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**MODELLING THE EXOTHERMIC HEAT AND THE DEMAND OF
COOLING IN PAPER AND PULP INDUSTRY BIOLOGICAL WASTE-
ATER TREATMENT**

Examiners: Assoc. Prof. Matti Heilio

Assoc. Prof. Tuomo Kauranne

ABSTRACT

Lappeenranta University of Technology
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Modelling the exothermic heat and the demand of cooling in paper and pulp industry biological wastewater treatment

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Abstract

This master thesis presents a study on the requisite cooling of an activated sludge process in paper and pulp industry. The energy consumption of paper and pulp industry and its wastewater treatment plant in particular is relatively high. It is therefore useful to understand the wastewater treatment process of such industries. The activated sludge process is a biological mechanism which degrades carbonaceous compounds that are present in waste. The modified activated sludge model constructed here aims to imitate the bio-kinetics of an activated sludge process. However, due to the complicated non-linear behavior of the biological process, modelling this system is laborious and intriguing. We attempt to find a system solution first using steady-state modelling of Activated Sludge Model number 1 (ASM1), approached by Euler's method and an ordinary differential equation solver. Furthermore, an enthalpy study of paper and pulp industry's vital pollutants was carried out and applied to revise the temperature shift over a period of time to formulate the operation of cooling water. This finding will lead to a forecast of the plant process execution in a cost-effective manner and management of effluent efficiency. The final stage of the thesis was achieved by optimizing the steady state of ASM1.

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Alphabetical Conventions

Symbol	Function	Unit
A	Matrix of a wastewater component concentration	
Area	Heat transfer surface area	
B	Matrix of a influent wastewater component concentration	
b_H	Decay coefficient for heterotrophic biomass	[day^{-1}]
C	Matrix of yield coefficient	
c_p	Heat capacity	[$J/kg K$]
f_P	Fraction of biomass transformed into inert particulate product rate	[dimensionless]
k_h	Maximum specific hydrolysis rate	[g slowly biodegradable COD]
K_{La}	Oxygen mass transfer rate coefficient	
K_{OH}	Oxygen half-saturation for heterotrophic biomass	[gO_2m^{-3}]
K_S	Half-saturation coefficient for heterotrophic biomass	[g COD m^{-3}]
K_X	Half-saturation coefficient for hydrolysis of slowly biodegradable substrate	[g slowly biodegradable COD]

P	Vector of process rate	$[ML^{-3}T^{-1}]$
Q_0	Influent flow rate	$[m^3/day]$
Q_1	Tank 1 out flow rate	$[m^3/day]$
Q_2	Tank 2 out flow rate	$[m^3/day]$
Q_3	Tank 3 out flow rate	$[m^3/day]$
Q_4	Settling tank inflow rate	$[m^3/day]$
Q_a	External recycling flow rate	$[m^3/day]$
Q_e	Effluent flow rate	$[m^3/day]$
Q_r	Recycling flow rate	$[m^3/day]$
Q_w	wasted sludge out flow rate	$[m^3/day]$
r	Reaction rate of system	
S_O	Dissolved oxygen concentration	
$S_{O,sat}$	Dissolved oxygen saturation	
T_c	Cooling water temperature	[K]
T_{in}	Inflow water temperature	[K]
T(t)	Temperature at given time	[K]
U	Heat transfer coefficient	
u	Vector of control variable	
V_1	Volume of tank 1	$[m^3]$
V_2	Volume of tank 2	$[m^3]$
V_3	Volume of tank 3	$[m^3]$

x	Vector of process variable	
X_1	Tank 1 wastewater component concentration	$[mgCODm^{-3}]$
X_2	Tank 2 wastewater component concentration	$[mgCODm^{-3}]$
X_3	Tank 3 wastewater component concentration	$[mgCODm^{-3}]$
X_4	Settling tank inflow wastewater component concentration	$[mgCODm^{-3}]$
X_a	External recycling wastewater component concentration	$[mgCODm^{-3}]$
X_e	Effluent wastewater component concentration	$[mgCODm^{-3}]$
X_r	Recycling wastewater component concentration	$[mgCODm^{-3}]$
X_w	Wasted sludge outflow wastewater component concentration	$[mgCODm^{-3}]$
Y_H	Yield for heterotrophic biomass rate	$[gCODoxidized^{-1}]$

Greek Conventions

Symbol	Function	Unit
$\hat{\mu}_H$	Max specific growth rate for heterotrophic biomass	$[day^{-1}]$
ΔH	Enthalpy change	$[kJ/mol]$
ρ	Density	$[Kg/m^3]$

List of Abbreviations

P&P	Paper and Pulp
WWTP	Waste Water Treatment Plant
AS	Activated Sludge
ASP	Activated Sludge Plant
ASM1	Activated Sludge Model no.1
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
BOD	Biological Oxygen Demand
MP	Mechanical Pulping

1 Introduction

Water is the most essential resource on this planet. Approximately, 70% of our planet is covered by water, and yet to meet the fresh drinking water demand of every individual on this earth is a big challenge. In the last few decades, our warming climate and population increase have made water scarcity an acute problem in many parts of the world. Water pollution and consumption is not caused just by household usage, but also by many industries, like food production, paper and pulp industry, pharmaceutical and chemical industries. They all contribute significantly to the consumption and contamination of water resources [2].

In the past few years, the European Union and its affiliate countries have sequentially executed several measures to ensure a sustainable water management process. Most of the pollutants released in water is by industries that do not satisfy the effluent discharge criteria, since these discharges are not easily biodegradable and sometimes contaminated with xenobiotic compounds [1]. Therefore, wastewater treatment plants for industries and municipalities become necessary to meet the water demand of a growing population and at the same time to maintain water quality and a healthy ecosystem. Wastewater treatment plants primarily execute biological degradation of waste compounds that are present in water using bacterial biomass under a process called activated sludge process. Activated sludge process is economical and produces a high quality effluent.

To meet the legislative standards imposed by The EU strategy for sustainable development (European Commission 2004), and lately by, Water Framework Directive (WFD), the effluent needs to be properly disposed of before, if they gets discharged into water bodies, to reduce its environmental impact [3]. As a consequence, it is required to get a good comprehension into the wastewater treatment plant and this is helped by modelling of the activated sludge process. Mathematical modelling will not only help us to understand the mechanism better but it also provides insight into process optimization and process control to improve effluent quality and quantity [1, 2, 3].

Paper and pulp (P&P) industry over the world is considered to be a heavy consumer of water. It also discharges a lot of pollutants, which contaminates the environment either through atmospheric discharge or through wastewater discharge. The effluent discharged from such industries contains gaseous, solid and liquid waste which can be toxic to receiving aquatic life. P&P discharge enhances slime formation in the water body, color problems, aesthetic problems and thermal problems, affecting

water ecosystems in a way that results in death of zooplankton and fish [6]. This is an outcome due to untreated discharge that contains a high concentration of COD, BOD and chlorinated compounds. Therefore, it is essential to minimize these effects [4].

In 1987, a numerical description of the biochemical process of activated sludge bioreactor was proposed by *Henze et al.* under International Water Association (IWA) in order to understand the design and operation of sludge processes. The Activated Sludge Model number 1 (ASM1) work is still used as a reference work for technical and educational purposes. Over the years, a number of modified versions of ASM1 have been established to overcome the limitations of ASM 1. Considering all the limitations of ASM1, it is still an extensively studied model to get insight into wastewater treatment plant biological processes [7].

1.1 Scope and outline of the thesis

The current work attempts to establish an answer to why it is essential to add cooling water in a paper and pulp industry wastewater treatment plant, since injecting cooling water not only increases water loading to the plant but it also requires energy consumption [10]. In an attempt to obtain an answer, we primarily try to understand the key pollutant degradation process [21] and the amount of heat transfer during this transaction. Later on, we have attempted to implement this finding into a modified activated sludge model number 1 and try to investigate the behavior of the temperature over a period of time as the activated sludge process proceeds.

To create an in-depth understanding on this topic, the research is partitioned into different sections. A brief synopsis of this thesis work is outlined below. The current chapter presents the purpose and significance of this research. Chapter 2 introduces a rudimentary insight into the paper making process and forms of waste released at each step of the various sub-processes. It also renders a brief introduction to wastewater treatment plants and the activated sludge process. Chapter 3 will give insight into the research problem and objective of the current work. Chapter 4 will discuss in detail a Modified Activated Sludge Model No. 1 (ASM1) and numerical integration techniques of the model outlined in this section. The chapter further gives insight into the Temperature Shift Model. Chapter 5 gives an explanation on enthalpy change calculation using Hess law as well as a dynamic behaviour study

on key pollutant degradation. Chapter 6 outlines the ASM1 matlab simulation results and presents a temperature study. The practical problem is supplemented with empirical evaluation and the results have been compared. Finally, chapter 7 provides the conclusions of this study.

2 Paper manufacturing process

2.1 Process description

Pollution from paper and pulp industry is a prime concern since paper production results in a large quantity of wastewater generation. Furthermore, pulp production uses only 40-45% of the total wood weight, and the resulting effluent is massively bulky in carbonaceous organic load. If such untreated discharge is released into a water body it can cause tremendous damage with high BOD and COD [6].

At present, paper and pulp industry encounters challenges like adopting stringent environmental regulations, energy efficient usage of resources and achieving financial growth by reducing processing cost [5]. This Thesis work is focused on the paper and pulp industry wastewater plant study. P&P manufacturing processes basically divided into five steps, each process step utilizing a number of chemicals to yield its final product. The steps are as follows debarking, pulp preparation, bleaching, washing and final step paper making. Pollutants are released during each process which results in air, water and environmental pollution. The details of each P&P manufacturing process step and description of pollutants released in each process are as follows [4, 5, 6].

Debarking: In this process, wood logs are first converted into smaller wood pieces called chips; in the following step; Soil, dirt and bark are removed as per the nature of the raw material used. The process results in the transfer of tannins, soil, dirt, suspended solids, resin acids, lignin present in the bark into the processed water.

