UNIVERSITI TEKNOLOGI PETRONAS

EFFECT OF DISSOLVED OXYGEN CONCENTRATION ON NITRIFICATION AND DENITRIFICATION

by

SHARIL NIZA B ABDUL AZIZ (2612)

Dissertation submitted in partial fulfillment of

Final Year Research Project

The requirement for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JULY 2005

Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Bandar Seri Iskandar, Tronoh, Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

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Ms. Ng Tze Ling
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CERTIFICATION OF ORIGINALITY

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

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ABSTRACT

The effect of the dissolved oxygen concentration on the nitrification and denitrification has been investigated worldwide by numbers of researcher. It has been proposed that several others factors also has affected the rate of the nitrification and denitrification process such as the pH, temperature, inhibitory and toxic materials. However, for this research, only the dissolved oxygen factor will be studied.

The main objective of this research is to study the effect of dissolved oxygen concentrations on the rate of nitrification and denitrification process. In addition to that, this research also will include the study of some of the equations which were developed by other researchers in order to determine the effect of DO concentrations on the rate of the nitrification and denitrification process.

For this research, the equation for mass transport which is solved by QUAL2E is going to be put to test by using the FEMLAB software. This equation includes the effects of advection, dispersion, dilution, constituent reactions and interactions, and sources and sinks. However, only the sources and sinks factor is being modified.

For nitrification, it is proven that as the DO concentration increases, the growth rate of the nitrifiers will also increase. Hence, the nitrification rate will also increase. For this nitrification process, the Double-Monod equation is found to best fit the research objective.

For denitrification, it is also proven that as the DO concentration increases, the growth rate of denitrifiers will decreases. Hence, the nitrification rate will also decrease. For this process, the Activated Sludge Model (Two-parameter Model) equation is found to best fit the research objective in determining the effect of dissolved oxygen concentration in denitrification.

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CHAPTER 1
INTRODUCTION

1.1. BACKGROUND OF STUDY

Nitrification-denitrification has long been recognized as a biological means of ammonia removal from soils, wastewaters, and rivers and lakes. Nitrification in wastewater treatment is increasing in importance due to more stringent effluent requirements, and need for nutrient removal.

Nitrification-denitrification appears to be one of the more promising methods of nitrogen removal. The subject of biological nitrogen removal has been investigated by and continues to be of interest to microbiologists, engineers, and biochemists.

1.1.1. Nitrification Process

The Nitrification process is carried out by bacterial populations that sequentially oxidize ammonium to nitrate with intermediate formation of nitrite. The two principle genera of importance for carrying out this process are *Nitrosomonas* and *Nitrobacter*. Both of these groups are classified as autotrophic organisms because they derive energy for growth from the oxidation of inorganic nitrogen compounds.

In contrast, heterotrophic bacteria derive energy from the oxidation of organic matter. Another feature of these organisms is that they use inorganic carbon for synthesis rather than organic carbon.

The two groups are distinguished from one another by their ability to oxidize only specific species of nitrogen compounds. While *Nitrosomonas* can oxidize ammonium to nitrite but cannot complete the oxidation to nitrate, *Nitrobacter* is limited to the oxidation of nitrite to nitrate. The overall stoichiometric reactions in the oxidation of ammonia into nitrate can be summed up as follows:

The process for the ammonium oxidizing bacteria is:

$NH_4^+ + 3/2\ O_2 \rightarrow NO_2^- + H_2O + 2H^+$

The process for the nitrite oxidizing bacteria is:

$NO_2^- + ½\ O_2 \rightarrow NO_3^-$

Since complete nitrification is a sequential reaction, treatment process systems must be designed to provide an environment suitable for the growth of both groups of nitrifying bacteria.

1.1.2. Denitrification Process

Biological denitrification involves the microbial reduction of nitrate to nitrite, and ultimately nitrite to nitrogen gas. Nitrate and nitrite replace oxygen for microbial respiration in this reaction; as such, denitrification is commonly thought to occur only in the **absence of molecular oxygen.** The conditions suitable for denitrification – oxygen is absent but nitrate is present – are commonly referred to as ***anoxic***.

Since nitrogen gas is relatively biologically inert, denitrification converts nitrogen from a potentially objectionable form (nitrate) to a form that has no significant effect on the environment (nitrogen gas). For example, using methanol as an electron donor, denitrification can be represented as a two-step process as shown below:

First Step:

$NO_3^- + 1/3\ CH_3OH \rightarrow NO_2^- + 2/3\ H_2O$

Second Step:

$NO_2^- + ½\ CH_3OH \rightarrow ½\ N_2 + ½\ CO_2 + ½\ H_2O + OH^-$

Nitrate in water can be objectionable if nutrient enrichment is a concern and/or if the water is intended to be potable. Denitrification in wastewater treatment applications may also provide process benefits in certain situations, including the development of alkalinity, the reduction of oxygen demand, and production of an activated sludge with better settling characteristics.

1.2. PROBLEM STATEMENT

Nitrification and denitrification have long been recognized as a biological means of ammonia removal from soils, wastewaters, and rivers and lakes. Both of these processes in wastewaters are increasing in importance due to more stringent effluent requirements, and need for nutrient removal. Nitrification-denitrification appears to be one of the more promising methods of nitrogen removal.

Nitrification and denitrification are functions of dissolved oxygen concentrations as stated in the project background. The effect of dissolved oxygen concentration on nitrification and denitrification to design a better wastewater treatment processes for nitrogen removal is important.

For the nitrification process, the basic model for the kinetics of the process is:

$\mu = \mu_{max}$ [S/ (K_s + S)] (Stenstrom and Poduska (1979)

μ = specific growth rate of microorganisms, d^{-1}

μ_{max} = maximum specific growth rate of microorganisms, d^{-1}

K_s = half-saturation or half-velocity coefficient (equivalent to the growth-limiting substrate concentration at half the maximum specific growth rate), mg/L

In this case, K_s and the growth rate of the nitrifying bacteria are affected by the dissolved oxygen at a certain concentration. Mean while, for denitrification, the basic model is as follows:

$r_D = r_{D,max}$ [1/(1+(DO/K_{O2}))] (Oh and Silverstein (1997)

where:

r_D = observed denitrification rate

$r_{D,max}$ = anoxic maximum specific denitrification rate

K_{O2} = the inhibition constant where the denitrification rate is half that of the anoxic rate.

For the denitrification process, the denitrifier growth rate is affected by the concentration of dissolved oxygen concentration in the water. So the main purpose of this project is to observe and concluded on what is the effect of DO concentration on nitrification and denitrification.

1.3. OBJECTIVES AND SCOPE OF STUDY

The objectives and purposes of this project are:-

- To identify the effect of dissolved oxygen concentration on nitrification.
- To identify the effect of dissolved oxygen concentration on denitrification.

The scope of this study is between the two processes involved in wastewater treatment which is the nitrification and denitrification process and the effect on the oxygen concentration in both of the processes.

It is clear that the growth rate of the nitrifier and denitrifier are affected by many factors such as pH, temperature, inorganic substrate concentration, inhibitory materials and dissolved oxygen concentration. For this study, only the effect of dissolved oxygen concentration will be taken into account. The findings of the kinetic rate by using several models will be simulated in the computers. No experiment will be done for this research.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1. Nitrification Process

A description of ammonium and nitrite oxidation can be derived from an examination of the growth kinetics of *Nitrosomonas* and *Nitrobacter*. *Nitrosomonas* growth is limited by the concentration of ammonium, while *Nitrobacter* growth is limited by the concentration of nitrite. The kinetic equation proposed by Monod is used to describe the kinetics of biological growth of either *Nitrosomonas* or *Nitrobacter*:

$$\mu = \mu_{max} [S / (K_s + S)]$$

μ = specific growth rate of microorganisms, d^{-1}
μ_{max} = maximum specific growth rate of microorganisms, d^{-1}
K_s = half-saturation or half-velocity coefficient (equivalent to the growth-limiting substrate concentration at half the maximum specific growth rate), mg/L
S = growth-limiting substrate concentration, mg/L

The concentration of dissolved oxygen (DO) has a significant effect on the rates of nitrifier growth and nitrification in biological waste treatment systems. By modeling the growth of *Nitrosomonas* according to the Monod equation with DO as the growth-limiting substrate concentration, value for the half-saturation coefficient have been reported as 0.15-2.0 mg/L O_2. Evidence suggests that the value for the coefficient increases with increasing temperature.

The influence of DO on nitrification rates has been controversial since the beginning. Qualitative observations imply that under certain conditions complete nitrification can be achieved in biological systems at DO levels as low as 0.5 mg/L.

In almost all treatment systems, oxygen is also required to oxidize other materials than ammonia present in the wastewater. This therefore often raises the total oxygen demand in a nitrifying plant.

The concentration of DO has a significant effect on the rates of nitrifier growth and nitrification in biological waste treatment systems. The Monod relationship has been used and modifies to model the effect of dissolved oxygen, considering oxygen to be a growth limiting substrate as follows:

$$\mu = \mu_{max} [DO/ (K_{O2}, n + DO)]$$

Where: DO = dissolved oxygen, mg/l and

K_{O2}, n = half-saturation constant for oxygen, mg/l, in the nitrification process.

Most mathematical models for biological growth take into account only one substrate, such as the Monod model, since experimental studies are usually performed with all other nutrients in excess. However, Stenstrom and Poduska (1980) used a double substrate-limiting kinetic expression to describe the combined effect of dissolved oxygen and ammonia-nitrogen on the growth rate, as shown in the following equation:

$$\mu = \mu_{max}[S_N/ (K_{S,N} + S_N)] [DO/ (KO_2, n + DO)] - K_d$$

where:

S_N = Ammonia concentration

$K_{S,N}$ = Half-saturation constant for ammonia nitrogen

K_d = decay or maintenance coefficient (d^{-1})

2.2. Denitrification Process

The kinetics of denitrification can be described using equations that the same form as those for other reactions such as nitrification. For example, zero-order, first order and Monod-type kinetics have all been used to describe the rate of denitrification.

