KINETIC PARAMETER STUDIES OF ACTIVATED SLUDGE PROCESS FOR ANAEROBIC PRE-TREATED PALM OIL MILL EFFLUENT

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UNIVERSITI SAINS MALAYSIA
2007

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by

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Thesis submitted in fulfillment of the
requirements for the degree
of Doctor of Philosophy (Environmental Technology)

MAY 2007

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to his thesis main adviser, Professor Ir. Dr. Mohd Omar Abdul Kadir and co-supervisor Dr. Norli Ismail for their excellent guidance and advice provided throughout this research.

The author also thanks Professor Teng Tjoon Tow and Associate Professor Dr. Mohammad Hakimi Ibrahim, both from Environmental Technology Division, School of Industrial Technology, University Sains Malaysia (USM) for their suggestions and valuable comments during my study. Special thanks also to Professor Madya Dr Nik Norulaini Nik Abdul Rahman, University Sains Malaysia (USM) for her great assistance as well as allowing the author to use a few of her microbiology equipments throughout the study.

The author also thanks Ir. Dr. Shamsudin Abdul Latif Deputy Director General (Development), Department of Environment for his great efforts in providing suggestions and review of this thesis. Special thanks and appreciation also go to Dr. Azhar Idris, Dr. Azri Azhar, Dr. Norina Lokman of the Regional Veterinary Laboratory Bukit Tengah, Penang for graciously allowing the author to conduct a part of the research at their respective laboratory facility. This study could not have been successful without the assistance of Professor Datuk Dr Zubir Hj. Din, Mr Omar Ahmad, and the late Mr Ahmad Abu from Cluster Laboratory of National Poison Centre, USM. The dedicated microscopes specialist Mr. Muthu and Mr. Johari from the School of Biology (Laboratory of Common User Microscopes), USM made this study possible. To them deep appreciation is extended.

This research would not have been possible without the help of the author's good friends, Mr. Rizol Md Ariff, Mr. Sadali Hj. Othman, and Mr. Hj. Ishak Zakaria, of Environmental Technology Division, School of Industrial Technology, and University Science Malaysia who gave a tremendous amount of assistance in the course of the study. The author would like to acknowdge several other technical staffs from the School of Industrial Technology whom the author fail to mention specifically but has contributed in the success of this study.

In addition, special thanks to Director General Department of Environment (DOE) and the Director General of Public Service Department (PSD) of Malaysia that granted the study leave to the author and provided financial support for the doctoral study at University Science Malaysia.

Finally yet importantly, I wish to thank my wife, Che Harifah Che Seman, our children, for their support, sacrifice and lots of patience over the years it took to complete the research. Her faith, love, and encouragement as well as prayer provided the strength to the author to continue when times were rough and until the author's achieve success of this study.

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LIST OF SYMBOLS

Ar		Archimedes dimensioless number
D		Dispersion dimensionless number
K		Geometric similarity scale up factor
k	d^{-1}	Maximum rate of substrate utilization
K_c	$mgL^{-1}d^{-1}$	Eckenfelder’s first order substrate removal constant
K'_c	d^{-1}	Eckenfelder’s second order substrate removal constant
K_m	$mgL^{-1}d^{-1}$	McKinney’s constant
K_b	mg/L	Substrate loading at which the rate of substrate utilization is one-half the maximum rate (kincannon and stover)
K_s	mg/L	The saturation constant (Lawrence & Mc Carty)
K_d	d^{-1}	Microorganism maintenance or decay coefficient
K_s	mg/L	Substrate concentration at one-half the maximum substrate utilization rate
K’	$mgL^{-1}h^{-1}$	Specific substrate utilization rate
Pe		Peclet dimensionless number
Q	m^3/d	Flow rate
Q_R	m^3/d	Recycle flow rate
Q_w	m^3/d	Wastage sludge
Re		Reynolds dimensionless number
S_o	mg/L	Influent substrate concentration
S_e	mg/L	Effluent substrate concentration
U	d^{-1}	Substrate utilization rate
U_{max}	d^{-1}	The maximum substrate utilization rate (Kincannon and Stover)
V	m^3	Volume of aeration basin volume
X	mg/L	Aeration basin microorganism concentration (Mixed Liquor Volatile Suspended Solids)

X_e	mg/L	Effluent liquid microorganism concentration
Y	mg/mg	Microorganism yield coefficient

Greek Letters

Θ	h	Hydraulic retention time
θ_c	d^{-1}	Sludge age
μ	d^{-1}	Specific growth rate
μ_{max}		Maximum microorganism growth rate
μ_{max}	d^{-1}	The maximum specific growth rate (Gaudy)
κ		Geometrical scale-up factor

LIST OF ABBREVIATION

BOD	Biochemical oxygen demand
BOD_3	Biochemical oxygen demand incubate for 3 days at 30^oC
COD	Chemical oxygen demand
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
POME	Palm oil mill effluent
TOC	Total organic carbon

UNITS

d	days
g	grams
h	hours
L	liters
mL	miliLiter
mg	milligrams
%	percentage

LIST OF PUBLICATIONS & SEMINARS

1. Ahmad Kamarulnajuib C. I. & Mohd Omar; A..K.; Evaluation of kinetic coefficients for the treatment of palm oil mill effluents, Paper presented at Second Bangi World Conference on Environmental Management, 13th-14th September, 2004.

2. Ahmad Kamarulnajuib C.I. & Mohd Omar, A.K.; Application of Mathematica ® for evaluation of kinetic parameters of activated sludge process treating palm oil mill effluent. Paper presented at Ecological and Environmental Modelling, 2005, Penang.