Pulp preparation/ delignification or cooking: wood chips in this process will get converted into pulp. The process removes majority of lignin and hemicellulose from the raw material and results in cellulose rich pulp. The delignification step can be carried out by mechanical or chemical (Kraft) method. In the chemical Kraft method, chips are cooked at high temperature and pressure in the presence of 'white liquid' (NaOH and Na₂S or sulphite (HSO₃) process. However, yield in Mechanical Pulping (MP) is high when compared with chemical pulping but, the quality of the product is significantly lower. Therefore, improvement of MP can be achieved by several techniques, such as thermo-mechanical pulping, chemo-mechanical pulping, and chemical thermo-mechanical pulping.

Subjected to the technique used, the above process releases various pollutants mixed with the process water such as resins, fatty acids, colors and chemicals such as $NaOH$, NaS_2 , H_2SO_3 , Na_2CO_3 , Na_2SO_4 , Na_2SO_3 , H_2SO_4 and $Na_2S_2O_3$. Treated water at this step is highly alkaline, with high COD and BOD content.

Bleaching: pulp produced from the Kraft process is brown in colour since major proportion of pulp that is made is used for the production of either, white or coloured papers for writing and printing purpose. On that account, pulp needs to be bleached in order to improve brightness.

Bleaching can be carried out using chlorine, chlorine dioxide, sodium hypochlorite, hydrogen peroxide, oxygen or ozone as bleaching agent. It removes virtually all of the lignin that still remains after cooking, as the lignin contains the chromophoric groups which make the pulp dark. In recent times, bleaching is carried out using the Elemental Chlorine Free (ECF) technique or Total Chlorine Free (TCF) bleaching processes. Elemental chlorine (Cl_2) was for many years the work horse of the bleaching process. It is efficient in bleaching the pulp and does not degrade the pulp strength. However, it produces a large amount of chlorinated organic compounds like dioxin or dioxin-like carcinogenic compound in the effluent, and strenuous efforts have therefore been made to decrease its usage. In the total chlorine free process, different combinations of bleaching acid (H_2SO_4), ozone, chelating agents or hydrogen peroxide steps are used.

The waste generated at this stage contains dissolved lignin, high COD, AOX, inorganic chlorinated compounds such as chlorate (ClO_3) and organic chlorinated compounds such as dioxins, furans, chlorophenol and volatile organic carbons such as chloroform, acetone, methylene chloride, carbon disulphide and chloromethane.

Washing: the above produced pulp is washed using alkaline caustic soda. It apply for the removal of the bleaching agents and hardly biodegradable compounds. It is also known as alkaline extraction stage.

Paper-making: pulp fibers are mechanically and chemically treated to form a dilute suspension, this further spread over a mesh surface. In the next step water is removed by suction, and the resulting pad of cellulose fibers pressed and dried to form paper. Various chemicals (sizing agent, fillers, dye) are add to improve paper qualities such as color, water resistance and sizing agents like rosin and starch to form the paper.

Sizing agents provides water resistance in order to have some kind of writing

quality. Rosin, alum and starch are normally used as sizing agents. Fillers are added in paper industry to increase brightness or to increase the optical and surface properties of paper. clay, chalk, titanium dioxide and talcum powder are some of the examples of fillers used in paper industry. Various dyes and pigments are also add to enhances whiteness or to color papers [4, 5, 6].

2.2 Wastewater treatment plant

The prime purpose of a wastewater treatment plant is to degrade pollutants which may be detrimental to water body from the sustainability aspect. Wastewater treatment plant consists of preliminary treatment, primary, secondary and tertiary treatment. In above mentioned process wastewater passes through various mechanical, biological and chemical processes before it gets discharged or reused. The activated sludge process (Secondary treatment), or Biological process, where bacterial biomass degrades organic pollutant compounds which are present in water by using them as their carbon and energy source. Subjected to reactor design, secondary treatment may achieve the degradation or removal of Carbon(C), Nitrogen(N) and Phosphorous (P) compounds [1].

The complexity of wastewater treatment processes has increased dramatically in the last two decades due to requirements to meet the effluent discharge criteria, to remove nutrients such as nitrogenous and phosphorous compounds, together with carbonaceous compounds. In P&P industry, a large quantity of pollutants come in the form of organic carbon (C) compounds, therefore P&P industry uses aerobic activated sludge processes, where carbon load get reduced in the presence of oxygen [1, 4].

2.3 Activated sludge process

The secondary treatment, also called activated sludge process, was first introduced by *Ardern* and *Lockett*. The wastewater is mixed with a consortium of microorganisms, which brings an accountable change in organic compounds (polymers) and/or nutrients that are present in waste by degrading them to simple compounds (monomers). This process is a complex mix of microbiology and biochemical transaction. In the activated sludge process bacteria secrete sticky substances that coat the minute particles (waste) carried in industrial waste stream. The particles stick

together to form aggregate of gel-like material, creating a support for bacteria to grow. This results in the formation of microfloc. Bacteria use those microfloc (particles or organic pollutants) existing in wastewater to grow and transform them to energy, water, CO_2 and new cell material. In the next stage, the following microflocs collide to form visible flocs which increases settling capacity in the settling tank. The activated sludge is aerated to dissolve oxygen which alleviates the removal of carbonaceous compounds faster and more efficiently [7, 8, 10].

Biological removal of nutrients like nitrogen is achieved by a nitrification and denitrification process, whereas, the removal of phosphorus in activated sludge systems can be done chemically or biologically [7, 9].

Since P&P industry waste is extremely loaded in lignin and other polysaccharide we restrict our study to aerobic activated sludge process [5].

2.4 Activated sludge model

Mathematical models are used as problem solving tools in many areas. Modelling of activated sludge process turn into an essential aspect for designing, operating, plant scaling and optimisation. In 1987, a model called Activated Sludge Model number 1 (ASM1) was established by *Henze et al.* under International Association on Water Pollution Research and Control (IAWPRC), which is now known as International Water Association (IWA) formally. ASM1 model was dealing with biological degradation of carbon and nitrogen removal aspect only. The phosphorous removal aspect was not taken into account for the simplicity, but later on various modified version of ASM1 are available [7].

The ASM1 characterises bacterial withdrawal of carbon and nitrogen compounds that are present in wastewater. It incorporates eight chief processes, which include carbon oxidation (aerobic), nitrification (aerobic) and denitrification (anoxic) process. ASM1 studies 13 biodegradable and non-biodegradable components which also includes dissolved oxygen and alkalinity. This transformation is carried out by aerobic and anoxic growth of heterotrophic bacteria and by aerobic growth of autotrophic bacteria [7, 8, 9].

3 Research problem and objectives

3.1 Problem definition

Presently, sustainability is a prime issue of concern across the globe. As a part of environmental management a lot of legislative regulation has been imposed by government organisations to reduce environmental impact. Therefore, for the efficient use of energy and for the preservation of water bodies, a substantial body of research has been directed on this sector concerning the energy consumption as well as the control of the effluent. Hence, it has become essential to understand the Activated Sludge Process as a part of operation cost to overcome financial hindrance.

3.2 Objective

The purpose of this work is to investigate and calculate the temperature flux in paper and pulp industry wastewater treatment processes to determine the requirement of inflow cooling water to maintain the optimum temperature of a plant. This solution will not only reduce the energy requirement but it will also cut down the water usage in P&P industries. Consequently, such an analysis will provide a sustainable solution to the problems of wastewater treatment. The prime objective of the work was to study the key pollutants of the paper and pulp industry and to understand their aerobic degradation process through the activated sludge model.

4 Research methodology

4.1 Mathematical Model

An activated sludge model provides assistance in understanding the process design, operation and control of wastewater treatment. Such models have been widely adopted by the scientific community to model activated sludge processes. This model delivers better knowledge on the biochemical processes in complex environmental conditions. The best known activated sludge model was developed by *Henze et al.* from the Institute of Water Association (IWA). Extension of this model have been produced over a period of time which deal with complex mechanisms like phosphorous and nitrogen removal [7].

Since the activated sludge process is derived from micro-organisms, the process is disturbed by changing operation conditions or by changing content. The modelling of the process is perplexing and bacterial population follows nonlinear and time-varying growth which disturbs effluent quality and quantity.

Modified Activated Sludge Model 1

As we discussed earlier, paper and pulp industry waste is opulent with carbonaceous components. In this research work our prime focus is to understand and study the aerobic hydrolysis of carbon compounds. We modify the ASM1 and we close down our evaluation study to 7 prime components which represent 3 vital bacterial metabolic processes. The 3 key aerobic processes of ASM1 are: growth of heterotrophic bacteria (X_{BH}), decay of heterotrophs and, lastly, hydrolysis of carbonaceous compounds. The operations embrace the dynamic behavior of the activated sludge process and its function [7, 8].

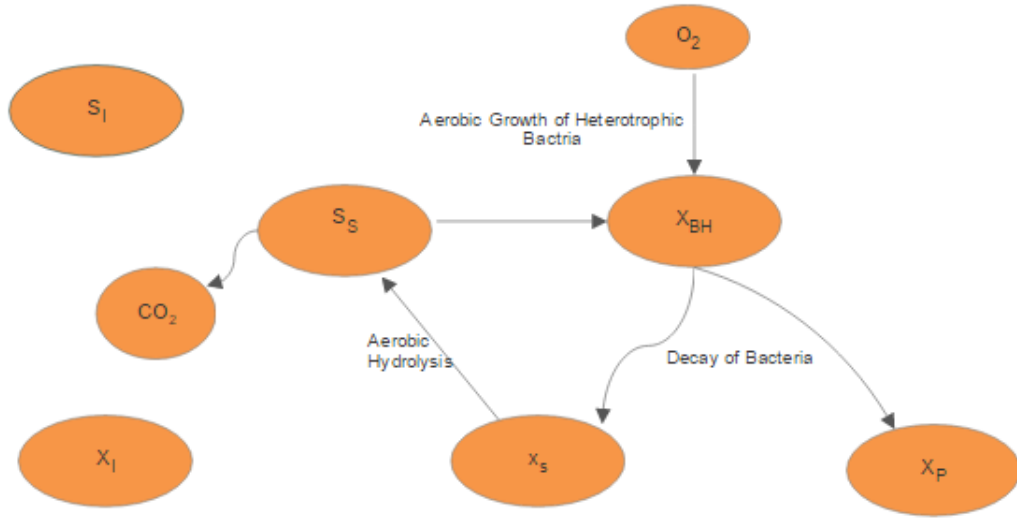


Figure 1: Schematic representation of aerobic degradation of carbon (C) compound in modified ASM1 [14].