A Monod-type expression can be used to relate the growth rate of denitrifying microorganisms to the concentration of nitrate:

$\mu_D = \mu_{max\,D}\ [D/\ (K_D+D)]$

where:

μ_D = specific denitrifier growth rate, d^{-1}

$\mu_{max\,D}$ = maximum specific denitrifier growth rate, d^{-1}

D = concentration of nitrate nitrogen, mg/L

K_D = half-saturation coefficient, mg/L

Denitrification is a process which takes place in an *anoxic* condition where oxygen is absent but nitrate is present. This is because, to accomplish denitrification, the denitrifier (bacteria) uses nitrate or nitrite to replaces oxygen in the respiratory process. This bacteria uses either nitrate or oxygen as the terminal electron acceptor while oxidizing organic matter. This is the condition where oxygen is less favored in the process, the anoxic condition. If the DO concentration is very high in time where denitrification occurs, the bacteria will choose to use oxygen rather than the nitrite or nitrate. This will cause the nitrogen cycle to be incomplete, and nitrogen will not be removed from the wastewater.

From the some of the journals, the effect of DO concentrations on denitrification process has been study for the activated sludge treatment. Some of the observed DO concentrations value ranged from 0.09 mg/L to 5.6 mg/L. For this activated sludge treatment, one-parameter model has been developed for oxygen-inhibition of denitrification in activated sludge which is called ASM-2 model 1. Below is the one-parameter model:

$r_D = r_{D,max}\ [1/(1+(DO/K_{O2}))]$

where:

r_D = observed denitrification rate

$r_{D,max}$ = anoxic maximum specific denitrification rate

K_{O2} = the inhibition constant where the denitrification rate is half that of the anoxic rate.

In order to account for more rapid decline in denitrification as the mixed liquor DO increased to a high enough level that all the flocs regions would be completely aerobic, another model was made:-

$r_D = r_{D,max} [1/(1+(DO/K_{O2}))][1-(DO/DO_{max})]$

where:

r_D = observed denitrification rate

$r_{D,max}$ = anoxic maximum specific denitrification rate

K_{O2} = the inhibition constant where the denitrification rate is half that of the anoxic rate.

DO = dissolved oxygen concentration.

DO_{max} = the threshold level of DO above which denitrification is completely inhibit (mg/L).

This activated sludge denitrification was carried out in a bench-scale sequencing batch reactor process (SBR).

Generally, for this research, the QUAL2E method for mass transport will be used. QUAL2E, which can be operated as steady-state or as a dynamic model, is intended for use as a water quality planning tool. The model can be used, for example, to study the impact of waste loads on in stream water quality or to identify the magnitude and quality characteristics of non-point waste loads as part of a field sampling program. The user also can model effects of diurnal variations in meteorological data on water quality (primarily on dissolved oxygen and temperature) or examine diurnal dissolved oxygen variations caused by algal growth and respiration.

The equation for the mass transport is as follows:

$$\partial M/\partial T = [\partial(A_X D_L (\partial C/\partial x))/ \partial x] \, dx - \partial[(A_X \hat{U} C)/ \partial x] \, dx + (A_X \, dx) \, dC/dT + s$$

This equation includes the effects of advection, dispersion, dilution, constituent reactions and interactions, and sources and sinks. In natural aerobic waters, there is a stepwise transformation organic nitrogen to ammonia, to nitrite, and finally to nitrate. The equations of transformation from one stage of formation to another are included in the **appendix**.

CHAPTER 3
PROJECT METHODOLOGY

For this final year research project, the methodology of the project has been divided into three parts which is:

1. *Research and Literature Review*

   Basically, this the most important parts in this project where a lot of research needs to be done in order to analyze the entire theoretical models of the kinetics of the nitrification and denitrification processes.

   The equation that is going to be use for the nitrification is the ***Double-Monod Equation*** which relates the effect of DO concentration with the concentration of Ammonia nitrogen in the modeled river. As for denitrification, the Equation from the Activated Sludge Model 2 will be put to test as the form of the equation does suits the theory of denitrification where as the DO concentration increases, the rate of denitrification will decrease.

   This is the **Double-Monod (Stenstrom and Poduska, 1979)** equation:-

   $$\mu = \mu_{max}[S_N/ (K_{S,N} + S_N)] [DO/ (K_{O2}, n + DO)] - K_d$$

   where:

   S_N = Ammonia concentration

   $K_{S,N}$ = Half-saturation constant for ammonia nitrogen

   K_d = decay or maintenance coefficient (d^{-1})

   And this is the ASM2 one-parameter equation **(Oh and Silverstein, 1997)** for the denitrification process:-

   $$r_D = r_{D,max} [1/(1+(DO/K_{O2}))]$$

   where:

   r_D = observed denitrification rate (mg-N/mg-MLVSS/h)

   $r_{D,max}$ = anoxic maximum specific denitrification rate

K_{O2} = the inhibition constant where the denitrification rate is half that of the anoxic rate.

For this process (denitrification), other model (two-parameter model) **(Oh and Silverstein, 1997)** for the activated sludge was also taken into account. The equation is as follows:-

$r_D = r_{D,max} [1/(1+(DO/K_{O2}))][1-(DO/DO_{max})]$

where:

r_D = observed denitrification rate (mg-N/mg-MLVSS/h)

$r_{D,max}$ = anoxic maximum specific denitrification rate

K_{O2} = the inhibition constant where the denitrification rate is half that of the anoxic rate.

DO = dissolved oxygen concentration.

DO_{max} = the threshold level of DO above which denitrification is completely inhibit (mg/L).

For these equation, the mixed liquor suspended solids concentration **MLVSS** is equal to 1340 mg/L.

Then, after all these equations have been tested, it will be suits in the nitrogen cycle equation as in the **appendix**. This is only for the ammonia nitrogen cycle and the nitrate nitrogen cycle.

2. *Analyzing Models*

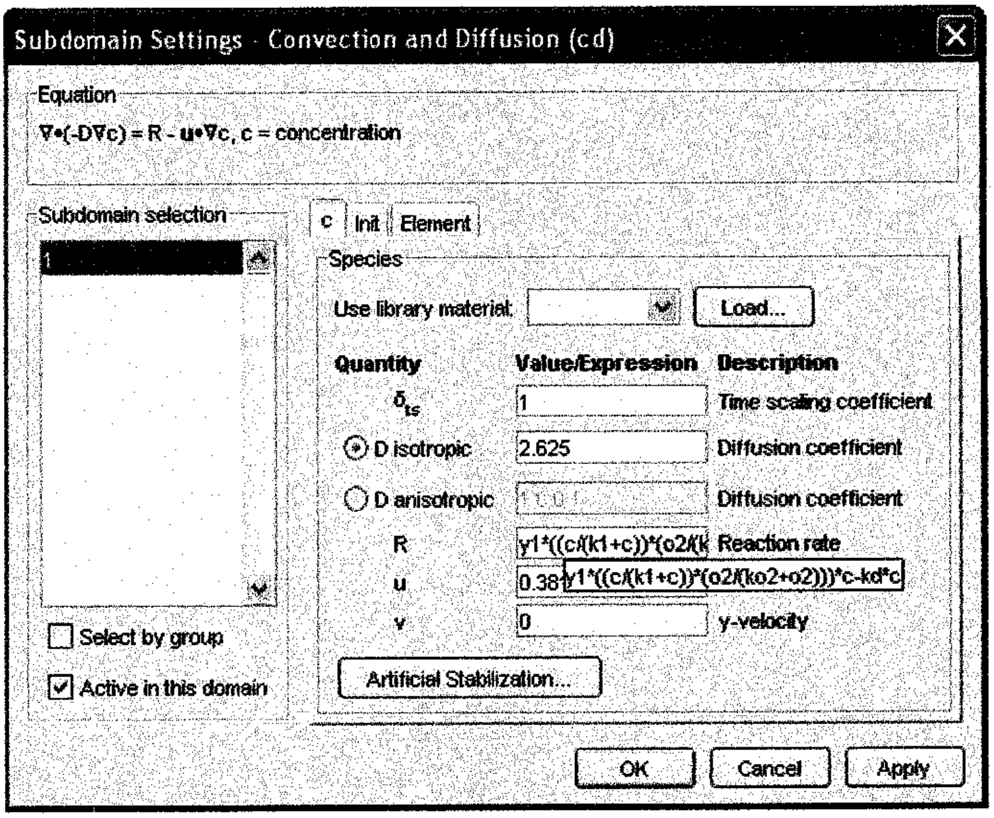
All 4 of the kinetic models which are obtained from journals and books will be analyze and compared to see which is more feasible and accurate in determining the effect of dissolved oxygen in nitrification-denitrification process.

3. *Computer Simulations*

The findings of the research will be put into computer simulations to produced results which can be compared in order to complete the task given.

The software which is going to be use is the **FEMLAB** software. FEMLAB supplies highly sought-after new technology for the modeling and simulation of physics in all science and engineering fields. Its main attribute is the ease with which modeling can be performed and its unlimited multiphysics capabilities in 1D, 2D, 3D - the perfect way to apply state-of-the-art numerical analysis in modeling such as the mass transport equation or the first order equation for nitrification or denitrification.