KAJIAN PARAMETER KINETIK TERHADAP PROSES ENAPCEMAR TERAKTIF UNTUK EFFLUEN KILANG KELAPA SAWIT PRA-TEROLAH SECARA ANAEROBIK

ABSTRAK

Kajian yang dilaporkan adalah mengenai penilaian parameter kinetik proses enapcemar teraktif bagi mengolah effluen dari kilang kelapa sawit. Hipotesis kajian ini adalah parameter kinetik yang dikaji boleh digunapakai untuk menilai keupayaan proses enapcemar teraktif bagi pengolahan effluen kilang kepala sawit berkeupayaan tinggi. Parameter kinetik yang diperolehi adalah melalui ujikaji skala penunjuk yang menggunakan kaedah ujikaji aliran berterusan dan kaedah berkelompok melalui teknik ‘respirometry’. Kajian yang dijalankan ini melibatkan persampelan melalui kolam fakultatif daripada kilang kelapa sawit sedia ada. Kajian skala makmal dijalankan dengan melakukan rawatan ke atas effluen kilang kelapa sawait yang menggunakan tiga kaedah iaitu pertama, sampel effluen yang bercampur dengan karbon teraktif, kedua, plastik berlubang digunakan sebagai media terendam dalam effluen kilang kelapa sawit dan ketiganya sampel effluen tanpa campuran karbon teraktif dan media. Karbon teraktif diperolehi melalui kenel biji kelapa sawit dan disediakan berdasarkan kepada piawai yang diperbuat di makmal. Penilaian koeffisien ke atas bio-kinetik berdasarkan kaedah sedia ada adalah berasaskan COD di mana ianya di dalam nilai julat; Y (0.34 hingga 0.75 mgVSS/mg COD), k_d (0.07 hingga 0.092 per hari), k (1.009 hingga 1.57 per hari), K_s (272 hingga 348 per hari) dan μ_m (0.54 hingga 0.85 per hari). Penilaian koeffisien yang serupa beasaskan BOD adalah: Y (0.78 hingga0.84 mg VSS/mg BOD), k_d (0.04 hingga 0.092 per hari), k (1.12 hingga 3.76 per hari) K_s (218 hingga 305 mg/L BOD) dan μ_m (0.54 hingga 0.85 pe hari). Bagaimanapun, melalui kaedah ‘respirometry’, penilaian ke atas kadar maksimum tumbesaran spesifik μ_{max} yang menggunakan penunjuk tumbesaran MLVSS dan kekeruhan adalah $0.336h^{-1}$ dan

$0.354h^{-1}$ manakala nilai sekata tepu K_s berdasarkan penunjuk tumbesaran MLVSS dan kekeruhan masing-masing adalah 331.57 mg/L dan 212.93 mg/L. Kajian ini juga berjaya mencadangkan satu piawai pelepasan yang sesuai untuk COD bagi meningkatkan lagi kawalan ke atas pencemaran air bagi effluen kilang kelapa sawit.

Kajian ini juga bertujuan menilai keupayaan skala penunjuk proses enapcemar teraktif dengan umur enapcemar mikrobial. Parameter kinetik yang diperolehi dalam kajian ini telah disesuaikan dengan beberapa model enapcemar teraktif seperti model enapcemar teraktif Eckenfelder's First Order, Eckenfelder's Second Order, McKinney, Lawrence dan Mc Carty's dan Gaundy's dan Kincannon dan Stover's bagi meramalkan kualiti effluen dan isipadu (saiz) tangki pengudaraan yang bersesuaian dengan proses kilang kelapa sawit berkapasiti 45 tan buah tandan segar (FFB)/jam.

Rekabentuk dan skala pembesaran yang sesuai bagi proses pengudaraan tambahan enapcemar teraktif untuk effluen kilang kelapa sawit telah dilakukan untuk membuktikan parameter kinetik dapat digunapakai bagi satu ciri kilang berkapasiti setara 45 tan buah tandan segar (FFB)/jam.

Kajian terhadap komposisi effluen kilang kelapa sawit telah dijalankan sebagai kajian awalan untuk mengesahkan komposisi air buangan berkeupayaan tinggi ini berdasarkan kepada ciri-ciri kimia, fizikal dan biologinya. Pecahan kandungan organik dan zarah pepejalnya telah dijalankan untuk menyiasat dengan terperinci komposisi yang menyumbang kepada air buangan berkeupayaan tinggi termasuk juga distribusi saiz partikel POME terutamanya dari segi kandungan pepejal, sifat pemendapan dan ujian reologi. Kajian komposisi juga penting untuk mengesahkan komposisis effluen kelapa sawit yang terdiri daripada jenis-jenis bakteria dan bagaimana morfologinya mempengaruhi kinetik microb dalam penyeleraian effluen yang tinggi keupayaan termasuk juga kelakuan proses enapcemar teraktif.

KINETIC PARAMETER STUDIES OF ACTIVATED SLUDGE PROCESS FOR ANAEROBIC PRE-TREATED PALM OIL MILL EFFLUENT

ABSTRACT

A study on the evaluation of kinetic parameters for activated sludge process treating palm oil mill effluents is reported. It is hypothesized that kinetic parameters are applicable for analyzing the performance of activated sludge process for treating high strength palm oil mill effluents (POME). The kinetic parameters were obtained through bench-scale continuous flow experimental studies and batch studies using respirometry technique. The studies utilized samples of POME obtained from a facultative pond from an existing palm oil mill. The bench scale studies were conducted by treating the POME in three modes: first, the sample POME was mixed with activated carbon; second, the sample as a perforated plastic as a medium was submerged in the sample and third, the sample was used as is without being mixed with the activated carbon or any medium. The activated carbon was made from palm kernel and was prepared as well as characterized in the laboratory. The evaluated bio-kinetic coefficients based on COD basis by conventional techniques were in the range of values: Y (0.34 to 0.75 mg/VSSmg COD), k_d (0.07 to 0.092 d^{-1}), k (1.009 to 1.57 d^{-1}), K_s (272 to 348 mg/L COD) and μ_m (0.54 to 0.85 d^{-1}). While similar coefficients evaluated based on BOD_3 were: Y (0.78 to 0.84 mg VSS/mgBOD), k_d (0.04 to 0.083 d^{-1}), k (1.12 to 3.76 d^{-1}), K_s (218 to 305 mg/L BOD) and μ_m (0.89 to 3.18 d^{-1}). However, by respirometry, the evaluated maximum specific growth rate μ_{max} using MLVSS and turbidity growth markers were 0.336h^{-1} and 0.354 h^{-1} respectively, whereas the saturation constants (K_s) values corresponding to the MLVSS and turbidity growth markers were respectively 331.57mg/L and 212.93 mg/L. The study also proposed an appropriate discharge standard for chemical oxygen demand (COD) to further enhance water pollution control for palm oil mill effluents.

The study also evaluated the performance of the bench scale activated sludge process with the microbial sludge age. The kinetic parameters obtained in the study were fitted with several activated sludge models of Eckenfelder's First Order, Eckenfelder's Second Order, McKinney, Lawrence and Mc Carty's and Gaundy's except Kincannon and Stover's for predicting the effluent quality and volume of the aeration tank equivalent to 45 ton FFB/h mill capacity.