Figure. 1 represent the modified ASM1 carbon compound degradation process in an activated sludge bioreactor. The configuration shown exemplifies the formation or the degradation of the 7 components under study. The soluble inert (S_I) and particulate inert (X_I) components do not get degraded throughout the ASM1 conversion process, but they contribute to the effluent Chemical Oxygen Demand (COD) concentration. These two components remain stable through out the process but since then contribute to COD concentration, they must be accounted for. The easily biodegradable (S_S) component disappears during the process of heterotrophic bacteria (X_{BH}) proliferation under aerobic conditions, whereas S_S is formed by hydrolysis of the slowly biodegradable (X_S) component. X_S component concentration increases during the bacterial biomass decay process. Particulate Product (X_P) is also produced during the bacterial decay process, but their concentration remains virtually unchanged since their degradation process is too slow to be captured. S_O represents the soluble or the dissolved oxygen concentration in a bioreactor. Dissolved oxygen concentration is a critical function in ASM1 modelling since it affects not only the bacterial growth but also determines the effluent quality [7].

Table 2: Process kinetics and stoichiometry for carbon oxidation in modified ASM1 [7].

Component	i	1	2	3	4	5	6	7	Process rate ρ_j [$ML^{-3}T^{-1}$]
j	Process	S_I	S_S	X_I	X_S	X_{BH}	X_P	S_O	
1	Aerobic growth of heterotrophs		$\frac{-1}{Y_H}$			1		$\frac{-1-Y_H}{Y_H}$	$\hat{\mu}_H \left(\frac{S_S}{K_S+S_S} \right) \left(\frac{S_O}{K_{OH}+S_O} \right) X_{BH}$
2	Decay of heterotrophs				$1-f_P$	-1	f_P		$b_H X_{BH}$
3	Hydrolysis of entrapped organics		1		-1				$K_h \left(\frac{X_S/X_{BH}}{K_X+(X_S/X_{BH})} \right) \left(\frac{S_O}{K_{OH}+S_O} \right) X_{BH}$

Table 3: Components evaluated for carbon oxidation in modified ASM1.

S_I	Soluble inert organic matter
S_S	Readily biodegradable substrate
X_I	Particulate inert organic matter
X_S	Slowly biodegradable substrate
X_{BH}	Active heterotrophic biomass
X_P	Particulate product arising from the biomass decay
S_O	Soluble oxygen

Table 4: Stoichiometry parameters for carbon oxidation in modified ASM1.

Symbol	Function	Unit
Y_H	Yield for heterotrophic biomass rate	(g COD oxidized) ⁻¹
f_P	Fraction of biomass transformed into inert particulate product rate	dimensionless

Table 5: Kinetic parameters for carbon oxidation in modified ASM1.

Symbol	Function	Unit
$\hat{\mu}_H$	Max specific growth rate for heterotrophic biomass	day^{-1}
b_H	Decay coefficient for heterotrophic biomass	day^{-1}
k_h	Maximum specific hydrolysis rate	g slowly biodegradable COD
K_S	Half-saturation coefficient for heterotrophic biomass	g COD m^{-3}
K_X	Half-saturation coefficient for hydrolysis of slowly biodegradable substrate	g slowly biodegradable COD
K_{OH}	Oxygen half-saturation for heterotrophic biomass	gO_2m^{-3}

Table 6: Observed conversion rate (r_i) for each component resulting from combinations of the basic processes:

1	$S_I(i = 1)$	$r_1 = 0$
2	$S_S(i = 2)$	$r_2 = \frac{-1}{Y_H}\rho_1 + \rho_3$
3	$X_I(i = 3)$	$r_3 = 0$
4	$X_S(i = 4)$	$r_4 = (1 - f_P)\rho_2 + \rho_3$
5	$X_{BH}(i = 5)$	$r_5 = \rho_1 - \rho_2$
6	$X_P(i = 6)$	$r_6 = 0$
7	$S_O(i = 7)$	$r_7 = \frac{-1 - Y_H}{Y_H}\rho_1$

4.2 Mass Balance Equation for modified ASM1

- For the Unit 1 the mass balance equation is written as:

$$\frac{dX_1}{dt} = \frac{1}{V_1}(Q_0X_0 + Q_aX_a + Q_rX_r + r_1V_1 - Q_1X_1) \quad (1)$$

For oxygen transfer in the unit 1 an ODE is written as follows:

$$\frac{dS_{O_1}}{dt} = \frac{1}{V_1}(Q_0X_0 + Q_aX_a + Q_rX_r + r_1V_1 - Q_1X_1) + (K_La)_1V_1(S_{O,sat} - S_{O_1}) \quad (2)$$

- For the unit 2 & 3 the mass balance equation reads:

$$\frac{dX_k}{dt} = \frac{1}{V_k}(Q_{k-1}X_{k-1} + r_kV_k - Q_kX_k) \quad \text{where, } k = 2, 3 \quad (3)$$

For oxygen transfer for the unit 2 & 3 an ODE is written as follows:

$$\frac{dS_{O_k}}{dt} = \frac{1}{V_k}(Q_{k-1}X_{k-1} + r_1V_1 - Q_1X_1) + (K_La)_1V_1(S_{O,sat} - S_{O_1}) \quad \text{where, } k = 2, 3 \quad (4)$$

4.3 Benchmark process with modified ASM1

WWTP follows a non-linear system and experiences perturbations subjected to influent flow rate, waste composition in order to operate such a system in controlled conditions is challenging either practically and in simulations. Therefore, in 1998 the development of benchmark tools for simulation-based evaluation of control strategies for activated sludge plants has been undertaken in Europe [15].

The prime purpose of the development of the benchmark simulation model was to boost up the compliance of contemporary control strategies for the activated sludge plant performance assessment that should be based on a rigorous methodology including a simulation model, plant layout, controllers, performance criteria and test procedures. The benchmark model allows various control strategies to be implemented. It facilitates the dynamic simulation on continuously varying input data and to optimize multiple process parameter simultaneously. In the benchmark simulation model the activated sludge model no.1 (ASM1) has been selected to describe the biological phenomena taking place in the activated sludge bioreactor [12, 13, 15].

Plant overview

Figure. 2 represents the activated sludge process carried out in a bioreactor with 3 aerobic compartments. The plant layout for aerobic degradation of carbonaceous compounds contains three aerobic compartments and a settling tank. All the three aerobic compartments of the bioreactor are assumed to be the same size, dimension and carrying capacity [16].

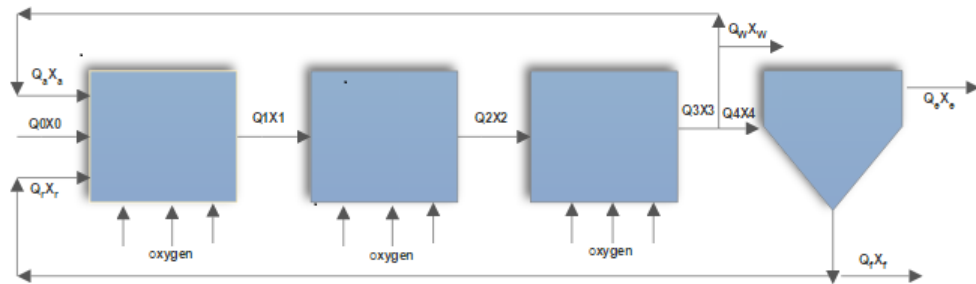


Figure 2: Example model plant layout. The plant modelled here has three identical compartment connected in a sequence [14, 16].

Model assumptions

1. The system is continuous.
2. The system is in a homogeneous state.
3. The total number of activated sludge bioreactor compartments is 3.
4. All three compartments are aerobic which means oxygen is supplying regularly to each, in order to maintain aerobic conditions.
5. The volume of the all three reactors is $1,333 \text{ m}^3$.
6. The Activated Sludge Model number 1 is used to model the activated sludge process.
7. Under aerobic condition only heterotrophic bacteria grows.

4.4 Mass-balance model for the benchmark plant

The mass-balance for the benchmark with the activated sludge model number 1 as follows:

1. Flow rate in each tank

$$Q_1 = Q_0 + Q_a + Q_r$$

$$Q_2 = Q_1$$

$$Q_3 = Q_2$$

$$Q_4 = Q_3 - Q_a - Q_w$$

$$Q_r = Q_4 - Q_e = Q_0 + Q_r - Q_w - Q_e$$

$$Q_e = Q_0 - Q_w$$

2. The recycled component calculation

$$X_r = \frac{(Q_0 + Q_r - Q_e)X_3 - (Q_0 - Q_w)X_e}{Q_r}$$

Since recycling waste will not have particulate material therefore , $X_e = 0$.

As a result the equation will be

$$X_r = \frac{(Q_0 + Q_r - Q_e)X_3}{Q_r}$$

The above equations will remain the same for the units 2 and 3 except that flow rate and mass transfer will change according to the mass-balance equation 3 for ASM1.

3. Discrete mass-balance equation for benchmark model

For the purpose of simplicity the mass-balance equation mentioned above is converted to a discrete form using Euler's method.

$$\frac{dx_n}{dt} = \frac{x_n(k+1) - x_n(k)}{\Delta t}$$

where, x_n is component concentration in different units and Δt is sampling time.