<u>For Nitrification</u>



<u>Figure 1 (Subdomain settings).</u>

Figure 1 shows the equation that is use for the reaction rate which is the nitrogen cycle equation for ammonia nitrogen as shown in the **appendix**. For the **diffusion coefficient** and **the X-axis velocity**, the value is based on the QUAL2E model for a certain river (also applied for the denitrification). The rate of nitrification which is the **μ** times the concentration of ammonia by using the ammonia nitrogen cycle equation is as follows:-

The Ammonia Nitrogen Cycle Equation:-

$$\frac{dN_1}{dt} = \beta_3 N_4 - \beta_1 N_1 + \sigma_3/d - F_1\ \alpha_1 \mu A$$

where

$$F_1 = P_N N_1/(P_N N_1 + (1 - P_N)N_3) \qquad \text{III-18}$$

N_1 = the concentration of ammonia nitrogen, mg-N/L

N_3 = the concentration of nitrate nitrogen, mg-N/L

N_4 = the concentration of organic nitrogen, mg-N/L

β_1 = rate constant for the biological oxidation of ammonia nitrogen, temperature dependent, day^{-1}

β_3 = organic nitrogen hydrolysis rate, day^{-1}

α_1 = fraction of algal biomass which is nitrogen, mg-N/mg-A

σ_3 = the benthos source rate for ammonia nitrogen, mg-N/ft^2-day

d = mean depth of flow, ft

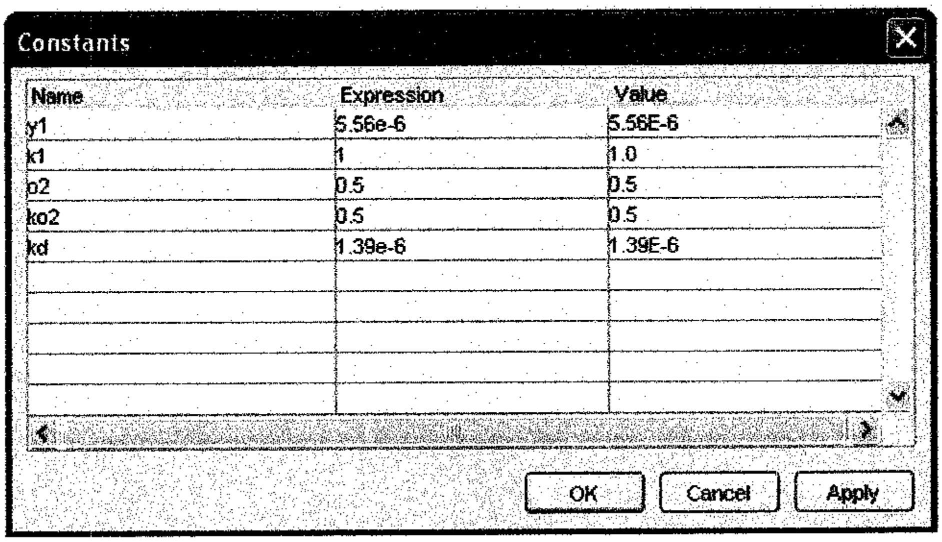
F_1 = fraction of algal nitrogen uptake from ammonia pool

μ = the local specific growth rate of algae, day^{-1}

A = algal biomass concentration, mg-A/L

P_N = preference factor for ammonia nitrogen (0 to 1.0)

For this case, all of the terms except for the N_1 and β_1 term can be neglected because this is the two terms which is being studied.


Constants

Name	Expression	Value
y1	5.56e-6	5.56E-6
k1	1	1.0
o2	0.5	0.5
ko2	0.5	0.5
kd	1.39e-6	1.39E-6

Figure 2(The constant values).

Figure 2 shows the constant value which is use in the nitrogen cycle equation for the nitrification process by using the FEMLAB software. Hence:-

Term	Value	Reference
μ_{max}	0.02 hr^{-1}	Stenstrom and Poduska (1979)
S_N	50 mg/L	Stenstrom and Poduska (1979)
$K_{S,N}$	1.0 mg/L	Stenstrom and Poduska (1979)
DO	Varies from 0.5 to 7.5 mg/L	Stenstrom and Poduska (1979)
K_{O2}, n	0.5mg/L	Stenstrom and Poduska (1979)
K_d	0.005 hr^{-1}	Stenstrom and Poduska (1979)

Table 1 (List of constant values use in the Monod Equation).

For Denitrification Model 1 (ASM-2)

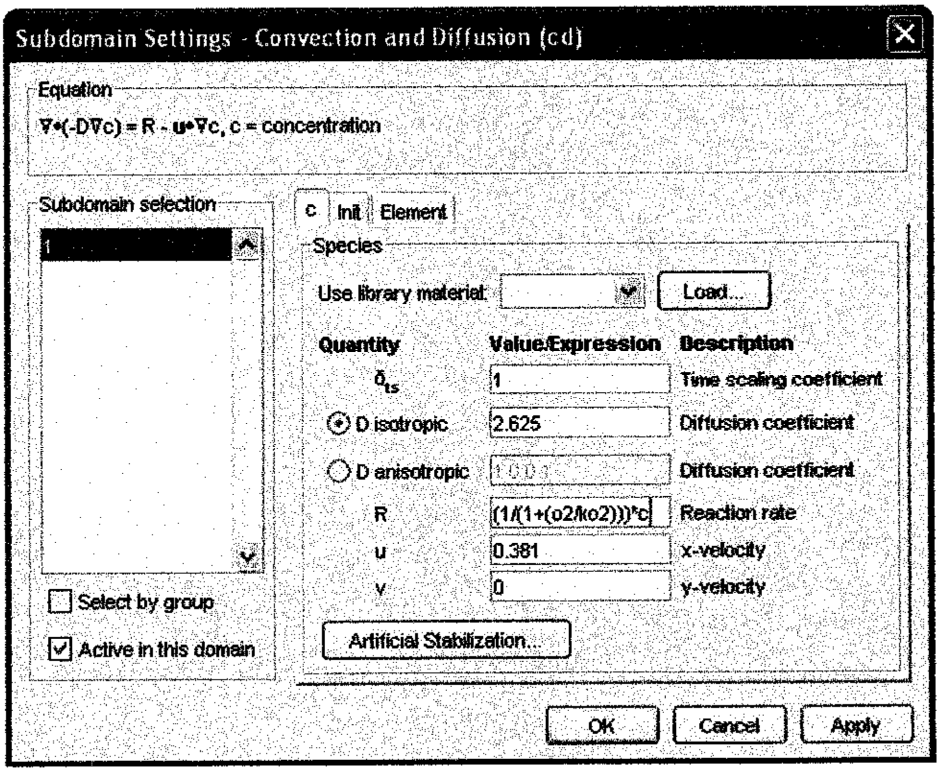


Figure 3 (The subdomain settings).

Figure 3 shows the equation that is use for the reaction rate which is the nitrogen cycle equation for nitrate nitrogen as shown in the **appendix**. For the **diffusion coefficient** and **the X-axis velocity**, the value is based on the QUAL2E model for a certain river (also applied for the denitrification). The rate of nitrification which is the r_D/r_{Dmax} times the concentration of nitrate by using the nitrate nitrogen cycle equation is as follows:-

Nitrate Nitrogen

$$\frac{dN_3}{dt} = \beta_2 N_2 - (1 - F)\alpha_1 \mu A$$

where

F = fraction of algal nitrogen taken from ammonia pool, as defined in Section 3.3.2

α_1 = fraction of algal biomass that is nitrogen, mg-N/mg-A

μ = local specific growth rate of algae, day^{-1}

For this case, all of the terms except for the N_2 and β_2 term can be neglect because this is the only two terms which is being studied. This is for both of the models which is Model 1 and Model 2.

Term	Value	Reference
DO	Varies from 0.09 to 5.6 mg/L	Oh and Silverstein(1997)
K	0.38 mg/L	Oh and Silverstein(1997)

Table 2 (List of constant values use in the ASM2 Model 1 equation for denitrification)