The proper design and scale up of extended aeration activated sludge process for treating palm oil mill effluents were performed to demonstrate the application of the kinetic parameters for a typical 45-ton FFB/h mill capacity.

Composition studies on palm oil mill effluent was also carried out as preliminary studies to determine the composition of the high strength wastewater in terms of chemical, physical and biological constituents. Fractionation of organic content and solids particles was carried out to investigate the detail composition that contributed to the high strength wastewater as well as to particle size distribution of the POME with respect to variability in the solids contents, settling behaviour and rheological tests. The composition studies were also important to justify the composition on types of bacteria present in palm oil mill effluent. The study is also to determine the composition on how its morphology influences the overall microbial kinetic degradation of the high strength wastewater as well as the performance of the activated sludge process.

CHAPTER 1
INTRODUCTION

1.1 Introduction

Over the years pollution from industrial sources has become more complex and its control more challenging as industrial processes noted for discharging wastewaters have expanded rapidly to meet economic growths and demand for new technologies for products. The complexity in dealing with the problems has promoted a lot of efforts on research and development for effective alternative industrial wastewater treatment methods so that industrial water pollution of receiving watercourses be minimized. The complexity can be attributed to the fact that most industrial wastewater exhibit considerable variability in quantity as well as quality. The extent of this variability depends, among others, on the types of products being manufactured, the manufacturing processes and technologies being employed, as well as the mode of wastewater treatment plants functions, in batch and continous operations. In certain circumtances, similar industries, may also exhibit a wide difference in quantity and quality of wastewaters owing to variation in production processes, level of housekeeping and water reuse practices, and the degree of cleaner technology and production process that have been employed.

Palm oil mill effluent (POME) is an agro-based industrial wastewater generated from the extraction processes of oil from the fresh fruit bunches (FFB) of oil palm trees (*Elaeis guineensis)*. Typically, POME is treated by the use of a series of earthern ponds and the treated wastewater is subsequently discharged into a watercourse. The oil palm considered here is sometimes also known as the ‘African oil palm’ to distinguish it from the ‘South American oil palm’ or *Corozo oleifera* (Turner and Gillbanks, 2003). POME poses a serious threat of industrial water pollution to watercourses unless proper pollution control technologies are employed.

Untreated POME which has just been discharged from a mill is a viscous brown liquid which can be classified as high strength organic wastewater with extremely high concentration of organic contents measured in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) as well as solids. The average corresponding concentrations of BOD and COD are usually within 25, 000 mg/L (100 times more polluting than the domestic sewage) and 100,000 mg/L respectively. The quantity of effluent produced varies widely among mills. As a rule of thumb, POME produced by a mill is often estimated as a minimum of just over 1 tonne POME for one tonne of crude palm oil produced. Another rule of thumb often used in the palm oil sector, is using a conversion factor of 0.67 tonne of POME generated for one tonne of FFB processed in an hour (Borja et al., 1995; Ma, 1999). Mill processing capacities range from 10 tonnes FFB/h to as high as 90 tonnes FFB per hour. Modern plants may process up to 120 tonnes FFB/h (Zin et al., 2000). Besides being high strength in organic contents, POME also exhibits substantial variability of solids suspensions distribution and excessive intensity of colour at various level of treatment processes (Chandrasekharan, 1997; Choo et al., 1997; Rusnani et al., 1999; Yusof & Sundram, 1999; Yusof & Chan, 2004).

Untreatred POME generally have pH below 5 and their temperature may range from 30^{o}C to 70^{o}C, hence their discharge to watercourses may have a deleterious impact on aquatic life. The problems are magnified when receiving watercourses are not able to provide enough dilution during dry weather conditions rendering them aesthetically unpleasant and limiting their usefulness for irrigation, fishing and other beneficial uses (Department of Environment Malaysia, 1999). Even in cases where the receiving streams afford high dilution, the discharge of POME still imposes limitation in their use as a source of portable water supply due to the colour and taste being imparted by POME. Additionally, the presence of fine size range of particles in POME is difficult to be removed effectively.

Although POME poses a serious environmental threat, the revenue obtained from the palm oil industry is an important contributor to the Malaysian economy. Malaysia contributes about 52 percent of the total palm oil production in the world (Chew et al.; 1999; Fuad et al., 1999; Ma, 1999; Malaysian Palm Oil Board, 2004; Malaysian Palm Oil Board, 2005a). The Department of Environment Malaysia (2004) reported there were 369 palm oil mills in full operation in Malaysia. From this statistics, 218 mills were granted permission to discharge treated effluent into rivers, 124 mills approved for land disposal of partially treated effluent, 26 mills allowed to adopt both methods of effluent disposal and one mill for effluent recycling.

1.2 Statement of Problems

Although several palm oil mill effluent (POME) wastewater treatment plants have been successfully operated, majority of the plants are still struggling to comply with the Malaysian discharge standards stipulated under the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations,1977. Indeed, POME is one of the contibutors of industrial (agro-based) water pollution in Malaysia (Ma, 1996; Palm Oil Research Institute of Malaysia, 1998; Zin et al., 2000; Shamsuddin 2002; Department of Environment Malaysia, 2003).

To comply with the discharge standards, the Department of Environment (DOE) imposes mandatory requirement for all palm oil mills to install appropriate individual wastewater treatment technologies within the factory premises. However, the types of wastewater treatment technologies are not specified and the mills are allowed to adopt the most suitable wastewater technologies taking into consideration not only their effectiveness but also their cost and availability in industry today.

In practice, it has been observed that palm oil millers prefer simple low cost wastewater treatment technology especially ponds or lagoon systems. The attractiveness of the treatment systems is due to their simplicity in design which is typically based on empirical design criteria or even rule of thumb. The drawback of this simplicity is that the design of wastewater treatment systems is not defensible on sound scientific basis.

Research is required to investigate alternative treatment technology for POME using well established engineering design fundamentals. The results of this study could provide a firm scientific and engineering basis for designing a wastewater treatment system for POME. Literature is abound with results of research on advance treatment of wastewaters of different characteristics in temperate countries but there is still scarcity of information in the literature on the use of advance systems for the treatment of POME (Chan & Chan, 2003).

This research is also important to establish a sound scientific basis for future decision on the possibilities of imposing more stringent or new discharge standard parameters such as chemical oxygen demand (COD). The revision to the existing Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977 is warranted to address the current demands and future challenges in water pollution and water quality management.