Discrete mass-balance equation for unit 1 reads as follows

$$S_{I_1}(k+1) = 0 \quad (5)$$

$$S_{S_1}(k+1) = S_{S_1}(k) + \frac{\Delta t}{V_1}(Q_0 S_{S_0}(k) + Q_r S_{S_3}(k) + Q_a S_{S_3}(k) - Q_1 S_{S_1}(k)) + \Delta tr_{S_{S_1}}(k) \quad (6)$$

$$X_{I_1}(k+1) = 0 \quad (7)$$

$$X_{S_1}(k+1) = X_{S_1}(k) + \frac{\Delta t}{V_1}(Q_0 X_{S_0}(k) + Q_r X_{S_3}(k) + Q_a X_{S_3}(k) - Q_1 X_{S_1}(k)) + \Delta tr_{X_{S_1}}(k) \quad (8)$$

$$X_{BH_1}(k+1) = X_{BH_1}(k) + \frac{\Delta t}{V_1}(Q_0 X_{BH_0}(k) + Q_r X_{BH_3}(k) + Q_a X_{BH_3}(k) - Q_1 X_{BH_1}(k)) + \Delta tr_{X_{BH_1}}(k) \quad (9)$$

$$X_{P_1}(k+1) = X_{P_1}(k) + \frac{\Delta t}{V_1}(Q_0 X_{P_0}(k) + Q_r X_{P_3}(k) + Q_a X_{P_3}(k) - Q_1 X_{P_1}(k)) + \Delta tr_{X_{P_1}}(k) \quad (10)$$

$$S_{O_1}(k+1) = S_{O_1}(k) + \frac{\Delta t}{V_1}(Q_0 S_{O_0}(k) + Q_r S_{O_3}(k) + Q_a S_{O_3}(k) - Q_1 S_{O_1}(k)) + \Delta tr_{S_{O_1}}(k) \quad (11)$$

The discrete mass-balance equation for the unit 2 and 3 can be derived from the equation 5-11.

4. State-space mass-balance for benchmark model

From the simulation prospect state space model offers a compressed illustration to analyse the system in a simple form. Therefore, for the simplicity purpose, the complete plant mass-balance equation which is mentioned in section 4.2 is transferred to the subsequent state space model. The equation reads as follows:

$$x_n(k+1) = Ax_n(k) + C^T P(x_n, k) + Bx_{n_i}(k) + K_L a(u_i)^T [S_{O,sat} - S_O(k)] \quad (12)$$

Where:

x_n = Vector of the component concentration

A = Matrix of component concentration coefficient

C^T = Yield coefficient matrix

P = Vector of process rate

B = Coefficient matrix of inflow concentration

x_{n_i} = Vector of inflow concentration

$K_L a$ = Oxygen transfer function vector

u_i = Vector of airflow rate

S_O = Vector of dissolved oxygen concentration

$S_{O,sat}$ = Saturated dissolved oxygen

5. State-space mass-balance component description as following

State-space process variable x_n for the modified ASM1

$$x_n = [S_{I,n} \ S_{S,n} \ X_{I,n} \ X_{S,n} \ X_{BH,n} \ X_{P,n} \ S_{O,n}]^T \in R^3 \quad \text{where, } n = 1, 2, 3$$

State-space model component u_i for the modified ASM1

$$u_i = [u_1 \quad u_2 \quad u_3]^T$$

component x_i is a vector of inflow concentration

$$x_i = [S_{I_{in}} \ S_{S_{in}} \ X_{I_{in}} \ X_{S_{in}} \ X_{BH_{in}} \ X_{P_{in}} \ S_{O_{in}}]$$

P is a vector for the process rates of the system

$$P = [P_1 \quad P_2 \quad P_3]$$

Weight matrix A for the system

$$\mathbf{A} = \begin{bmatrix} \text{diag}(1 - \frac{\Delta t}{V_1}Q_1) & 0 & \text{diag}(1 - \frac{\Delta t}{V_1}(Q_a + Q_r)) \\ \text{diag}(\frac{\Delta t}{V_1}Q_1) & \text{diag}(1 - \frac{\Delta t}{V_1}Q_2) & 0 \\ 0 & \text{diag}(\frac{\Delta t}{V_1}Q_2) & \text{diag}(1 - \frac{\Delta t}{V_1}Q_3) \end{bmatrix}$$

Matrix C for the system

$$\mathbf{C} = \Delta t \begin{bmatrix} c_1 & 0 & 0 \\ 0 & c_2 & 0 \\ 0 & 0 & c_3 \end{bmatrix}$$

Matrix B for the system

$$\mathbf{B} = \begin{bmatrix} \text{diag}\left(\frac{\Delta t}{V_1}Q_0\right) & 0 & 0 \end{bmatrix}$$

4.5 Kinetic parameter and temperature dependency

Kinetic parameter such as max specific growth rate for heterotrophic biomass ($\hat{\mu}_H$), decay coefficient for heterotrophic biomass (b_H) and maximum specific hydrolysis rate (k_h) mentioned in modified ASM1 are temperature dependent. Temperature dependency of reaction kinetic parameter can be studied using Arrhenius equation. Bacteria illustrate a comparably narrow temperature range where they actively perform their function. However, within that temperature range reaction rate coefficient increase as the temperature increases until it reach its optimum temperature. Once it attain its optima, the temperature will start decreasing with increase in the temperature. Figure 3 shows the effect of temperature on bacterial specific growth rate. The Arrhenius equation adapted for the study of temperature range where coefficient increases with increasing temperature, however it fails to track the decrease in specific growth rate as the temperature goes beyond its optima. In this work, we assumed that system temperature remains at its constant and therefore, we

are eliminating the concept of kinetic parameter temperature dependency [21]. In the future work, reasonable next challenge would be to include the kinetic parameter temperature dependence in the model by introducing a suitable function for kinetic parameter such as $\hat{\mu}_H(T)$, $b_H(T)$ and $k_h(T)$, where T is the temperature.

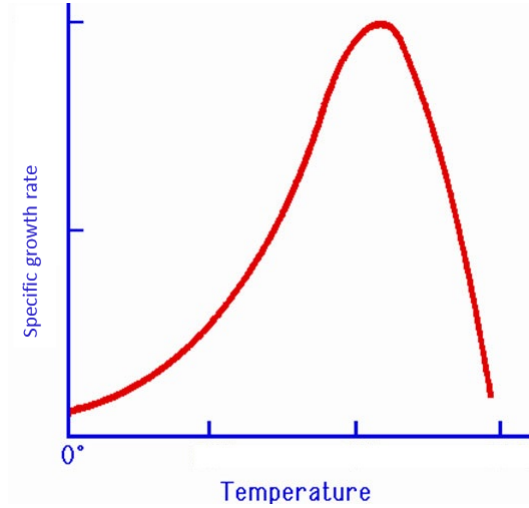


Figure 3: Effect of temperature on bacterial growth rate.

4.6 Temperature shift model

The biological process or activated sludge process for waste degradation in water is supported by bacterial biomass. Bacterial biomass reduces the organic components that are present in waste by utilising it as their food and energy source. Bacterial growth is quite sensitive to environment conditions. Their proliferation performs best under optimal conditions, but modest changes in environmental conditions, such as pH, temperature and substrate concentration can alter or halt their growth and processes. Therefore, it is important to operate a bioreactor at bacterial optimal conditions. We will see in section 5 that the activated sludge process in paper and pulp industries is an exothermic process which releases energy into the system. This results in a raise in system temperature as activated sludge process increases. To overcome this situation cooling water is added into the bioreactor. This cooling water addition utilizes energy, therefore to make the plant energy efficient and to improve effluent quality it is essential to study the temperature.

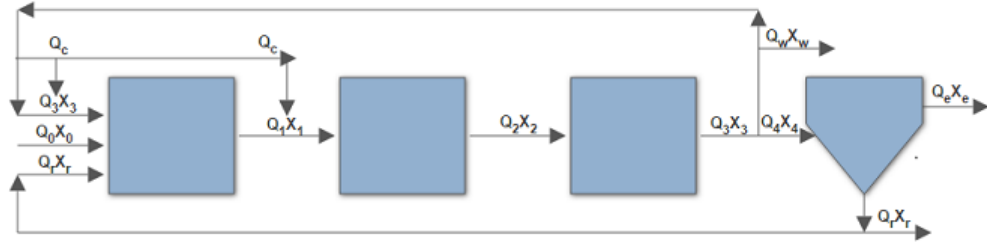


Figure 4: Example model plant layout with inflow cooling water for temperature shift model. The plant modelled here has three identical compartments connected in a sequence.

Chemical reactions are either exothermic or endothermic in nature and hence, constructed energy over a period of time needs either be removed or added to the reactor for a constant temperature to be maintained. Exothermic reactions are interesting to study because of potential problems of multiple steady-states, which can be studied using a temperature shift model. The temperature shift model study provides in depth understanding of the dynamic behaviour based on an analysis of the heat generated by the reaction and reduced by the addition of cooling water [18].

A temperature shift model is derived upon the variation in energy caused by the wastewater inflow and outflow in the various compartments. This causes a change in the energy balance over a period of time. The change in tank temperature can be measured using enthalpy change (ΔH). The below equation is considered for the an exothermic, irreversible reaction in a cooling CSTR [18].

$$\frac{dT}{dt} = \frac{Q_n}{V_n}(T_{in} - T(t)) + \frac{\Delta H r}{\rho c_p} - \frac{UA}{\rho V_n c_p}(T(t) - T_c) \quad \text{where, } n=1,2,3 \quad (13)$$

Where:

Q_n = Flow rate in respective Tank

V_n = Volume of respective Tank

ΔH = Enthalpy change of the system

r = Reaction rate of the system

ρ = Density

c_p = Heat Capacity

U = Heat Transfer Coefficient

A = Heat Transfer Surface Area

T_{in} = Inflow water Temperature

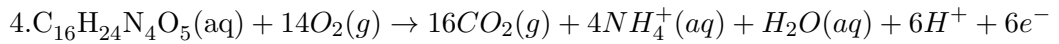
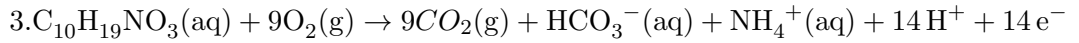
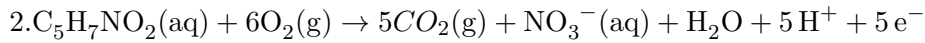
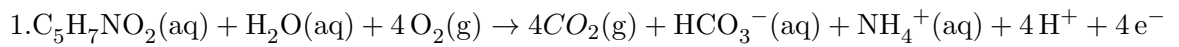
$T(t)$ = Temperature at given time

T_c = Cooling substance temperature

5 Kinetic study of biochemical reaction

5.1 Biochemical reaction

There are a number of organic and inorganic waste compounds released into the paper and pulp industry wastewater treatment plant. In this thesis we restrict our study to five vital organic pollutants and their biochemical degradation in a waste treatment plant [21, 22]. The biochemical reactions are as follows:



Where:

$C_5H_7NO_2$ = Chemical composition of empty (dead) bacterial cell.