For Denitrification Model 2

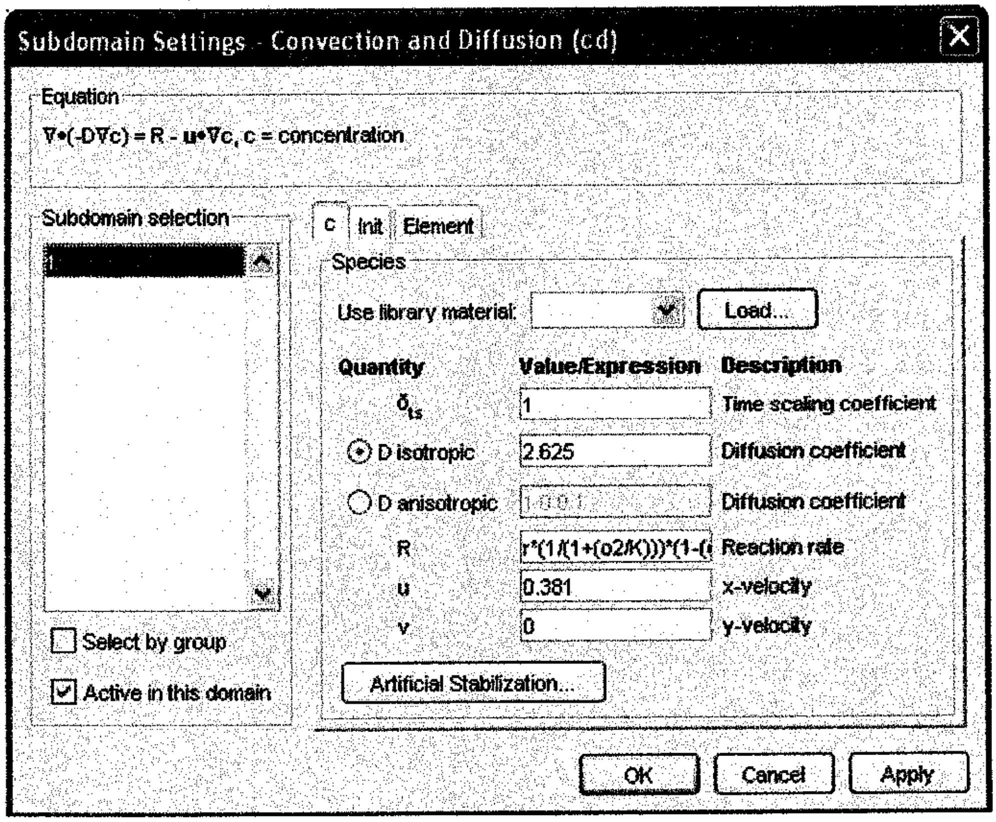


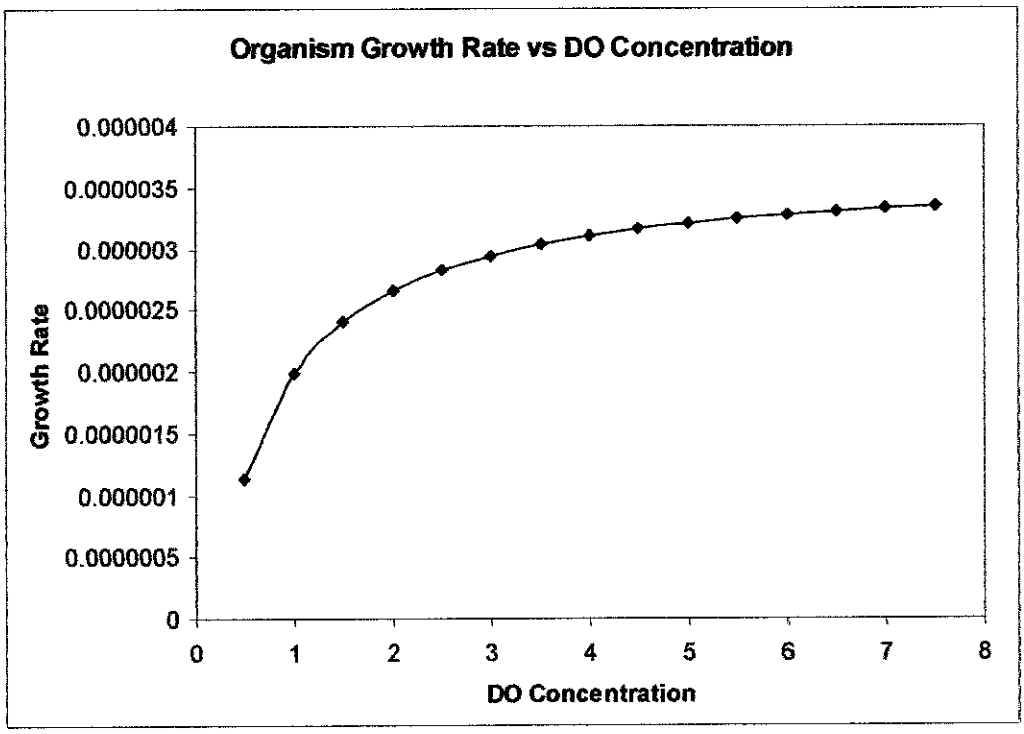
Figure 4 (The subdomain settings)

Term	Value	Reference
$r_{D,max}$	28.676 mg/hr	Oh and Silverstein(1997)
DO	Varies from 0.09 to 5.6 mg/L	Oh and Silverstein(1997)
DO_{max}	4.5 mg/L	Oh and Silverstein(1997)
K	0.69	Oh and Silverstein(1997)

Table 3 (List of constant values use in the ASM2 Model 2 for denitrification)

CHAPTER 4
RESULTS AND DISCUSSION

<u>For Nitrification</u>



<u>Figure 5 (Organism growth rate against DO concentration)</u>

Figure 5 is a graph that shows the organism growth rate against the DO concentration. The result is that at different DO level of concentration, the growth rate will change. By looking at the trend of the graph, as the DO level of concentration increases, the growth rate will also increases. This means that if the growth rate increases, the rate of nitrification will also increases. Hence, the relationship of the nitrification rate with the DO concentration is proportional. However, this graph is based on this equation:-

$$\mu = \mu_{max}[S_N / (K_{S,N} + S_N)]\ [DO / (KO_2, n + DO)] - K_d$$

where:

S_N = Ammonia concentration (mg/L)

$K_{S,N}$ = Half-saturation constant for ammonia nitrogen

K_d = decay or maintenance coefficient (d^{-1})

And the ammonia concentration, S_N, is **fixed at 50 mg N/L**. So, in order to justify the liability of this equation, another graph is produced based on this equation:-

$$\mu = \mu_{max} [DO / (KO_2, n + DO)]$$

Where: DO = dissolved oxygen, mg/l and

KO_2, n = half-saturation constant for oxygen, mg/l, in the nitrification process.

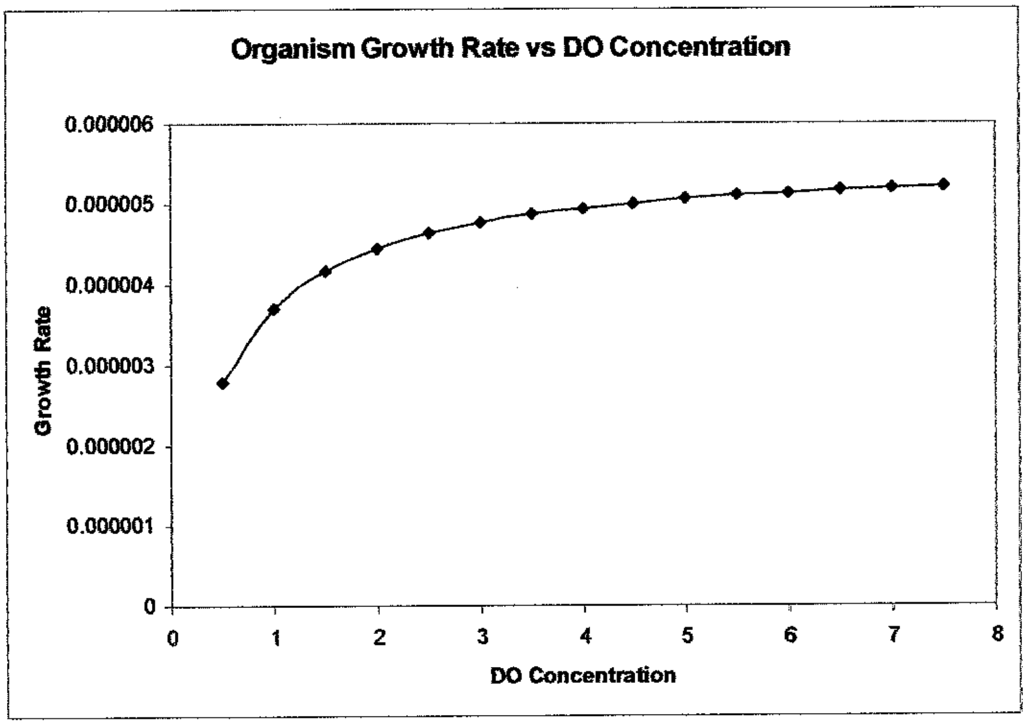


Figure 6 (Organism growth rate against DO concentration)

Even though this graph give a similar trend line as the graph in Figure 6, but the equation does not take into account the ammonia concentration, S_N, value. This is quite arguable because the rate of ammonia concentration, S_N, disappearance must be taken into account. So, in this research, the double Monod equation will be use.

FEMLAB (Nitrification)

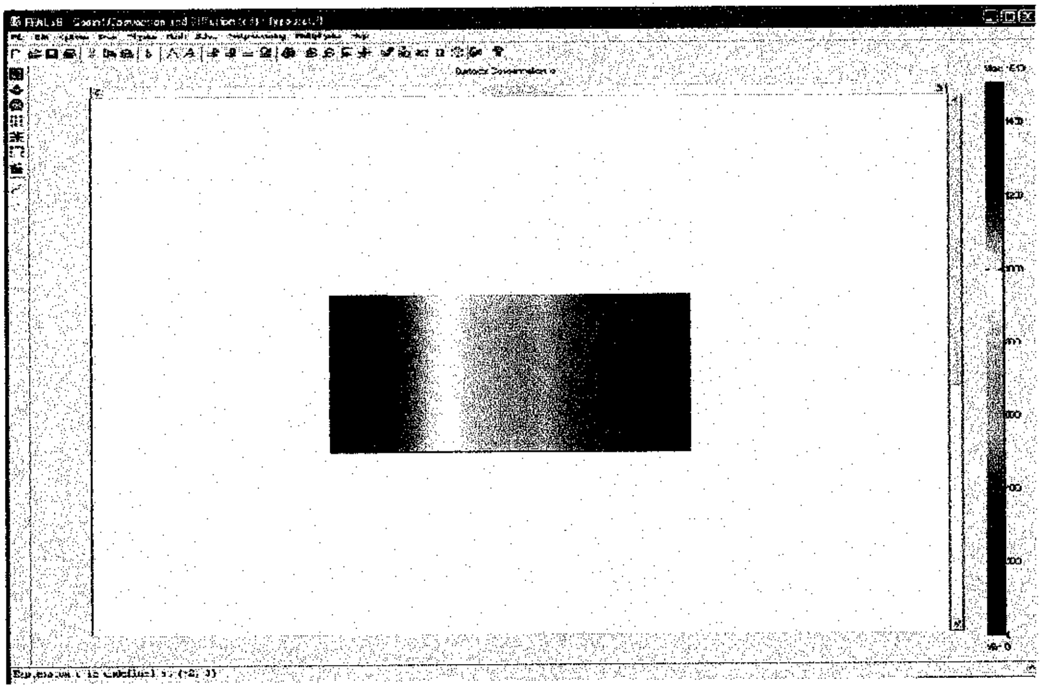


Figure 7 (The concentration decreases as the distance of the river increases)

By using FEMLAB, the process of nitrification in a river can be modeled. As shown above, as the distance increases (moving to the right side), the ammonia concentration decreases. This is shown by the changes of colors in Figure 7.