As mentioned earlier, the majority of treatment techniques employed for POME is still conventional by using either pond systems or to a limited extent using the mechanical systems like aerated lagoon, apart from ‘land disposal’ of partially treated POME within the oil palm estates (Chooi, 1984; Department of Environment, 1999). According to Borja & Banks (1994), the increasing stringent water quality regulations also already been imposed in many ASEAN countries that have forced mills to consider alternative POME treatment techniques. An attractive option for the palm oil industry is to shift treatment of anaerobic pre-treated POME using the current conventional pond systems to advanced technology like the activated sludge process (Ma, 1999; Zin, 2000).

Furthermore, the well known mathematical models of activated sludge process available in temperate included the Eckenfelder's First Order Model, Eckenfelder's Second Order Model, McKinney's Model, Lawrence and McCarty's Model, Gaundy's Model and Kincannon and Stover's Model and other approximated model are needed to be investigated in order to gain an insight and understanding of the tools for predicting design parameters of activated sludge process in treating palm oil mill effluent generated from a certain mill capacity. In fact, it is hypothesized in this study that kinetic parameters are applicable for analyzing the performance of activated sludge process and its variant whether in batch or continuous aeration mode for treating high strength anaerobic pre-treated POME. The associated data from this study have to be tested in the local context (tropical climatic condition) even though, the complexity and the importance of microbial kinetics in the treatment of organic industrial wastewater are already well recognised in temperate regions. It is envisaged that the results of the study will be useful in resolving the hesitation about the use of kinetic parameters for analyzing the design performance of the activated sludge process for treating anaerobic pre-treated POME.

1.3 Significance of the Study

Wastewater treatment systems to treat POME are commonly designed using empirical methods. This approach however, suffers from a number of difficulties in data interpretation and rigidity of optimisation processes. With the emergence of kinetics concepts, the process of designing biological wastewater treatment plants for palm oil mill effluent to achieve optimal treatment results can be made on a sound basis by merely optimizing the kinetic and pertinent design parameters such as sludge age, hydraulic retention time, and mixed liquor suspended solids. Design based on kinetics offers more flexibility in selecting treatment efficiency and operational characteristics. In fact, as stated by Hanqing et al., (1998) process kinetics provided a rational basis for process evaluation, control and design of an activated sludge process treating various types of wastewaters. Although many kinetic studies for activated sludge process are reported in literature, research about kinetic studies on palm oil mill effluents especially in Malaysian conditions and tropical climate is still scarce. This study is significant to gain a better understanding of how to use kinetic approach to operate and design the activated sludge process applied in the treatment of anaerobic pre-treated POME.

Secondly, this study will determine the kinetic parameters of activated sludge process specifically for the treatment of anaerobic pre-treated POME the basis of on biochemical oxygen demand (BOD) and chemical oxygen demand (COD) removal. Thirdly, this study also demonstrate the application of both conventional and modern techniques of generating the kinetics parameters data for the activated sludge process treating a typical characteristic of high strength wastewater for palm oil mill effluent. Additionally, this research also provides a firm basis for justifying an appropriate COD discharge standard to be imposed in Malaysia. Another significant contribution of this study is that the applicability of the activated sludge process models can be tested using the kinetic data obtained in this research.

Finally, the research also contribute to the understanding of solids variability in palm oil mill effluent. The method of dimensional analysis used to study settling behaviour of the solids elucidates the typical range of solids sizes, settling velocity and time required for clarification. The use of dimensional analysis is demonstrated to be a useful tool in wastewater treatment although Cheremisinoff (2002) referred it as the lost art because it is usually not heavily emphasized in engineering education today. Based on the information obtained from the dimensional analysis, discharge of solids from palm oil mill effluent into the watercourses can be controlled and managed more effectively.

1.4 Objectives of the Study

The specific objectives are:

<u>Preliminary Studies</u>

(a) To conduct preliminary studies to characterize the physical and chemical properties of activated carbon prepared from oil palm kernel shell wastes for its application in the bench-scale continuous-flow kinetic studies, and

(b) To conduct physical, chemical and biological composition tests on untreated POME and anaerobic pre-treated POME in influent and effluent of activated sludge process.

Batch Studies

(c) To conduct respirometry studies using batch reactors to investigate biodegradability of anaerobic pre-treated POME, and

(d) To conduct respirometry studies using batch reactors to generate kinetic parameter (specific growth rate) on COD removal basis for activated sludge process in treating anaerobic pre-treated POME.

Continuous Flow Studies

(e) To conduct bench-scale continuous-flow stirred-tank reactor studies to evaluate kinetic parameters for activated sludge process in treating anaerobic pre-treated POME and anaerobic pre-treated POME with powdered activated carbon, as well as anaerobic pre-treated POME with submerged perforated plastic media;

(f) To evaluate effect of sludge age upon performance parameters of activated sludge process for treating anaerobic pre-treated POME;

(g) To evaluate several established activated sludge mathematical models for predicting design parameters (volume, and effluent quality) appropriate for the activated sludge process in treating anaerobic pre-treated POME of a certain mill capacity; and

(h) To conduct design analysis and mathematical scale-up of activated sludge process for treating anaerobic pre-treated POME.

(i) To conduct an analysis on the effect of the kinetic parameters for activated sludge process in treating anaerobic pre-treated POME in terms of cost of sludge disposal, final effluent quality as well as size and cost of aeration tank.

1.5 Limitations of the Study

A study on activated sludge process can be very broad and covers various aspects including the behaviour of microorganisms during aeration process and the settling of solids. However, the emphasis of this research is on the kinetic parameters analysis of bench-scale studies involving continuous-flow stirred tank and batch (respirometry approache). The results of the study are applicable only to the .condition prevailing in this study. Applicability to the actual field conditions needs further investigation.

This study emphasizes on candidate samples of anaerobic pre-treated POME obtained from an existing anaerobic tank digester from a palm oil mill of capacity 45 tonnes FFB/h at Kuala Gula, Taiping District, Perak. The samples were mainly use for composition and kinetic studies. However, a fresh wastewater (untreated POME) samples just discharged from a mill, which consisted of a combination of wastewaters generated and discharged from three principal sources namely sterilizer condensate, clarification wastewater and clay bath wastewater from the palm oil mill were collected for composition studies only.