$C_{10}H_{19}NO_3$ = Solid waste.

$C_{16}H_{24}N_4O_5$ = Protein.

$C_{10}H_{12}O_3$ = Soft lignin.

5.2 Hess law and enthalpy change

The heat transfer property of any biochemical reaction is determined using the enthalpy change of that biochemical reaction under constant pressure. It is a thermodynamic unit that estimates the amount of energy per mole either released or produced in a reaction. The changes in enthalpy (H) are correlated with changes in internal energy (U) and changes in volume (V) at a constant pressure (P) [23, 29].

$$H = U + PV$$

Hess law is used to study the variation in enthalpy along with changes in chemical reaction. For the constant heat summation Hess law states that; “Enthalpy (energy) changes per reaction is a state function. The total enthalpy change of the reaction depends merely on the state of the reactant and that of the products, irrespective of intermediate steps.”

Reaction standard enthalpy changes can be calculated using Hess law through mainly two methods:

1. Combustion ΔH_c° , or formation ΔH_f° of compounds at 25 °C temperature at 1 molar concentration, and 1 atmosphere of pressure.
2. And secondly using bond enthalpy.

Since standard enthalpy formation of combustion data is available only for commonly used chemical compounds but not ones reactant for activated sludge process, we decided to study standard enthalpy using bond enthalpy. The bond enthalpy can be define as the amount of energy utilised or released during the bond formation between atoms. A standard bond enthalpy table is available for single, double or multiple bonds between molecules. Figure. 5 represents the bond enthalpy table. The molecule structure of a chemical compound is required in order to study bond enthalpy. If molecular structure of an interesting molecule is not available or is unknown, then estimation is based upon their empirical formula i. e. on one available for one other compound with a similar molecular formula. Calculations described above will give a subtle variation in enthalpy since enthalpy calculation is highly depending upon the atom arrangement in the formation of the molecule [23, 29].

Average Bond Enthalpies (kJ/mol)							
Single Bonds							
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Multiple Bonds							
C=C	614	N=N	418	O ₂	495		
C≡C	839	N≡N	941				
C=N	615			S=O	523		
C≡N	891			S=S	418		
C=O	799						
C≡O	1072						

Figure 5: Standard bond enthalpy table (image credit: Chemistry: the central science by Brown [23]).

Bond dissociation enthalpy and mean bond enthalpy

The bond dissociation enthalpy is the energy required to disrupt one mole of the bond for the formation of separate atoms from the given molecule. The molecule under consideration has to be in the gaseous state. Therefore, bond enthalpy cannot be calculated straight from substances starting in the liquid or solid state. Heat of vaporization i.e., the amount of energy required to convert a substance from liquid or solid state to gaseous form is required to be considered. The extra energy which is required to convert a liquid into the gaseous state is known as enthalpy change of vaporization (ΔH_{vap}° or ΔH_v°) [23, 29].

The standard enthalpy of formation of a compound is the amount of enthalpy change that is, energy released or consumed, for the formation of one mole of substance in its standard state from its elements in standard state. The following equation is used to calculate the standard enthalpy of formation

$$\Delta H_{Reaction}^\circ = \sum \Delta H_{Substrate}^\circ - \sum \Delta H_{Product}^\circ$$

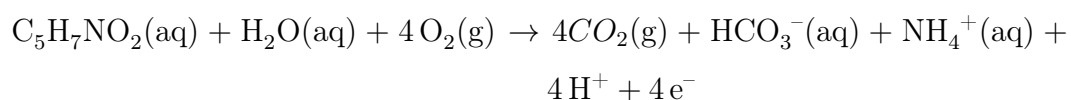
If sum of the enthalpy of formation i. e. $\Delta H_{Reaction}^\circ$, is positive, then the reaction is endothermic (energy consuming) whereas, if $\Delta H_{Reaction}^\circ$ is negative, the reaction is exothermic (energy releasing). Heat released in the reaction process will increase the temperature of the system, which may affect the

process and end product formation.

5.3 Bond enthalpy calculation

Bond Enthalpy Calculation was performed for the five prime organic pollutants and for their biodegradation process, as discussed earlier [23, 24, 25, 26, 29]. The chemical structure used for the enthalpy study were derived from the ChemSpider database, which is maintained by the UK based Royal Society of Chemistry.

Reaction 1



Assumptions

- We considered chemical composition of empty bacterial cell ($\text{C}_5\text{H}_7\text{NO}_2$) as Ethyl Cyanoacetate ($\text{C}_5\text{H}_7\text{NO}_2$).
- The reaction is taking place under standard conditions.

Ethyl cyanoacetate structure:

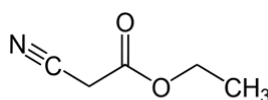


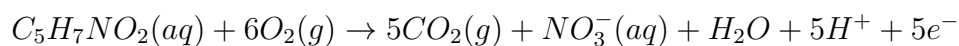
Figure 6: Ethyl cyanoacetate structure (image credit: www.ChemSpider.com).

Bond enthalpy calculation table for Ethyl cyanoacetate

Compound	ΔH_v° (kJ/mol)	Compound (gaseous form)	Number of molecules (V)	Total bond enthalpy of component	V * total bond enthalpy (kJ / mol)
$C_5H_7NO_2(aq)$	44.0	$C_5H_7NO_2(g)$	1	6341	6341
$H_2O(aq)$	40.7	$H_2O(g)$	1	926	926
$O_2(g)$	0	$O_2(g)$	4	499	1996
$CO_2(g)$	0	$CO_2(g)$	4	1598	6392
$HCO_3^-(aq)$	63.4	$HCO_3^-(g)$	1	1487	1487
$NH_4^+(aq)$	23	$NH_4^+(g)$	1	1567	1567
$H^+(aq)$	-	$H^+(g)$	4	0	0

$$\begin{aligned}
 \Delta H_{Reaction} &= \sum \Delta H_{Substrate} - \sum \Delta H_{Product} \\
 &= (44.0 + 6341 + 40.7 + 926 + 1996) - (6392 + 63.4 + 1487 + 23 + 1564) \\
 &= (9347.7 - 9529.4) \\
 &= -181.7 \text{ (kJ/mol)}
 \end{aligned}$$

Reaction 2



Assumptions

- We considered chemical composition of empty bacterial cell ($C_5H_7NO_2$) as Ethyl cyanoacetate ($C_5H_7NO_2$).
- The reaction is taking place under standard conditions.

Ethyl cyanoacetate structure:

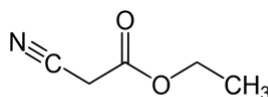


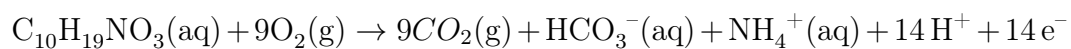
Figure 7: Ethyl cyanoacetate structure (image credit: www.ChemSpider.com).

Bond enthalpy calculation table for Ethyl cyanoacetate

Compound	ΔH_v° (kJ/mol)	Compound (gaseous form)	Number of molecules (V)	Total bond enthalpy of component	V * total bond enthalpy (kJ / mol)
$C_5H_7NO_2(aq)$	44.0	$C_5H_7NO_2(g)$	1	6341	6341
$O_2(g)$	0	$O_2(g)$	6	499	2994
$CO_2(g)$	0	$CO_2(g)$	5	1598	7990
$NO_3^-(aq)$	-	$NO_3^-(g)$	1	1009	1009
$H_2O(aq)$	40.7	$H_2O(g)$	1	926	926
$H^+(aq)$	-	$H^+(g)$	5	0	0

$$\begin{aligned}
 \Delta H_{Reaction} &= \sum \Delta H_{Substrate} - \sum \Delta H_{Product} \\
 &= (44.0 + 6341 + 2994) - (7990 + 1009 + 40.7 + 926) \\
 &= (9379.9965.7) \\
 &= -586.7 \text{ (kJ/mol)}
 \end{aligned}$$

Reaction 3



Assumptions

- We considered solid waste ($C_{10}H_{19}NO_3$) as N-Boc-3-piperidinol ($C_{10}H_{19}NO_3$).
- The reaction is taking place under standard conditions.

N-Boc-3-piperidinol Structure:

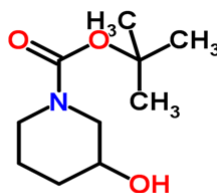


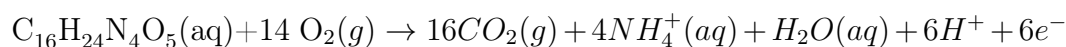
Figure 8: N-Boc-3-piperidinol structure (image credit: www.ChemSpider.com).