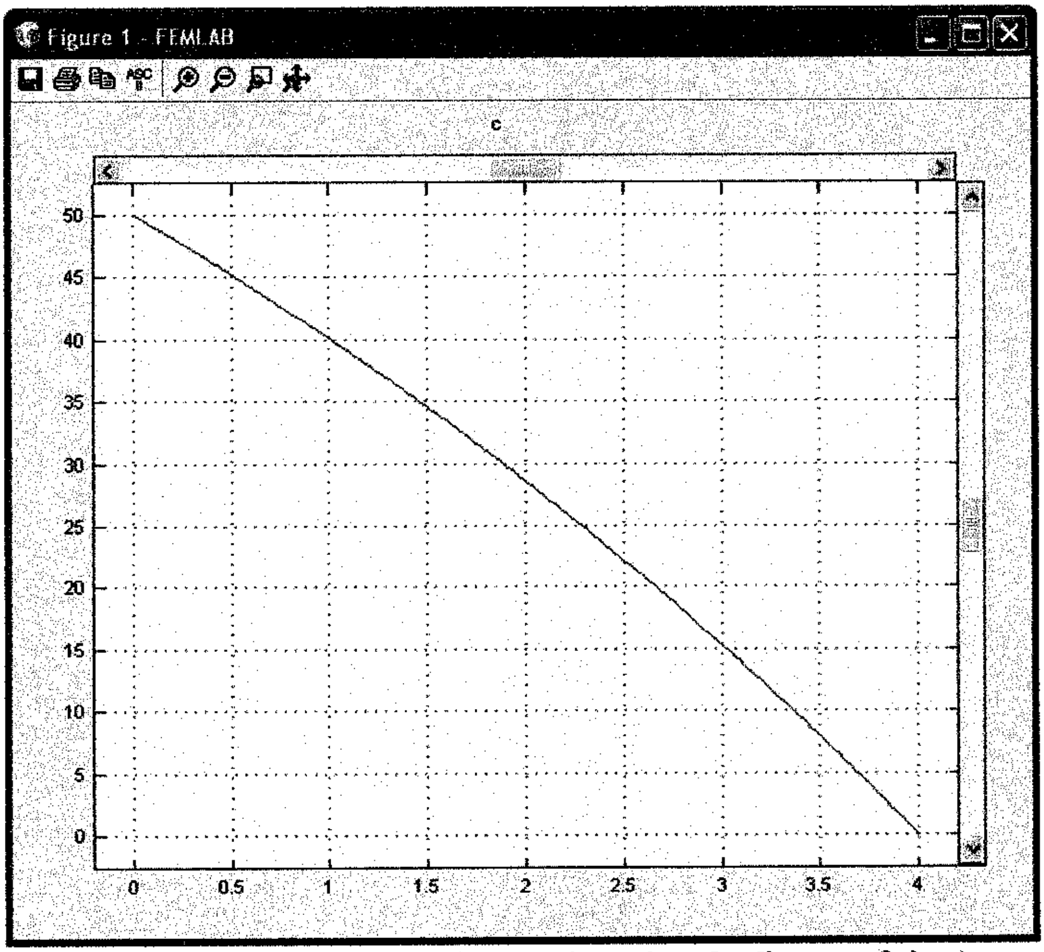


Figure 8 (The concentration of ammonia against the distance of river).

Figure 8 is actually similar to Figure 3. It shows the rate of disappearance of ammonia as the distance of the river increases. Hence, as the distance increases (X-axis), the concentration of the ammonia decreases.

For Denitrification

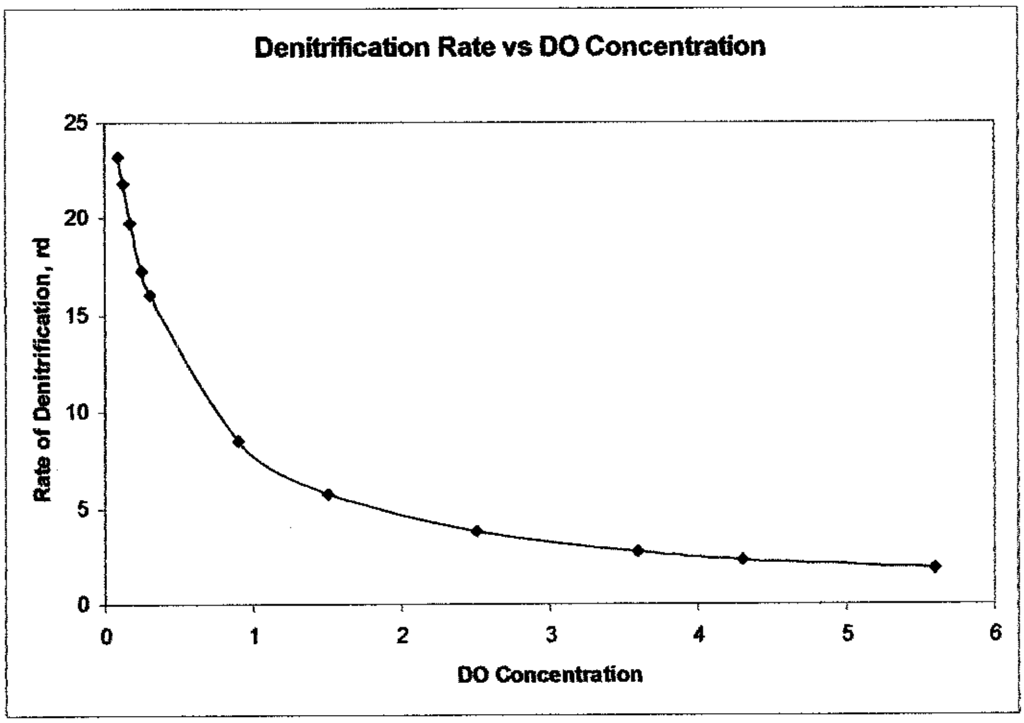


Figure 9 (Denitrification rate vs DO concentration).

Figure 9 shows the rate of denitrification against the DO concentration. This process is not as similar to the nitrification process. As shown above, as the DO concentration increases, the rate of denitrification decreases. However, according to ***Oh and Silverstein (1997),*** the effect of dissolved oxygen (DO) on denitrification by activated sludge in a bench-scale sequencing batch reactor (SBR) was investigated over a range of 0.09 to 5.6 mg/L DO. This means that the rate of denitrification will not change much even though the DO concentration is increasing more than 5.6 mg/L. For this graph, the equation is:-

$r_D = r_{D,max} [1/(1+(DO/K_{O2}))]$

where:

r_D **= observed denitrification rate**

$r_{D,max}$ **= anoxic maximum specific denitrification rate**

K_{O2} **= the inhibition constant where the denitrification rate is half that of the anoxic rate.**

This equation is from the Activated sludge model 2 (ASM2).

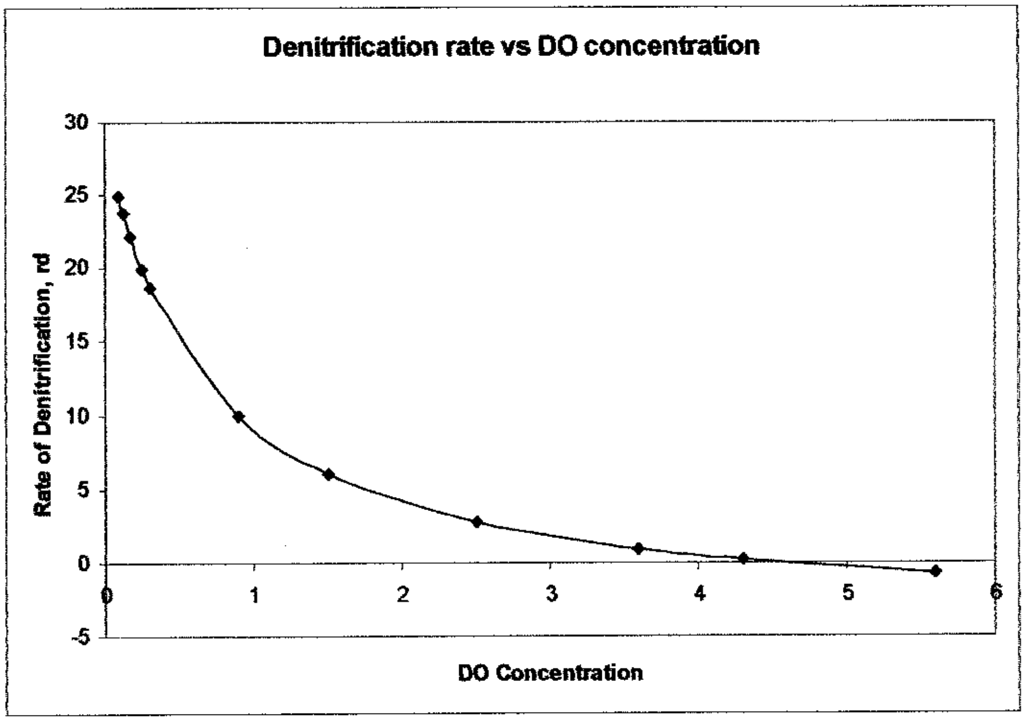


Figure 10 (Denitrification rate vs DO concentration).

Figure 10 shows the rate of denitrification against the DO concentration by using this equation, the ASM2 Model 2 equations:-

$r_D = r_{D,max}$ [1/(1+(DO/K_{O2}))][1-(DO/DO_{max})]

where:

r_D = observed denitrification rate

$r_{D,max}$ = anoxic maximum specific denitrification rate

K_{O2} = the inhibition constant where the denitrification rate is half that of the anoxic rate.

DO = dissolved oxygen concentration.

DO_{max} = the threshold level of DO above which denitrification is completely inhibit (mg/L).

In this model, an attempt was made to add a parameter to account for more rapid decline in denitrification as the mixed liquor DO increased to a high enough level that all the floc regions would be completely aerobic.