A comprehensive composition study would require considerable study period but due to time and resource constraints, only a few significant constituents of palm oil mill effluent for both samples that have environmental consequences were studied.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

For the purpose of this study, there are several scientific literatures needed to be reviewed. Although the main intention of this study is focused on evaluation of kinetic parameters of activated sludge process for treating palm oil mill effluent (POME), other important related subjects need to be exploited. These subjects included the known concepts and technology of activated sludge process, the conventional and modern biokinetic theory, activated sludge design models and principles of design and scale up of activated sludge systems. Other important related subjects include solids particle size distribution and its settling behaviour that affects the performance of activated sludge process needed to be exploited. In addition, literature subjects related to composition including physical, chemical and biological constituents of the wastewater focussed in this study also need a special review. The amount of published literature for kinetic analysis of activated sludge process is huge. However, most of the previous works tend to be the foundation of the most up to date literature on the subject. This sequential progress facilitates the understanding of the importance of the kinetic parameters of activated sludge process for treating typical high strength palm oil mill effluent.

2.2 Activated Sludge Process

“Activated Sludge” is really a misleading notion as the ‘sludge’ is in fact a flocculent microbial culture. According to Chudoba (1995), activated sludge is a mixed culture of microorganisms cultivated under non-sterile conditions on organic substances present in wastewaters.

Mines & Sherrard (1995) and Lee et al., (1989) reported the activated sludge process has been used successfully for treating domestic and industrial wastewaters. The process has been employed extensively and current research efforts further profoundly improved the understanding of the process kinetics. Two major steps (Nayar & Sylvester, 1979) characterize the activated sludge process. The first step involves substrate utilization and the second, solids/liquid separation. As shown in Figure 2.1, wastewater flows into the aeration basin where it is brought into contact with oxygen and a heterogeneous culture of microorganisms, primarily bacteria. The microbes for growth and energy requirements use organic pollutants and nutrients.

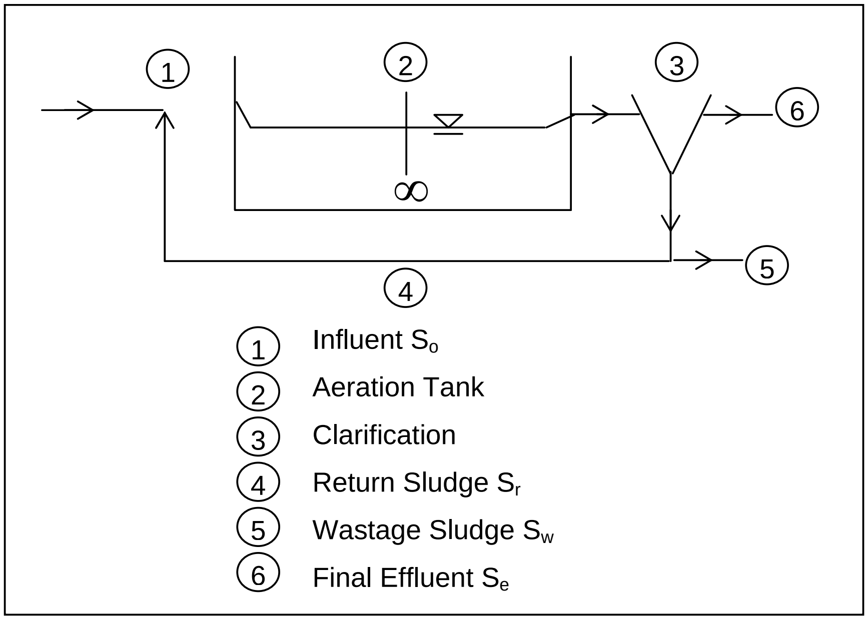

Figure 2.1: Flow diagram for a completely mixed with sludge recycle activated sludge wastewater treatment process

The activated sludge process performed the conversion of dissolved and suspended organic pollutants to biomass and evolved gases (CO_2, CH_4, N_2 and SO_2) which are separable from the treated waters (Low & Chase, 1999). According to Kiely (1998) the biochemical reaction in the activated sludge process involves bacterial cell respiration and synthesis using organic pollutants as substrate. The overall biochemical reaction in the activated sludge process is generalized in Equation 2.1.

$$\begin{array}{l} \text{Organic matter + Oxygen} \\ \text{+ nutrients + bacteria} \end{array} \rightarrow \begin{array}{l} CO_2 + H_2O + NH_3 + \text{New Biomass} \\ \text{+ other end products} \end{array} \quad \ldots\ldots(2.1)$$

The overall biochemical reaction of Equation 2.1 may be represented by three distinct processes as expressed by the following Equation 2.2, Equation 2.3 and Equation 2.4.

Oxidation (Catabolism)

$$\begin{array}{l} \text{CHON or CHONS} + O_2 + \\ \text{bacteria} \end{array} \rightarrow \begin{array}{l} CO_2 + H_2O + NH_3 + \text{waste products} \\ \text{(small molecules) + Energy} \end{array} \quad \ldots\ldots.(2.2)$$

Synthesis (Anabolism)

$$\begin{array}{l} \text{Small molecules} \\ \text{(CHONS)} + O_2 + \text{Energy} \end{array} \rightarrow C_5H_7NO_2 \text{ (New cell tissue)} + H_2O \quad \ldots\ldots\ldots.(2.3)$$

Endogenous respiration (Endogenous metabolism)

$$C_5H_7NO_2 \text{ (New cell tissue)} + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 \ldots\ldots\ldots..\ldots\ldots\ldots..(2.4)$$

During biological wastewater treatment, organic matter is used up, and endogenous respiration takes place with new cells begin to consume their own cell tissue to obtain energy for their cells maintenance and simultaneously, release carbon dioxide, water and ammonia. Throughout the respiration process, large compounds of high-energy content are broken down to small molecules of low energy content. The respiring organisms capture much of the energy lost by the large compounds (Gerardi, 2003). It is worth mentioning that the empirical chemical composition of the new bacterial cells growth in Equation 2.1 is most commonly expressed as $C_5H_7NO_2$ whereby the corresponding percentages of carbon, hydrogen, nitrogen, and oxygen are 53,6,12, and 28 respectively (Crites & Tchnobanoglous, 1998; Eweis et al., 1998). However, some literatures also quoted the empirical formula as $C_5H_7O_2NP_{0.2}$ (Bishop, 2000) or $C_{42}H_{100}N_{11}O_{13}P$ (Kiely, 1998).