Bond enthalpy calculation table for N-Boc-3-piperidinol

Compound	ΔH_v^o (kJ/mol)	Compound (gaseous form)	Number of molecules (V)	Total bond enthalpy of component	V * total bond enthalpy (kJ / mol)
$C_{10}H_{19}NO_3(aq)$	61.7	$C_{10}H_{19}NO_3(g)$	1	13085	13085
$O_2(g)$	0	$O_2(g)$	9	499	4491
$CO_2(g)$	0	$CO_2(g)$	9	1598	14382
$HCO_3^-(aq)$	63.4	$HCO_3^-(g)$	1	1978	1978
$NH_4^+(aq)$	23	$NH_4^+(g)$	1	1567	1567
$H^+(aq)$	-	$H^+(g)$	14	0	0

$$\begin{aligned}
 \Delta H_{Reaction} &= \sum \Delta H_{Substrate} - \sum \Delta H_{Product} \\
 &= (61.7 + 13085 + 4491) - (14382 + 63.4 + 1978 + 23 + 1564) \\
 &= (17637.7118010.4) \\
 &= -372.7 \text{ (kJ/mol)}
 \end{aligned}$$

Reaction 4



Assumptions

We considered protein ($C_{16}H_{24}N_4O_5$) as Ethyl 4-hydroxy-2-(4-[(2-methyl-2-propanyl) oxy] carbonyl -1-piperazinyl) -5-pyrimidinecarboxylate ($C_{16}H_{24}N_4O_5$).

The reaction is taking place under standard conditions.

Ethyl 4-hydroxy-2-(4-[(2-methyl-2-propanyl) oxy] carbonyl -1-piperazinyl) -5-pyrimidinecarboxylate Structure:

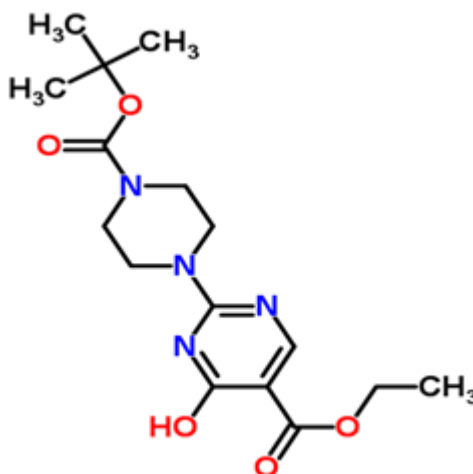


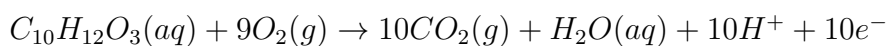
Figure 9: Ethyl 4-hydroxy-2-((2-methyl-2-propanyl)oxy)carbonyl-1-piperazinyl-5-pyrimidinecarboxylate structure (image credit: www.ChemSpider.com).

Bond enthalpy calculation table for Ethyl 4-hydroxy-2-((2-methyl-2-propanyl)oxy)carbonyl-1-piperazinyl-5-pyrimidinecarboxylate

Compound	ΔH_v° (kJ/mol)	Compound (gaseous form)	Number of molecules (V)	Total bond enthalpy of component	V * total bond enthalpy (kJ / mol)
$C_{16}H_{24}N_4O_5(aq)$	79.5	$C_{16}H_{24}N_4O_5(g)$	1	19737	19737
$O_2(g)$	0	$O_2(g)$	14	499	6986
$CO_2(g)$	0	$CO_2(g)$	16	1598	25568
$NH_4^+(aq)$	23	$NH_4^+(g)$	4	1567	6256
$H_2O(aq)$	40.7	$H_2O(g)$	1	926	926
$H^+(aq)$	-	$H^+(g)$	6	0	0

$$\begin{aligned}
 \Delta H_{Reaction} &= \sum \Delta H_{Substrate} - \sum \Delta H_{Product} \\
 &= (79.5 + 19737 + 6986) - (25568 + 92 + 6256 + 40.7 + 926) \\
 &= (26802.5132790.7) \\
 &= -5988.2(kJ/mol)
 \end{aligned}$$

Reaction 5



Assumptions

- We considered softwood lignin ($C_{10}H_{12}O_3$) as p-Methoxyhydrocinnamic acid ($C_{10}H_{12}O_3$).
- The reaction is taking place under standard conditions.

p-Methoxyhydrocinnamic acid structure:

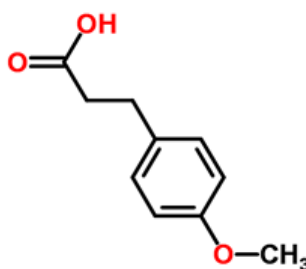


Figure 10: p-Methoxyhydrocinnamic acid structure (image credit: www.ChemSpider.com).

Bond enthalpy calculation table for p-Methoxyhydrocinnamic acid

Compound	ΔH_v° (kJ/mol)	Compound (gaseous form)	Number of molecules (V)	Total bond enthalpy of component	V * total bond enthalpy (kJ / mol)
$C_{10}H_{12}O_3(aq)$	59.0	$C_{10}H_{12}O_3(g)$	1	10809	10809
$O_2(g)$	0	$O_2(g)$	9	499	4491
$CO_2(g)$	0	$CO_2(g)$	10	1598	15980
$H_2O(aq)$	40.7	$H_2O(g)$	1	926	926
$H^+(aq)$	-	$H^+(g)$	10	0	0

$$\begin{aligned}
 \Delta H_{Reaction} &= \sum \Delta H_{Substrate} - \sum \Delta H_{Product} \\
 &= (59 + 10809 + 4491) - (15980 + 926) \\
 &= (15359 - 16906) \\
 &= -1547 \text{ (kJ/mol)}
 \end{aligned}$$

5.4 Total system enthalpy

$$\begin{aligned}\text{Total system energy} &= \sum_{i=1}^5 \text{reaction}_i \\ &= -181.7 - 586.7 - 372.7 - 5988.2 - 1547 \\ &= -8676.3 \text{ (kJ/mol)}\end{aligned}$$

Hence, the reaction is an exothermic reaction which produces heat.

5.5 Dynamic behaviour study

Modelling of biochemical reactions

A system of Ordinary Differential Equations (ODE) can be built from the system of chemical or biochemical reactions to study the rate of change in concentration of chemical species over time. It is used to study the dynamic behaviour of chemical or biochemical reaction kinetics. It will be helpful to conduct a study of the effect of kinetic and stoichiometry parameters on the reaction rate. A differential equation model depicts the rate at which reactants are consumed and products are formed over a period of time. Thus, an ODE system will be useful in developing models of physical, chemical, biological or biochemical phenomena, and to determining whether the models are mathematically “well-posed” or not.

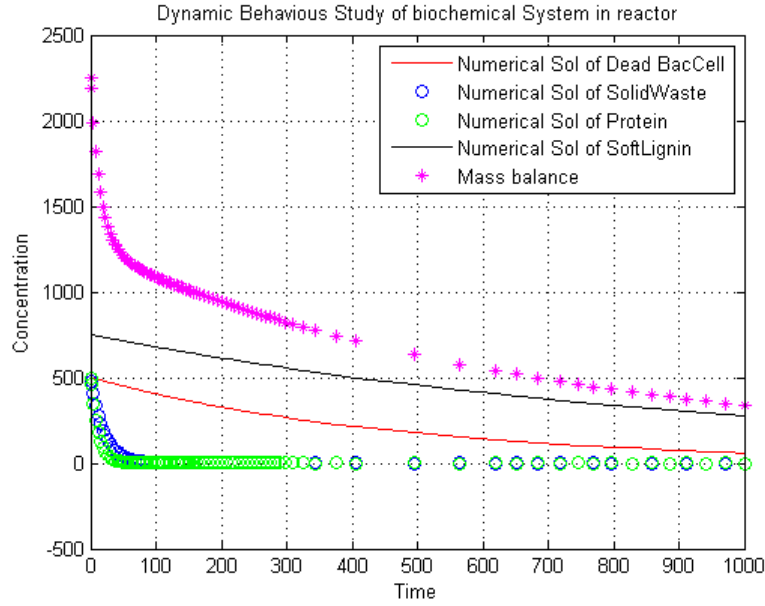


Figure 11: Dynamic behaviour of biochemical reaction system.

In Figure. 11 a series of plots of reactant concentration versus time for a constant temperature is shown. The concentration of all the biological waste decreases as the time increases.

Stochastic simulation of biochemical reaction

For the biochemical system of large molecules, discrete and stochastic approaches are more appropriate than continuous and deterministic approaches. In 1976, Gillespie proposed a time-evolution method which describes the probability density function of species in biochemical reactions.

Gillespie algorithm

As per Gillespie, "Suppose a biochemical system involves N molecule species $\{S_1, \dots, S_N\}$. $X_i(t)$ denotes the number of molecules of species S_i at time t . The method studies the evolution of the state vector $X(t) = (X_1(t), \dots, X_N(t))$ given that the system was initially in the state vector $X(t_0)$. Suppose the system is composed of M reaction channels $\{R_1, \dots, R_M\}$. In a constant volume, assume that the system is homogeneous and in thermal equilibrium at some constant temperature. There are two important quantities in reaction channels R_j : the state change vector

$v_j = (v_{1j}, \dots, v_{Nj})$, and propensity function a_j . v_{ij} is defined as the change in the S_i molecule population caused by one R_j reaction, and $a_j(x)dt$ gives the probability that one R_j reaction will occur in the next infinitesimal time interval $[t, t + dt)$. [27, 28].

The Gillespie algorithm or Stochastic Simulation Algorithm (SSA) reproduces the correct probability distribution of a reaction. This method is mathematically exact with no artifacts but it is computationally expensive and time consuming [27, 28]. It is a time-evolution method. The following pseudo-code provides a slower, but often more intuitive, means of modeling chemical kinetics.

- Label system of molecules of N chemical species $\{S_1, \dots, S_N\}$, which interact through M chemical reactions $\{R_1, \dots, R_M\}$.
- calculate propensities (a_1, \dots, a_N) .
- $a_0 \leftarrow \sum_{i=1}^N a_i$.
- $\tau \leftarrow \frac{1}{a_0} \log\left(\frac{1}{S_2}\right)$
- pick reaction index i with $P_i = \frac{a_i}{a_0}$
- $n_j \leftarrow n_j + v_{ij} \quad \forall j = 1, \dots, M$
- $t \leftarrow t + \tau$
- repeat steps 1-6 until $t \geq t_{max}$.