FEMLAB (Denitrification-Model 1)

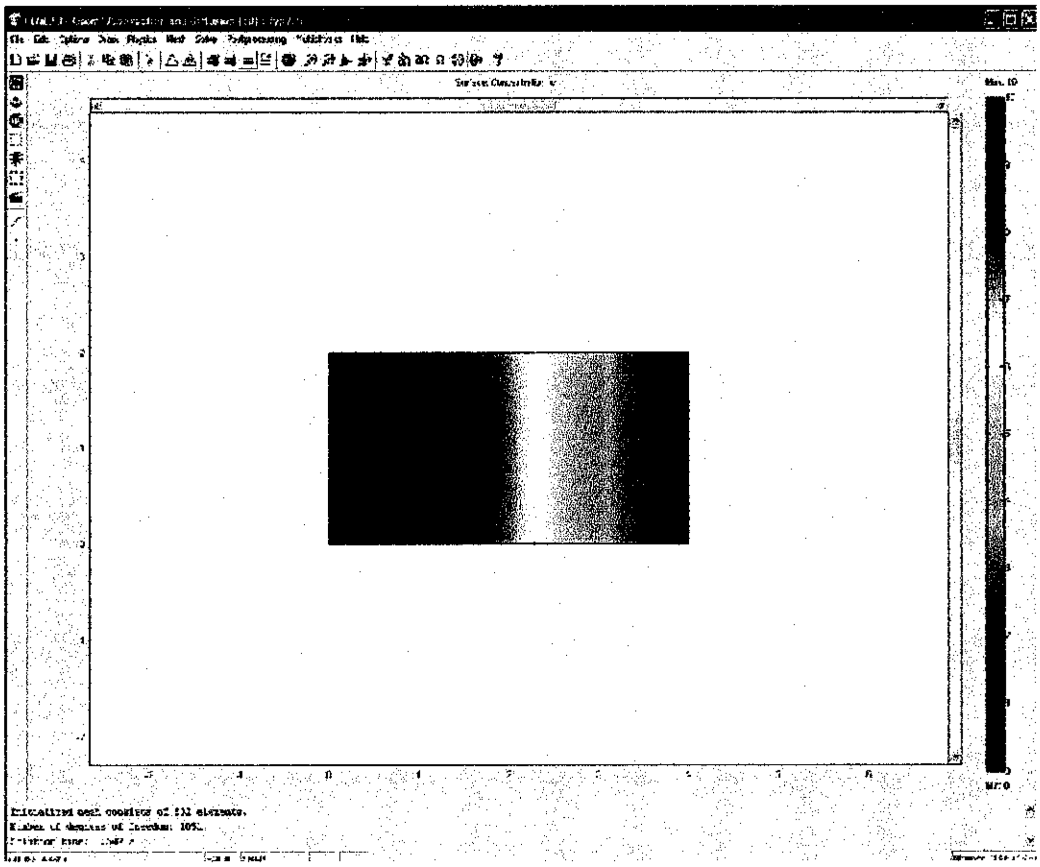


Figure 11 (The concentration of nitrate changes as the distance of the river increases).

By using FEMLAB, the process of denitrification in a river can be modeled. As shown above, as the distance increases (moving to the right side), the nitrate nitrogen decreases. This is shown by the changes of colors in Figure 11.

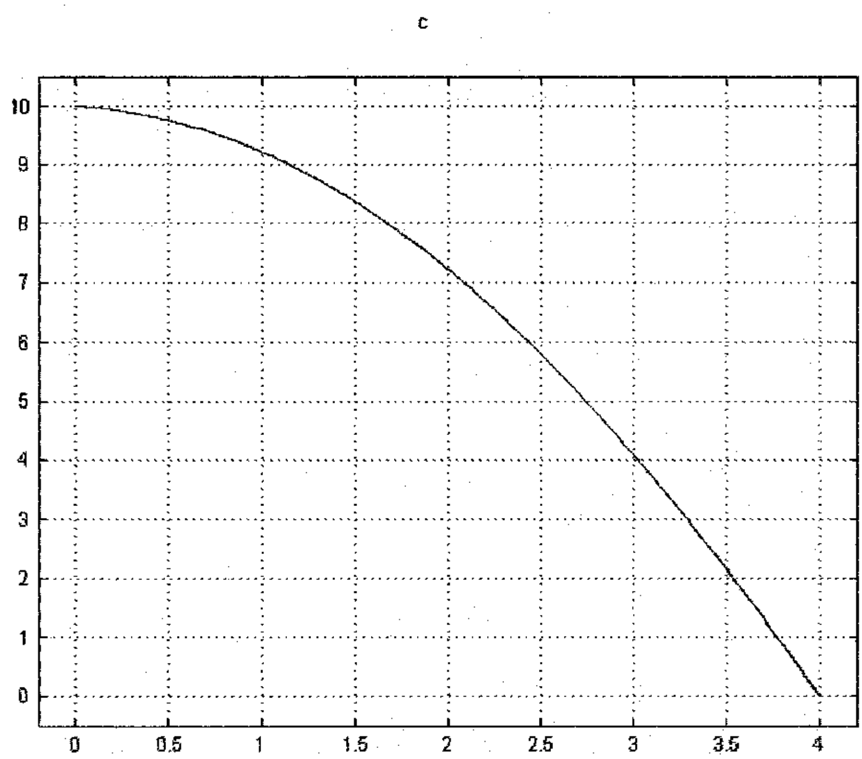


Figure 12 (The concentration of nitrate against the river distance)

Figure 12 is actually similar to Figure 8. It shows the rate of disappearance of nitrate as the distance of the river increases. Hence, as the distance increases (X-axis), the concentration of the nitrate in the river decreases.

For Denitrification (Model 2)

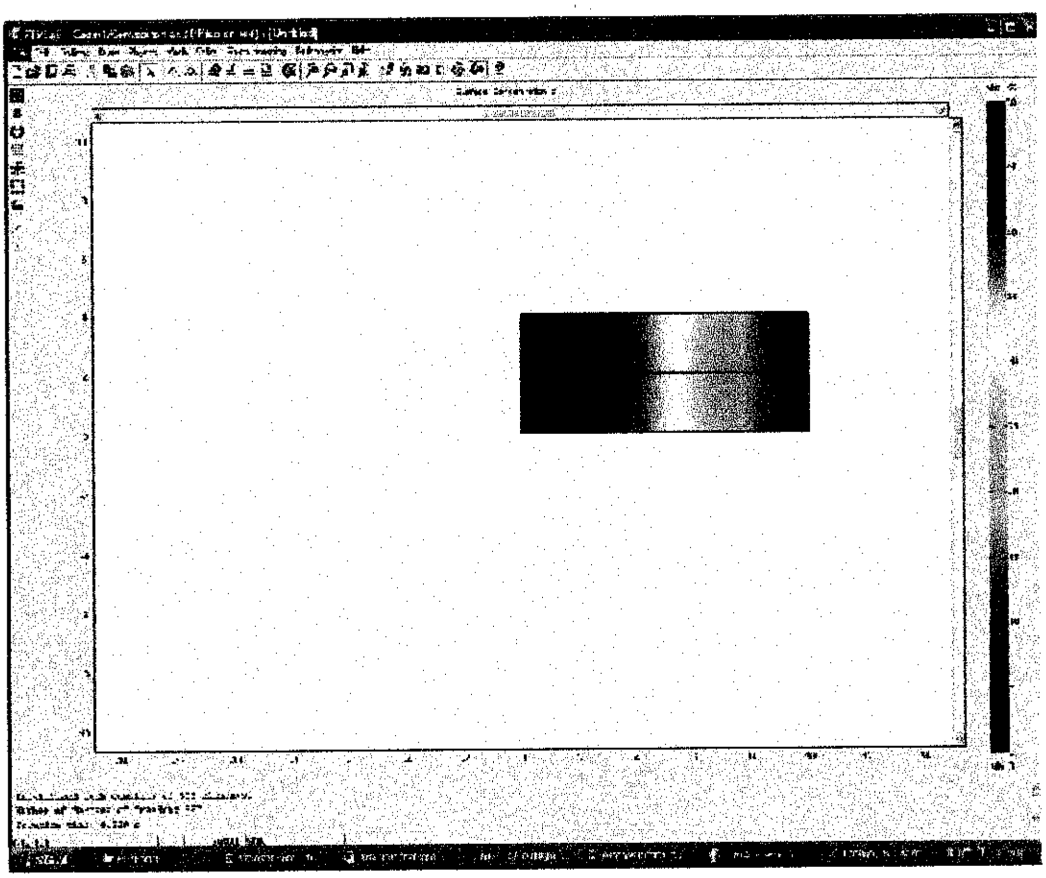
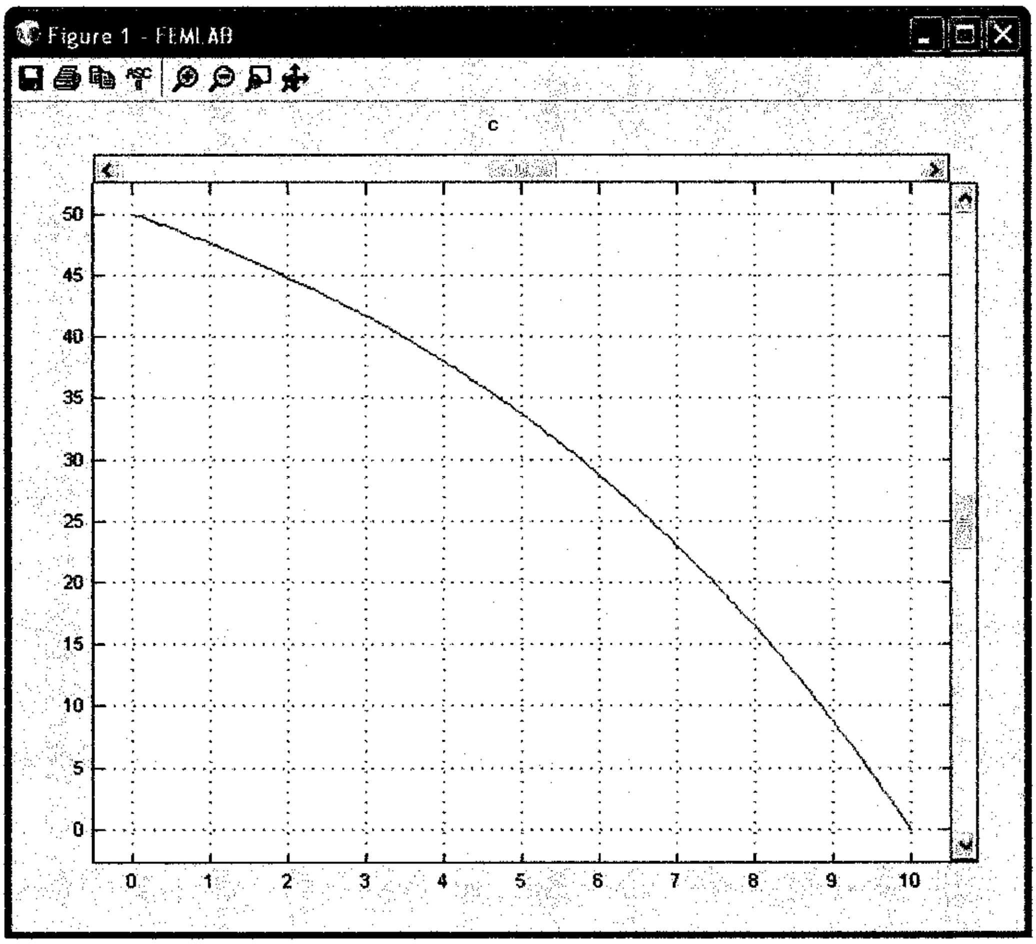


Figure 13(The dissolved oxygen concentration at 4.5 mg/L)

For this figure, it shows the same trend or pattern as the result for the nitrification where the concentration of the nitrate is decreasing as the distance of the modeled river increases. The changes can be observed as the colors changes as the distance increases to the right.