Activated sludge process is very reliable for a number of reasons. Firstly, the presence of bacterial viruses or bacteriophage can cause rapid and large shifts in dominant bacterial species. Since various bacterial species always are present, if one species is destroyed by a phage, another can substitute it rapidly so that significant disorder in treatment efficiency are not detected. This probably is a main basis why activated sludge works reliably. Secondly, redundancy in microbial ecosystems and the great competition for energy resources that occurs within activated sludge, slight changes in the treatment process can result in major changes in the microbial population composition and the floc physical characteristics. Thus, redundancy allows the microbial strains most capable of surviving to dominate quickly as conditions change. Thirdly, the growth and maintenance of a large, diverse, and active population of bacteria over time developed firm and dense mature floc particles (floc formation) which ensure adequate oxidation of carbonaceous BOD and nitrogenaceous BOD. The dense flocs are resistant to shearing action and readily settleable. Moreover, the surface area of bacteria per unit mass is relatively high, 5-6 cm^2/g. This factor also explains the reason bacteria are more successful in degrading pollutants than the other prostists do (Luria, 1960; Qasim & Stinehelfer, 1982; Eweis et al., 1998; Rittmann & Mc Carty, 2001; Gerardi, 2002a). Nevertheless, Petrasek et al. (1983) reported that the conventional activated sludge process is not a totally effective system for controlling the discharge of toxic compounds, most notably lindane, phenol, bis-(2-ethyhexyl)-phthalate, and di-butylphtalate.

2.2.1 Activated Sludge Process Technology

Over the years, a number of modifications have been made to the conventional activated sludge process to accommodate specific wastewater characteristics, problems and treatment performance requirements. Generally, the nature of wastewater will dictate the preferred process modification, mainly for maintaining mixed liquor settling quality. The most common of these variations of the activated sludge process includes the extended aeration process which utilizes long aeration time (hydraulic retention time, 18 to 24 hr) and low organic loading (i.e. low food to biomass ratio) to maintain suspended culture in endogenous phase of the growth curve (Goranszy, 1979). High rate process, on the other hand, utilizes a short retention time and high food to biomass ratio to maintain culture in log-growth phase curve (Eckenfelder & Musterman, 1995).

The PACT (Powdered-activated carbon technology) is a variant of the activated sludge process typified by the addition of powdered activated carbon to the aeration basin of the activated sludge system. This process is a combination of physical adsorption with biological oxidation and assimilation has been shown to be particularly effective in treating wastewaters which variable in concentration and composition, highly colored or contain pollutants, which are potentially toxic to biological growth (Sublette et al., 1982; Dietrich et al., 1988; O'Brien, 1992; Najm et al., 1993). In fact, du Pont (Sublette et al., 1982) has patented the PACT enhancement of the activated sludge process.

Other alternative activated sludge process variant includes trickling filter (Shipin et al., 1999), rotating biological contactors (Najafpour et al., 2005) and biological aerated filter (BAF) which consist of non-adsorbing materials including shale, coke, sand, granular media as attached media for suspension microorganisms in the aeration process (Zhang et al.,1991; Mann & Stephenson, 1997; Eckenfelder, 2000). Sequencing batch reactor (SBR) is also another variant of the activated sludge process, which involves a fill-and-draw process operated under a non-steady state condition where equalization, biological oxidation and clarification are all carried out sequentially in the same tank (Ibrahim & Abasasaeed, 1995).

Grady et al., (1999), reported that although different modifications of activated sludge are available, the common characteristic of all of them, is that they use a flocculent suspended growth culture of microorganisms in an aerobic bioreactor and employ some means of biomass recycle. However, more importantly, both conventional and modern activated sludge process is to ensure successful substrate utilization rate, which is governed by the net microorganism growth rate. For the activated sludge process shown in Figure 2.1, to achieve a required level of treatment (soluble substrate BOD removal), the process is operated at a specified sludge age that is independent of the hydraulic retention time (θ). A constant sludge age (θ_c) can be maintained by proper control of sludge wasting.

2.2.2 Performance Monitoring of Activated Sludge Process

The applicability of activated sludge process is also contingent upon proper operation and maintenance of the system. Thus, performance monitoring or process control of the activated sludge process is essential for its effective operation and control in order to maintain high levels of treatment performance under a wide range of operating conditions. Performance monitoring comprises of operational monitoring and analytical monitoring. The basic process control parameters and standards essential for an activated sludge process are summarized in Table 2.1. The Department of Environment (2006a and 2006b) recommended performance monitoring parameter tests and operating ranges for different activated sludge systems commonly used in Malaysia.

Table 2.1: Performance Monitoring Parameter for Activated Sludge Process

Process Control Parameter	**Indicator or Standard**	**Frequency of Monitoring**	**Reference**
<u>Aeration Basin</u>			
Dissolved Oxygen	2mg/L to 5mg/L	In-situ and continuous basis or once per eight hour	Palm et al. (1980); Raj & Anjaneyulu (2005)
Oxygen uptake rate (OUR)	A sudden rise in OUR an upsurge of organic load while a sudden decrease indicates a toxic	At least once per day	Chandra et al. (1987); Droste (1997)
Mixed Liquor Solids (MLSS and MLVSS)	Must maintained constant	Daily	Alleman et al. (1982)
pH	Continuous basis	6.5 to 8.5	Water Environment Federation (1994); Gerardi (2002b)
Sludge volume index (SVI)	80 to 120 mL/mg	Daily	Bye & Dold (1998); Sperling & Froes (1999)
Zone settling velocity (ZSV)	Decrease ZSV indicative poor settling	Once a while or when necessary	Bye & Dold (1998)
Nutrient	BOD_5:N:P around 100:5:1	Daily	Eckenfelder & Musterman (1995)
Foam	Anaerobic condition	Daily	Gerardi (2002a); Gerardi (2002b); Gerardi & Zimmerman (2003)
Odour	Anaerobic Condition	Daily	Metcalf & Eddy (2003)
<u>Clarifier</u>			
Sludge Blanket Level	Acceptable recycle ratio & waste sludge ratio	Regularly	Davis & Cornwell (1991)
Returned Activated Sludge	Acceptable recycle ratio & waste sludge ratio	Regularly	Cho et al. (1996)

Chandra et al. (1987) reported oxygen uptake rate (OUR) is an important parameter for activated sludge process to assess the biological activity occurring in the aeration tank. However, Shamas & Englande (1992) and Gerardi (2002b) suggested specific oxygen uptake rate (SOUR) is essential for an activated sludge process control parameter. Cho et al. (1996) suggested the optimum operating parameters namely, recycle ratio and waste sludge ratio, are important deciding factor of controlling the performance of activated sludge process that included both aerator and secondary settling tank. Palm et al. (1980) reported that by maintaining minimum dissolved oxygen (DO) of 2 mg/L in the aeration basin DO will prevent filament out growth (bulking sludge) from the floc. Bye & Dold (1998) reported a decrease in zone settling velocity (ZSV) is indicative of “poor” settling. Casey (1997) reported normal flocculent activated sludge have sludge volume index of 80-120 mL/g while bulking sludge may exceed SVI of 200 mL/g. Alleman et al. (1982) offered a review of literatures pertaining to process control parameter for activated sludge process.