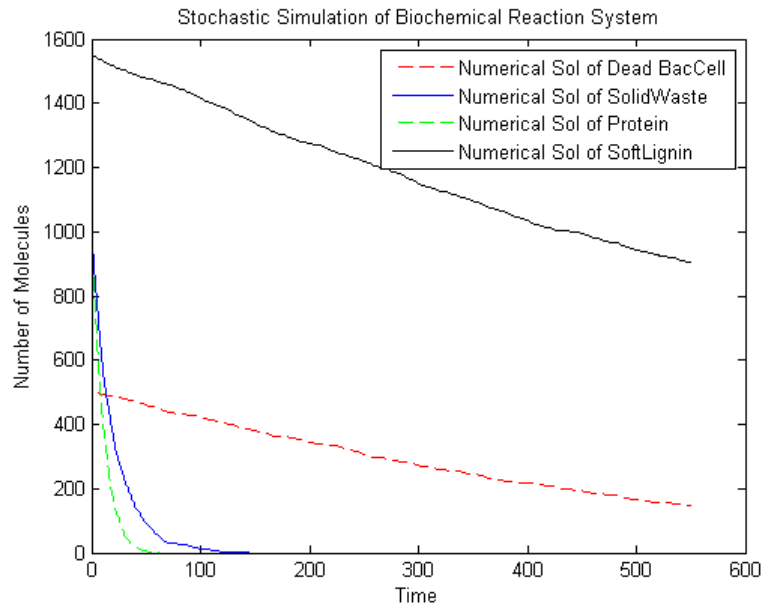


Figure 12: Gillespie simulation of biochemical reaction system.

Figure. 12 presents the molecule hydrolysis against time plot. We can observe from the plot that soft lignin requires maximum duration and the degrade process is significantly slow compare to the solid waste, although both components have the same number of carbon molecules. However, as mentioned earlier, the carbon-carbon bond arrangements also influence the degradation process. Therefore, it can be concluded from the plot that the solid waste and protein can be grouped into the soluble solid (S_S) whereas, dead bacterial cell and lignin are part of slowly biodegradable (X_S) components.

6 RESULTS

6.1 State space mass-balance model simulation for the benchmark plant

The Benchmark plant is a simulation condition with the three aeration sequential units introduced in section 4.3. For simplicity the continuous mass-balance model equation in section 4.2 is transferred into a discrete form. For the validation of the modified ASM1 several simulations are carried out. A benchmark state-space mass balance model based upon Euler's method was implemented first using equation (12) for all three tanks. The model was studied for all 7 constituent concentration shifts over a period of time. Figures 13, 14 and 15 illustrate the result for tank 1, 2 and 3 respectively in the form of Chemical Oxygen Demand (COD). The stoichiometric and kinetic parameter data for the model simulation is taken from the activated sludge model by *Henze et al.* [7, 9]. As expected, an aerobic carbon hydrolysis process resulted in the degradation of suspended solid material (S_S) in all three tanks. The heterotrophic biomass (X_{BH}) is increasing with time and the concentration of slowly biodegradable substrate (X_S) and particulate products that are formed by biomass decay (X_P) is raising slowly, since bacterial biomass is in an actively growing state and therefore, bacterial decay rate is slow.

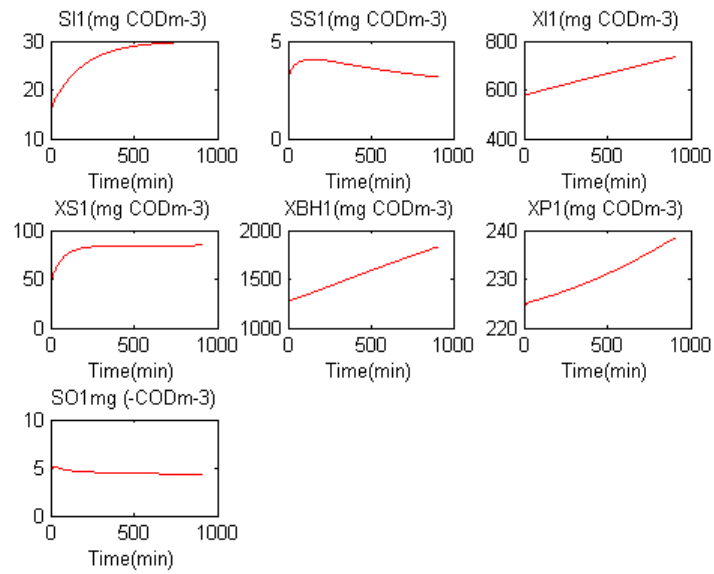


Figure 13: Tank 1 process variable study using benchmark model.

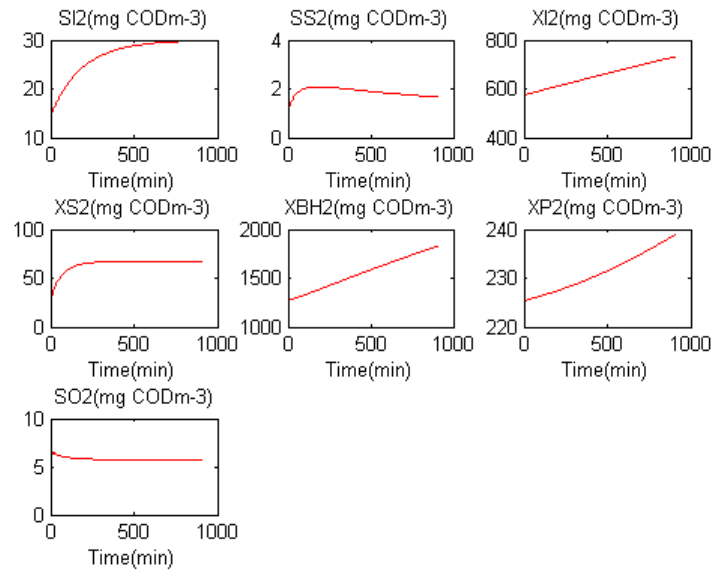


Figure 14: Tank 2 process variable study using benchmark model.

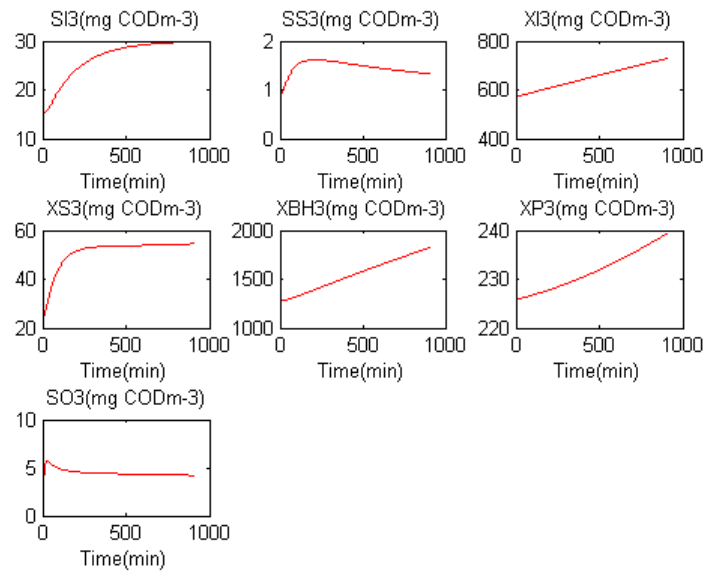


Figure 15: Tank 3 process variable study using benchmark model.

6.2 Modified ASM1 process variable study

Benchmark model solution obtained using Euler's method. Since, Euler's method is simple but provides less accuracy, we decided to solve the ASM1 mass-balance equation mentioned in section 4.2 using an ODE solver. Figure 16, 17 and 18 shows the implementation of mass-balance model of ASM1.

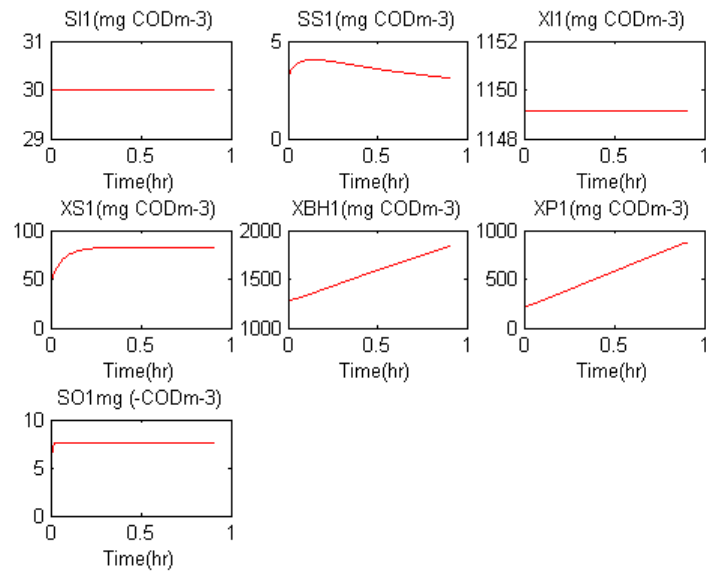


Figure 16: Tank 1 process variable study using modified ASM1.

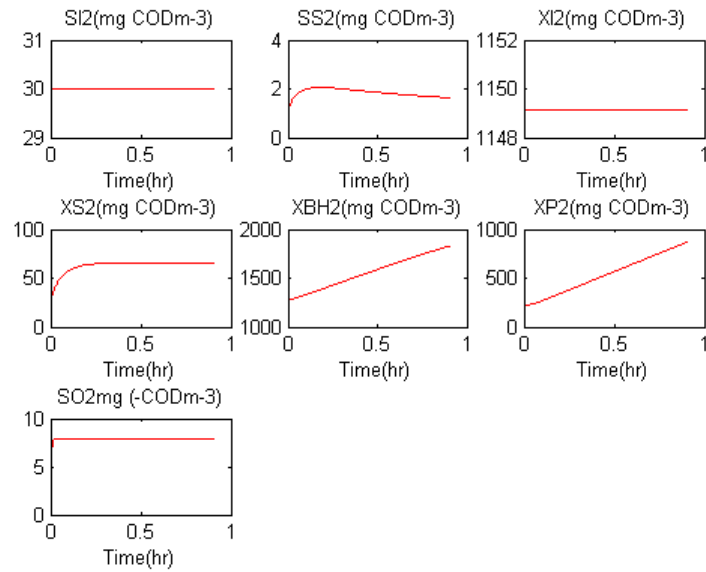


Figure 17: Tank 2 process variable study using modified ASM1.