<u>Figure 14 (Dissolved oxygen concentration at 4.5mg/L)</u>

Figure 14 is actually similar to Figure 12. It shows the rate of disappearance of nitrate as the distance of the river increases. Hence, as the distance increases (X-axis), the concentration of the nitrate (Y-axis) in the river decreases.

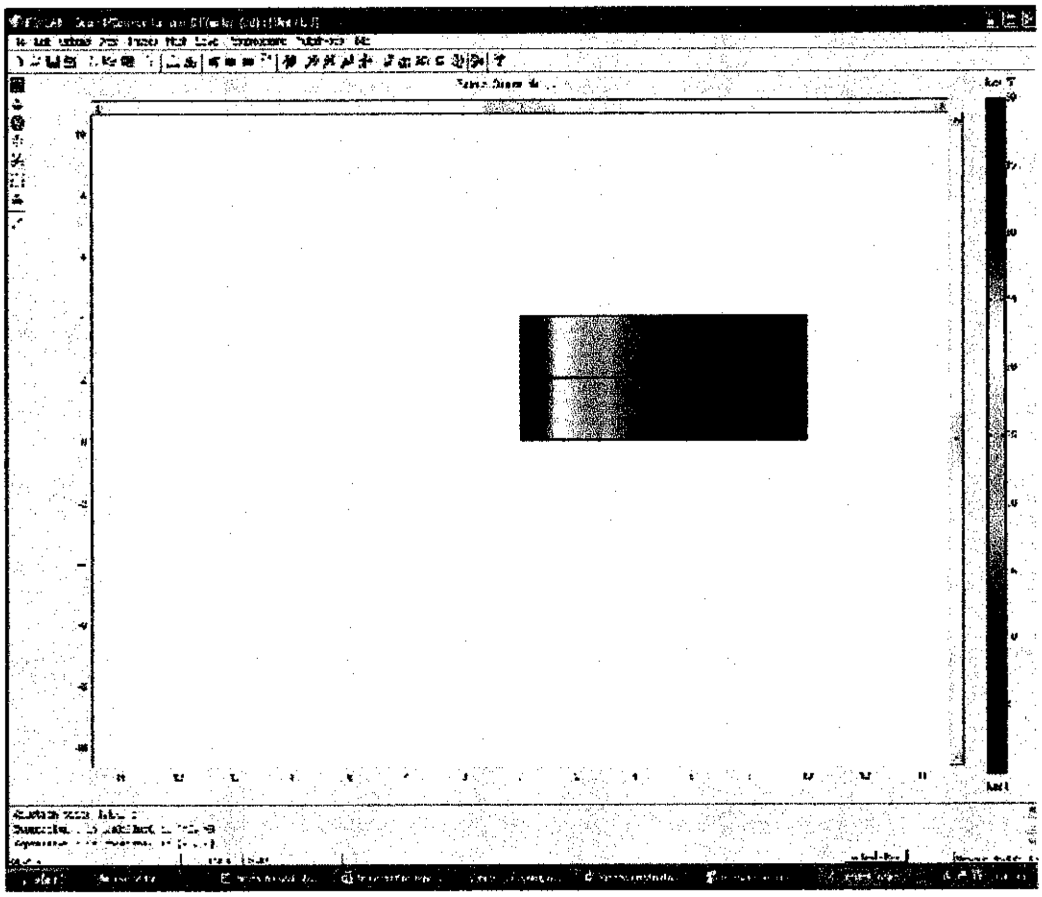


Figure 15 (Dissolved oxygen concentration at 5.0mg/L)

For this figure, it shows the same trend or pattern as the result for the nitrification where the concentration of the nitrate is decreasing as the distance of the modeled river increases. The changes can be observed as the colors changes as the distance increases to the right.

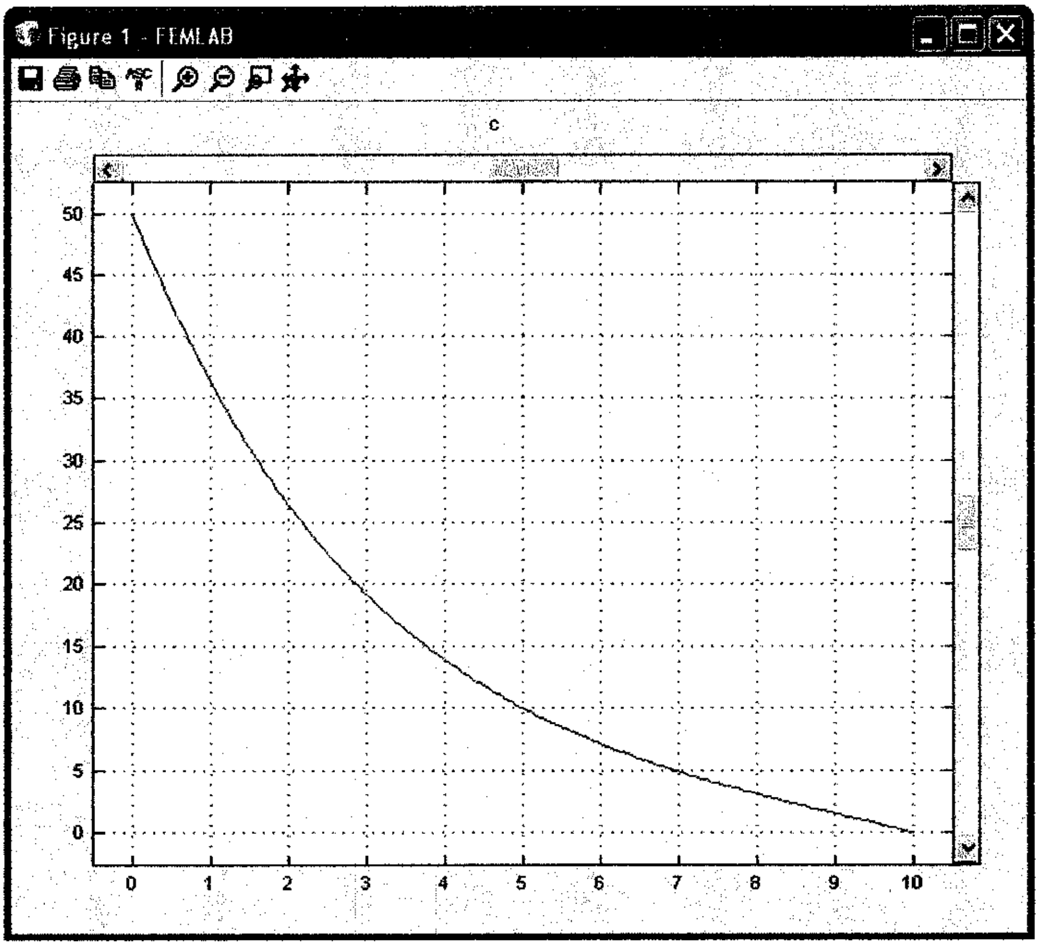


Figure 16 (Dissolved oxygen concentration at 5.0mg/L)

Even though this graph is quite different from the one with the DO concentration at 4.5 mg/L, it stills produce an acceptable result which is the nitrate concentration decreases as the distance of the river increases (Y-axis is the nitrate concentration while the X-axis is the distance).

For Nitrification

For now, the modify Monod first order equation which is the **Double-Monod Equations** seems to be suitable to be put to test for the simulations for the nitrification process because the equation has relate the DO concentrations with the rate of nitrifiers growth. All that can be stated here is that, for nitrification, as the dissolved oxygen concentrations increases, the growth rate of the nitrifier will also increase. Hence, the rate of nitrification process will also increase. However, for this research, other factors such as pH and temperature will be neglected because the main purpose of this study is to determine the effect of DO concentration on nitrification. For nitrification, the initial concentration of the ammonia is set at 50 mg/L.

From the results, the finding does follow the theory where as the DO concentration increases, the rate of nitrification will also increase. This mean, in the modeled river, the ammonia concentration will decreases as the distance of the river increases at a fixed DO. However, the results which were produced by FEMLAB for different DO concentration for the modeled river does not make any differences. For this process (nitrification), the range of the DO concentration that is being studied is from 0.5 mg/L up to 7.5 mg/L. From **figure 5**, as the DO concentration increases higher and higher, the growth rate of the nitrifier become constant. From the graph, the effect of dissolved oxygen concentration on the growth rate of both nitrification reactions is from 0.5 mg/L to as much as 4.0 mg/L. This mean, that the DO concentration will only affect the rate of nitrification at a certain range because the graph in figure 5 shows a trend line that is becoming constant and does not change as the DO concentration increases.

