0.791	15.886	0.130	67.487	0.672	21.408
28	0.099	78.999	0.790	16.858	0.121	71.761	0.717	21.636
29	0.100	78.415	0.784	16.018	0.126	69.250	0.690	20.124
30	0.097	80.023	0.798	16.517	0.120	71.899	0.718	23.352
31	0.096	79.956	0.799	15.936	0.124	70.576	0.699	22.237
32	0.096	79.923	0.799	16.558	0.131	66.954	0.668	19.634
33	0.097	79.902	0.799	15.612	0.122	71.047	0.710	19.663
34	0.102	77.702	0.776	15.223	0.124	70.404	0.702	19.690
35	0.098	79.296	0.792	16.128	0.127	69.589	0.686	21.159

Table G.6: Tansig-Purelin number of neurons tested and the score for evaluation parameters for the MSBR

Neurons	Training				Validation			
	RMSE	VAF	R^2	MAPE	RMSE	VAF	R^2	MAPE
5	0.104	76.897	0.767	16.870	0.121	72.436	0.714	19.359
6	0.100	78.465	0.784	17.547	0.119	72.909	0.724	20.247
7	0.101	78.283	0.781	16.562	0.120	72.722	0.720	18.658
8	0.102	77.752	0.777	16.908	0.118	72.756	0.727	18.302
9	0.100	78.205	0.782	15.906	0.127	69.123	0.688	18.816
10	0.101	78.322	0.782	16.296	0.120	71.994	0.720	18.887
11	0.100	78.295	0.783	17.028	0.123	71.064	0.707	20.080
12	0.101	78.326	0.781	16.570	0.126	74.407	0.690	19.579
13	0.101	78.161	0.782	16.618	0.119	72.914	0.725	19.359
14	0.101	78.315	0.779	15.821	0.117	73.391	0.734	18.596
15	0.099	78.767	0.788	16.021	0.133	66.061	0.655	21.003
16	0.100	78.552	0.785	15.788	0.122	71.332	0.712	19.329
17	0.099	79.054	0.787	16.214	0.122	68.552	0.711	20.360
18	0.099	78.840	0.788	16.525	0.124	70.454	0.702	19.593
19	0.099	78.947	0.789	16.691	0.159	52.134	0.511	19.192
20	0.099	78.839	0.787	15.600	0.124	68.236	0.700	19.329
21	0.098	79.401	0.791	15.484	0.118	73.534	0.730	20.167
22	0.098	79.486	0.795	16.575	0.130	67.056	0.671	21.658
23	0.100	78.873	0.785	16.515	0.127	68.522	0.685	19.884
24	0.099	79.006	0.790	15.856	0.122	71.355	0.710	19.465
25	0.099	78.970	0.788	15.887	0.130	67.833	0.670	22.929
26	0.100	78.555	0.785	16.777	0.131	71.169	0.664	21.695
27	0.100	78.594	0.785	16.684	0.135	64.444	0.644	26.680
28	0.099	78.822	0.787	15.525	0.121	66.404	0.715	22.866
29	0.096	80.374	0.800	15.913	0.153	54.569	0.546	19.908
30	0.100	78.661	0.786	16.629	0.128	66.806	0.680	23.759
31	0.100	78.644	0.786	16.534	0.125	69.537	0.695	24.622
32	0.099	79.562	0.790	15.529	0.127	69.204	0.685	19.803
33	0.100	78.567	0.784	15.916	0.128	69.343	0.683	25.853
34	0.100	78.960	0.785	15.443	0.133	66.155	0.654	22.928
35	0.093	81.433	0.812	16.443	0.140	61.838	0.616	23.002

nts Form No. 22
ATENTS ACT 1983
 	
STATEMENT JUSTIFYING THE APPLICANT'S
RIGHT TO A PATENT/CERTIFICATE
(Regulations 10(2))
 	
To : The Registrar of Patents
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I. IN THE MATTER OF :
    Patent Application No. : .... Filing Date : ....
    Certificate Application No. : .... Filing Date : ....

II. TITLE OF INVENTION : **Multi-Stage Biological Reactor for Maximum Treatment of Wastewater**

III. APPLICANT (S) :
      Name   : **Universiti Teknologi Petronas**
      Address : **Bandar Seri Iskandar, 31750 Tronoh, Perak.**

IV. I we believe that the inventor(s)/innovator(s) of the above mentioned application is as follows :

     1. **Shamsul Rahman bin Mohamed Kutty**
     2. **Mohamed Husnain Isa**
     3. **Gasim Hayder Ahmed Salih**

V. Statement justifying the applicant's right to a patent/certificate :

    Being the inventor's employer

VI. ADDITIONAL INFORMATION accompanies this Form :

                 Yes [   ]   No [X]

VII. SIGNATURE ....   **13 February 2012**
                       ** (Applicant/Agent)   (Date)

      If Agent, indicate Agent's Registration No. **PA04/0141**

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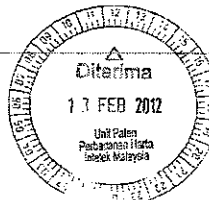Perbadanan Harta
Intelek Malaysia

Figure H.1: Patenting "Multi-Stage Biological Reactor for Maximum Treatment of Wastewater". (Patent filed).