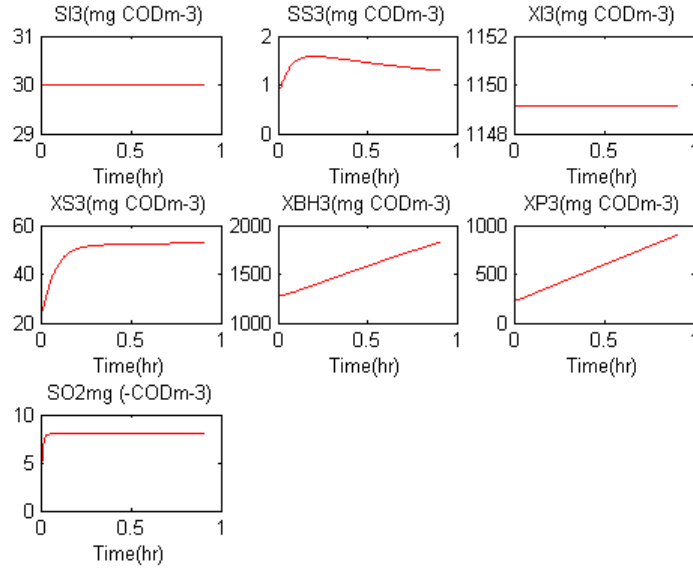


Figure 18: Tank 3 process variable study using modified ASM1.

The simulation results obtained for tank 1, 2 and 3 with the benchmark model and with the modified activated sludge model number 1 represent similar results for some components: easily biodegradable (soluble solids (S_S)), slowly biodegradable (particulate solid (X_S)) and for heterotrophic bacterial cell biomass (X_{BH}). However, inert components like soluble inert (S_I), particulate inert material (X_I) and particulate product (X_P) formed due to the decay of bacterial cells, all mentioned three component plots show simulation result variation compared to modified ASM1 due to the fact that in Euler's method the initial inflow concentration of each components was taken into account along with the initial concentration of each component in respective tank whereas, in modified activated sludge model nu. 1 the initial concentration of the component in each tank only is taken into account. Therefore, in modified ASM1 simulation result shows a flat line for all three components since those component do not get degraded in modified ASM1 and their concentration remains unchanged throughout the process. Furthermore, in benchmark model soluble oxygen concentration decreases over time whereas, in modified ASM1 its in steady state. Therefore, for the oxygen control study, the benchmark model gives good result compare to the modified ASM1.

6.3 Temperature shift and enthalpy change

As mentioned before, it is essential to maintain the plant temperature at optimal for the efficient performance of activated sludge process by microorganism. The temperature shift was simulated using equation (13). Figure 19 represents the temperature change estimation using the total system enthalpy for the 9 hours of time span. It is clearly visible that the temperature in all three tanks follows a linear function. The temperature increase is highest in tank 2 compared to all three compartments, whereas in tank 3 the temperature variation is noticeably low. Therefore, from the graph it can be concluded that tank 1 and tank 2 require cooling to maintain the temperature at optimum level for ASP process to work effectively.

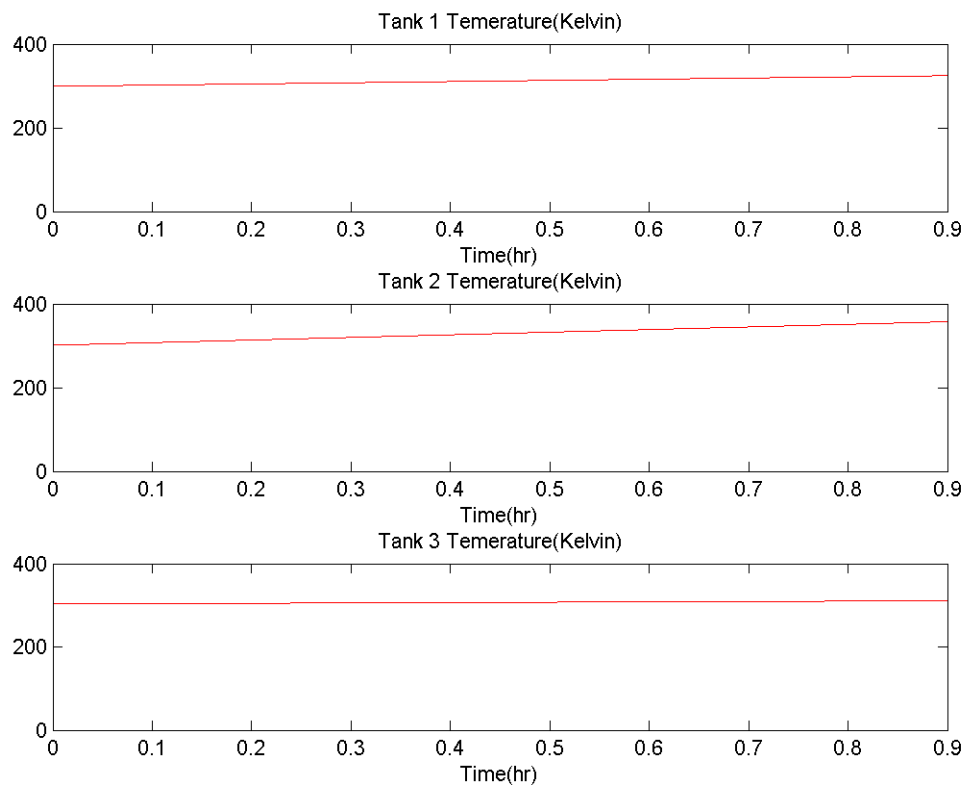


Figure 19: Temperature shift and system enthalpy.

Figure 20 represents the temperature against time plot. After addition of cooling water in both the tank it can be seen that temperature remains of + 300 in tank 1 and + 303 for the tank 2. Considering Figure. 19 and Figure. 20 simulation result,

we come to the conclusion that in tank 1, in presence of 73% of wastewater, 27% of cooling water needs to be added in order to maintain optimum temperature of process, whereas, in tank 2, in presence of 63% of wastewater 37% of cooling water is required to maintain the temperature.

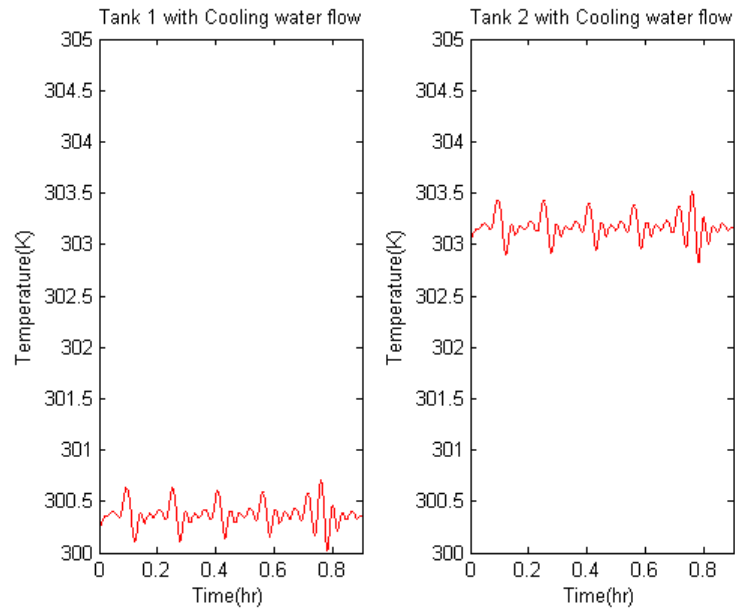


Figure 20: Effect of cooling water and temperature shift.

7 DISCUSSION

Recently, there is increasing interest in discovering efficient modes of operation and controlling of Paper and Pulp (P&P) industry waste water treatment plants. This is in the interest of P&P industries because of energy savings, but especially in order to regulate pollutant release so as to minimize their environmental effect or water consumption. This study attempts to find a solution to the above problem by studying the effect of enthalpy change on plant temperature and by conducting an evaluation of ASP using modified ASM1.

To find a solution on the given topic the research work was divided into following steps:

- A Literature review on P&P industry waste was carried out. Later, a detailed analysis and understanding was built up on WWTP, ASP and ASM1 and Benchmark simulation model.
- ASM1 model is modified for the aerobic degradation of carbon compounds.
- Next, enthalpy change calculation was evaluated for key pollutants of P&P industry and stochastic simulation of degradation process was performed for the pollutant.
- The modified ASM1 and Benchmark Simulation Model was implemented in Matlab to simulate the AS process. Furthermore, a temperature shift model was evaluated and the quantity of cooling water required to maintain optimum system temperature was determined.

8 CONCLUSIONS

In this research work, wastewater treatment of the paper and pulp industry has been analysed. A modified activated sludge model number 1 simulating the aerobic degradation of carbonaceous compounds was developed. To reproduce the activated sludge process for the paper and pulp industry waste, the benchmark simulation model and the modified activated sludge model number 1 are simulated in matlab.

The key pollutant of P&P waste was identified and bond enthalpy study was performed for its degradation process. The above process was classified as exothermic which generates energy. The generated energy result was implemented into the temperature shift model to determine the amount of water required to be added in order to maintain the activated sludge process at its optimum temperature. Furthermore, using a stochastic simulation study, the P&P pollutant was classified into the soluble solid (S_S) and slowly biodegradable (X_S) components.

From this thesis work, it can be concluded that the efficiency of wastewater plant operation is highly dependent upon the type of waste. Especially slowly decaying carbonaceous components like lignin require a longer processing time than faster decaying components in municipal waste. Therefore, it is important to have a separate wastewater plant for industries before the effluent water gets discharged either into the municipal plant or to the natural water body.

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