Another consideration for the successful operation of the activated sludge process necessitates an efficient solid/liquid separation process, which can be achieved by proper design of clarifier. Proper design of the clarifier requires microbial solids be prevented from escaping in the effluent and thickened sludge be recycled back to the aeration tank or wasted from the system for maintaining the required sludge age. For effective sludge settling, the sludge age, wastewater characteristics (constituents) and major species of microbes are important consideration. As reported by Bye & Dold (1998), secondary settling tanks play an important role in the performance of suspended-growth activated sludge processes. In fact, sludge volume index is the best measure of solids settleability and it should be used as one of the performance monitoring parameters.

2.2.3 Bacteria Associated with Activated Sludge Process

Despite there are other microorganisms than bacteria in activated sludge process, a review of bacteria is of special interest of this study. Scragg (1999) and Suwa et al. (1994) reported that through the application of environmental biotechnology, in particular, DNA technology, the culture techniques commonly used currently are not capable of providing full details of the bacterial population in activated sludge process. The bacterial population proven to be diverse in the activated sludge process.16S rRNA probes has shown that the dominant organisms were those of the beta class of the Proteobacteria, whereas the culture methods had shown that the gamma sub-class of proteobacteria was dominant in the activated sludge process.

Some past studies reported that majority of bacterial genera in activated-sludge systems belong primarily to the Gram negative species however, more recent studies using oligonucleotide probes show that Gram-positive bacteria are significant in activated sludge process. The Gram-negative genera identified included *Pseudomonas*, *Arthrobacter, Comamonas, Lophomonas, Zoogloea, Sphaerotilus, Aztobacter, Chromobacterium, Achromobacter, Flavobacterium, Bacillus,* and *Nocardia.* Generally, this group of bacteria may be involved in carbon oxidizers, nitrogen oxidizers, floc-formers, nonfloc-formers, predators, nuisance organisms, aerobes and facultative anaerobes. Saprophytes (carbon oxidizers) are heterotrophic bacteria for the degradation of organic matter. The principal carbon oxidizers genera are Gram-negative and include *Achromobacter, Alcaligenes, Bacillus, Flavobacterium, Micrococus, and Pseudomonas*. Table 2.2 show a summary of some principal genera of bacteria found in activated sludge process compiled from several reported literatures (Hammer & Hammer, 1996; Grady et al., 1999; Liu & Liptak, 2000; Rittman & Mc Carty, 2001; Gerardi, 2002).

Table 2.2: Common Genera of Organotrophs in the Activated Sludge

Genus	Strict Aerobes	Facultative Anaerobes
Achromobacter		X
Acinetobacter	X	
Actinomyces		X
Aerobacter		X
Arthrobacter		
Bacillus		X
Beggiatoa		X
Cornynebacterium		X
Enterobacter		X
Esherichia		X
Flavobacterium		X
Klebsiella		X
Micrococcus	X	
Microthrix	X	
Nitrosomonas	X	
Nitrobacter		X
Nocardia	X	
Proteus		X
Pseudomonas	X	
Sphaerotilus	X	
Thiothrix	X	
Zoogloea	X	

(Source: Horan,1990; Gerardi, 2002a)

Floc-forming bacteria play a very important role in suspended growth biochemical operations because without them, the biomass cannot be separated from the treated wastewater nor can colloidal-sized organic pollutants be removed (Grady et al., 1999; Gerardi, 2002b).

Nitrogen oxidizers bacteria involves in conversion of ammonia-N to nitrate-N. during nitrification process in activated sludge. The primary bacterial genera in the aeration tank of activated sludge process that are capable for nitrification are *Arthrobacter, Bacillus, Nitrosomonas, Nitrobacter, Proteus, Pseudomonas, and*

Vibrio (Grady et al.,1999; Gerardi, 2002a). Denitrification, on the other hand, is significant in activated sludge process because this process helps strengthening of the floc particles, control undesired filamentous growth and returns of alkalinity to the treatment process. The reduction of nitrites ions (highly toxic) discharged to the receiving water reduces toxicity concerns related to aquatic life. The denitrifying bacteria included *Bacillus,* and *Pseudomonas.* Numerous oxidation states of nitrogen in the activated sludge process are *Nitrate ion, Nitrite ion, Nitric oxide, Nitroxyl, Nitrous oxide, Molecular nitrogen, Hydroxylamine, Ammonia, Ammonium ion.*

Furthermore, the group of Gram-negative bacteria in aeration tank of activated sludge process responsible for aerobic respiration is *Nitrosomonas* and *Nitrobacter*. The Gram-positive aerobic bacteria are Sarcina. While those responsible for aerobic or anaerobic (facultative) respiration is E. coli, Salmonella, Aerobacter, Shigella, Bacillus and Pseudomonas. Those facultative bacteria belong to Gram negative. The oxidizing bacteria that degraded sulphur in the form of sulphite ion are *Sulfolobus*. The filamentous bacteria *Leptothrix* and *Crenothrix* deposit oxidized iron, Fe $(OH)_3$, in their sheath and forming yellow or reddish-colored slimes (Horan, 1990; Hammer & Hammer, 1996; Gerardi, 2002a; Gerardi, 2003).

Many types of filamentous organisms could be responsible for bulking (a poor-settling of biomass).The main filamentous bacteria are *E. coli, Sphaerotilus natans, Nocardia spp, Thiothrix spp, Sphaerotilus natans, Microthrix parvicella, Halsicomenocbacter hydrossis, Nostocoida limicoda (Types* I, II, and III)*, Beggiotoa spp, type 1701, type 021N, type 0041, type 0041, type0675, type0803, type1851, type0961, type0581, type0092 and type0914.* The conditions that promoted filamentous bacteria in activated sludge are low dissolved oxygen (DO); low food to microorganism’s ratio, nutrient deficiency and low pH. Although *Nocardia* is a commonly found filamentous organism, it does not normally cause bulking because its filaments do not extend beyond the floc particle. Foaming is another major nuisance associated with suspended growth cultures in activated sludge process. This condition is caused primarily by bacteria of the genus *Nocardia* and *Rhodococcus* under the group of *Actinomycetess* and the species *Microthrix parvicella* (Palm et al., 1980; Viessman et al., 1985; Horan, 1990; Blackall et al., 1991; Chudoba, 1995; Grady et al. 1999; Rittmann & McCarty, 2001; Gerardi, 2002b).

The ability to remove phosphate (Phosphorus) in activated sludge mixed liquor is a bacteria species known as Acinetobacter *junii* (Momba & Cloete, 1996). In addition, deficiency in certain nutrients can cause stress for the bacteria growth. Bacteria growths needs to maintain the weight ratio for BOD_5: N: P: Fe to be 200:10:2:1. Beside, a pH of 6.5 to 8.5 and moderate temperatures (approximately 10 ^oC to 40^oC) also essential to be maintained in the aeration tank (Gerardi, 2002a; Gerardi, 2002b).

2.3 Review of the Importance of Kinetic Analysis

In the past the design of activated sludge process was based on empirical parameters developed by experience. Many of these empirical parameters included organic loading, hydraulic loading, aeration period etc. However, empirical methods suffer from a number of disadvantageous including they cannot be used to interpret data; and optimize processes. Moreover, design of activated sludge process based on empirical methods often led to operational failure and non-compliance with effluent standards. However, nowadays, due to enhanced knowledge of fundamentals, design is based on process kinetics.

The emergence of microbial or biological kinetic (in short, biokinetic) theory, proper design and operation of activated sludge processes can be successfully achieved, by employing rational parameters based on biological kinetic equations. These equations express biological (sludge) growth and substrate utilization rates in terms of biological kinetic coefficients, food-to-biomass ratio, and the mean cell residence time. Using biokinetic theory allows for the prediction of soluble effluent substrate concentration (BOD, COD, TOC), aeration basin mixed liquor suspended solids concentration (MLSS), nutrient requirements (nitrogen and phosphorus), oxygen requirements, and daily sludge production. Of utmost importance, the success of the model is dependent upon the biokinetic coefficients used. The values of kinetic coefficients growth yield (Y), maximum rate of substrate utilization per unit mass of biomass (k), saturation coefficient (k_s) and microbial decay coefficient (k_d) greatly influence the design of the activated sludge process. These values very much dependent on the characteristics of the wastewater to be treated especially when it contains industrial wastes. Numerous investigators have enhanced the treatment efficiency through the development of microbial kinetics and substrate utilization equations (Lee & Lin, 1999).

The basic biological kinetic equations governing the kinetics of processes for organic substrate (BOD, COD, and TOC) removal and microbial growth in activated sludge processes are well documented in the literature (Ghosh et al., 1976). The biological kinetic expression is based on the Monod Model of population dynamics (Viessman & Hammer, 1985; Degremont, 1991; Mihelcic, 1998).

Substrate removal

Equation 2.5 gives the general steady–state mass balance equation for the substrate entering and leaving the aeration basin (substrate removal). Figure 2.2 shows the complete mix activated sludge scheme.

$$\frac{Q(S_o - S_e)}{XV} = U = KS_e \qquad \text{……………………………………………………}(2.5)$$

Where:

Q = volumetric flow rate of wastewater;

S_o = influent substrate concentration;

S_e = effluent substrate concentration;

X = biomass concentration in the aeration tank;

V = volume of aeration basin;

U = specific substrate uptake rate, time;

K = substrate uptake constant, mass. Time

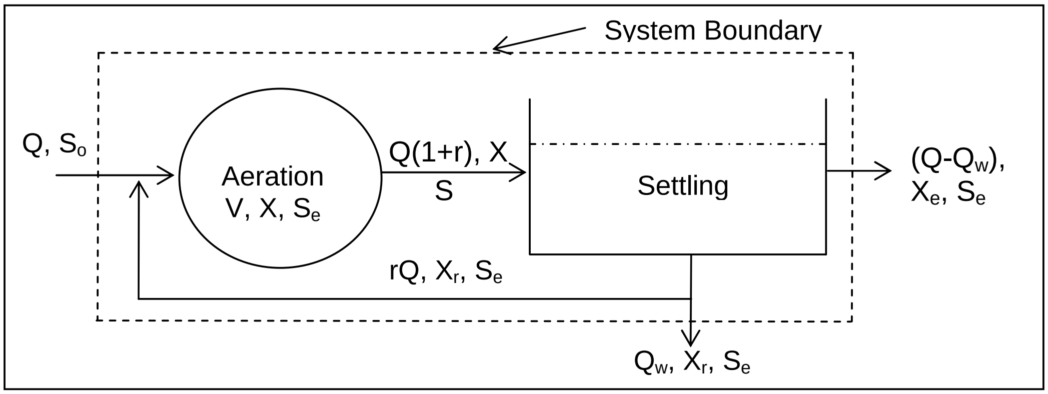

Figure 2.2: Complete-mix activated sludge process scheme

The specific substrate utilization rate can also be represented by;

$$U = \frac{kS_e X}{K_s + S_e} \qquad \text{……………………..…………………………………………}(2.6)$$

Where:

k = maximum rate of substrate uptake time^{-1}

K_s = half-saturation constant, mass volume^{-1} (mg/L)

The Monod kinetic model as in Equation 2.6 is an empirical relationship of mixed–order reaction, which can be described by a rectangular hyperbolic curve and analogous to the Michaelis-Menton equation, which describes enzyme reaction kinetics (Bailey & Ollis, 1986; Horan, 1990). According to Cheremisinoff (1994) and Stephenson & Blackburn (1998) the Monod model were first developed by Michaelis-Menton, and the constants k and K_s are often known as the Michaelis-Menton constants.

Cell yield

Microbial growth rate can be expressed by:

$$\frac{dX}{dt} = Y_t \frac{ds}{dt} - k_d X \quad \text{……………………………………………………………(2.7)}$$

Where:

(dX / dt) = net rate of change in biomass

Y_t = true cell yield coefficient

k_d = cell decay coefficient

The observed cell yield in complete system decreases as the sludge age increases. Cell yield in systems can also be expressed as:

$$\frac{dX}{dt} = Y_{obs} \frac{ds}{dt} \quad \text{..……………………………………………………………..………(2.8)}$$

Where:

Y_{obs} = observed cell yield coefficient