For Denitrification

For denitrification process, there are some of the researchers who did some experiments and studies on the effect of DO on denitrification of the activated sludge treatment. For this case, there are two models which have been developed which relate the DO concentrations with the denitrification rate. The range of the DO concentrations that is applied in this study is between 0.09 mg/L up to 5.6 mg/L. In this study, mixed liquor DO concentrations as low as 0.09 mg/L was found to significantly inhibit denitrification, resulting in a decrease of rate of denitrification process. However, as the DO concentration increases, the rate of denitrification decreases.

From **figure 9**, as the DO concentration increases, the rate of denitrification is approaching constant value. This mean that the rate of denitrification will keep on decreasing as the DO concentration increases until at certain value of DO concentration, the rate of denitrification will remain constants. From the graph, the range of DO concentration that has an effect on the rate of denitrification is from 0.09 mg/L to as much as 3.6 mg/L. To fit the observed inhibition of denitrification rate, r_D **(mg-N/mg-MLVSS/h)**, in the presence of DO as a fraction of the anoxic rate, $r_{D,max}$, for this research, two models were calibrated. The one parameter model which is as follows:-

$$r_D = r_{D,max} [1/(1+(DO/K_{O2}))]$$

appear to best fit the inhibition of SBR activated sludge denitrification over the entire range of DO studied (0.09 mg/L to 5.6 mg/L) with an inhibition constant, K, value of 0.38 mg/L DO. And the two-parameter model which as follows:-

$$r_D = r_{D,max} [1/(1+(DO/K_{O2}))][1-(DO/DO_{max})]$$

incorporating a threshold DO concentration after which denitrification would be completely inhibited also fitted the results well with fitted K and DO_{max} values of 0.69 and 4.5 mg/L DO.

For the FEMLAB results for both of the models, it appears that the result is as expected where the nitrate nitrogen concentration decreases as the distance of the modeled river increases at fix DO concentration.

CHAPTER 5
CONCLUSIONS

The main purpose of this project is to determine the effect of dissolved oxygen concentration in the nitrification and denitrification process. Nitrification is a process which oxidizes ammonia into nitrite and subsequently to nitrate while denitrification is the reduction of nitrate into nitrogen gas. These two processes are part of the natural nitrogen cycle and are crucial in biological process for removing nitrogen from wastewater.

For nitrification and denitrification, the DO concentration will affect the growth rate for both of the nitrifier and denitrifier. From the research, the relationship between the growth rate of the nitrifying and denitrifying bacteria with the kinetics (rate) of the nitrification and denitrification is proportional. Hence, if the growth rate increases, the rate of the process will also increase. This is where the DO concentration plays an important factor in determining the rate of the process.

For nitrification, from the graphs, we can see that the higher the DO concentration, the higher it will be for the growth rate of the nitrifier. But for denitrification, it is vice versa. In order to determine the value and to see the effect of DO concentration on both of the process, the mass transport equations and the nitrogen cycle equations is used along with the equations for the nitrification and denitrification and was simulated by using FEMLAB software.

Hence, for the nitrification process, the Double-Monod Equation is found to best fit for this kind of research in determining the rate of nitrification because the equation does somehow relates the DO concentration along with the ammonia concentration and the growth rate of the nitrifier. The equation is as follow:-

$$\mu = \mu_{max}[S_N / (K_{S,N} + S_N)]\ [DO / (KO_2, n + DO)] - K_d$$

Hence, the range of values for the DO concentration that affect the nitrification rate is from 0.5 mg/L to 4.0 mg/L.

While for denitrification, there are two models which were found to best fit the needs of this research in studying the effect of DO concentration on denitrification. For the first model (one-parameter model), the equation is as follow:-

$$\mathbf{r_D = r_{D,max}\,[1/(1+(DO/K_{O2}))]}$$

As for the second model (two-parameter model), the equation is as follow:-

$$\mathbf{r_D = r_{D,max}\,[1/(1+(DO/K_{O2}))][1-(DO/DO_{max})]}$$

Hence, the range of values that affect the denitrification rate is from 0.09 mg/L to 3.6 mg/L.

For future works, it is recommended to study the growth rate of the nitrifiers and the denitrifiers in pure cultures and mixed liquor in order to justify the true effect of DO concentration to these bacteria. Hence, the study of nitrification and denitrification process in a river can be compared with the one in an activated sludge treatment or in the wastewater treatment system.

CHAPTER 6

REFERENCE

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3. Linfield C. Brown and Thomas O.Barnwell, Jr. *The Enhanced Stream Water Quality Models QUAL2E and QUAL2E-UNCAS: Documentation and User Manual.* Environmental research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia:May 1987: *www.coe.uncc.edu/~jdbowen/6141/qual2e_info/manual.pdf*

4. B. Hailing-Sorensen, S.E. Jorgensen (1993), The Removal of Nitrogen Compounds from Wastewater, Elsevier.

5. Jeill Oh and Joann Silverstein, *Oxygen Inhibition of Activated Sludge Denitrification,* Dept. of Civil, Environmental and Architectural Engineering, University of Colorado, Boulder, CO, U.S.A.

APPENDIX

ACTIVITIES	WEEK NO / DATE													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Jan 24-30	Jan31-Feb6	Feb7-13	Feb14-20	Feb21-27	Feb28-Mac6	Mac7-13	Mac14-20	Mac21-27	Mac28-Apr3	Apr4-10	Apr11-17	Apr18-24	Apr25-May1
Topic Selection														
Preliminary Research Work • Study the nature of the process • Study the DO effect														
Literature review • Study of the constant k • Study the kinetic rate of all the models • Research of the first model • Research of other models														
Engineering Analysis • Analyzing of the k constant • Analyzing of the first order model and other models														
Data interpretations and comparisons • Modeling and simulation														
Final Report														

3.3.2 Ammonia Nitrogen

$$\frac{dN_1}{dt} = \beta_3 N_4 - \beta_1 N_1 + \sigma_3/d - F_1 \alpha_1 \mu A \qquad \text{III-17}$$

where

$$F_1 = P_N N_1/(P_N N_1 + (1 - P_N)N_3) \qquad \text{III-18}$$

N_1 = the concentration of ammonia nitrogen, mg-N/L

N_3 = the concentration of nitrate nitrogen, mg-N/L

N_4 = the concentration of organic nitrogen, mg-N/L

β_1 = rate constant for the biological oxidation of ammonia nitrogen, temperature dependent, day^{-1}

β_3 = organic nitrogen hydrolysis rate, day^{-1}

α_1 = fraction of algal biomass which is nitrogen, mg-N/mg-A

σ_3 = the benthos source rate for ammonia nitrogen, mg-N/ft^2-day

d = mean depth of flow, ft

F_1 = fraction of algal nitrogen uptake from ammonia pool

μ = the local specific growth rate of algae, day^{-1}

A = algal biomass concentration, mg-A/L

P_N = preference factor for ammonia nitrogen (0 to 1.0)

The QUAL2E model includes an algal preference factor for ammonia, P_N (Bowie et al., 1985; JRB Associates, 1983). The ammonia preference factor is equivalent to the fraction of algal nitrogen uptake from the ammonia pool when the concentrations of ammonia and nitrate nitrogen are equal.

3.3.3 Nitrite Nitrogen

$$\frac{dN_2}{dt} = \beta_1 N_1 - \beta_2 N_2 \qquad \text{III-19}$$

where

N_1 = the concentration of ammonia nitrogen, mg-N/L

N_2 = the concentration of nitrite nitrogen, mg-N/L

β_1 = rate constant for the oxidation of ammonia nitrogen, temperature dependent, day^{-1}

β_2 = rate constant for the oxidation of nitrite nitrogen, temperature dependent, day^{-1}

3.3.4 Nitrate Nitrogen

$$\frac{dN_3}{dt} = \beta_2 N_2 - (1 - F)\alpha_1 \mu A \qquad \text{III-20}$$

where

F = fraction of algal nitrogen taken from ammonia pool, as defined in Section 3.3.2

α_1 = fraction of algal biomass that is nitrogen, mg-N/mg-A

μ = local specific growth rate of algae, day^{-1}

3.3.5 Inhibition of Nitrification at Low Dissolved Oxygen

QUAL2E has the capability of inhibiting (retarding) the rate of nitrification at low values of dissolved oxygen. This inhibition effect has been reported by others (Department of Scientific and Industrial Research, 1964; Texas Water Development Board, 1984).

Nitrification rates are modified in QUAL2E by computing an inhibition correction factor (having a value between zero and one) and then applying this factor to the values of the nitrification rate coefficients, β_1, and β_2. The nitrification rate correction factor is computed according to a first order equation:

$$CORDO = 1.0 - \exp(-KNITRF * DO) \qquad \text{III-21}$$

where

CORDO = nitrification rate correction factor

exp = exponential function

KNITRF = first order nitrification inhibition coefficient, mg/L^{-1}

DO = dissolved oxygen concentration, mg/L

The correction factor is applied to the ammonia and nitrite oxidation rates by:

Ammonia: $(\beta_1)_{inhib.} = CORDO * (\beta_1)_{input}$ III-22

Nitrite: $(\beta_2)_{inhib.} = CORDO * (\beta_2)_{input}$ III-23

A value of 0.6 for KNITRF closely matches the inhibition formulation in QUAL-TX, the Texas Water Development Board version of QUAL-II, whereas, a value of 0.7 closely simulates the data for the Thames Estuary (DSIR, 1964).

3.4 PHOSPHORUS CYCLE

The phosphorus cycle operates like the nitrogen cycle in many respects. Organic forms of phosphorus are generated by the death of algae, which then convert to the dissolved inorganic state, where it is available to algae for primary production. Phosphorus discharged from sewage treatment plants is generally in the dissolved inorganic form and is readily taken up by algae (Bowie et al., 1985). QUAL2E revises the SEMCOG version of QUAL-II, which included only dissolved phosphorus, to simulate the interactions between organic and dissolved phosphorus. Below are the differential equations governing transformations of phosphorus from one form to another.

3.4.1 Organic Phosphorus

$$\frac{dP_1}{dt} = \alpha_2 \rho A - \beta_4 P_1 - \sigma_5 P_1 \qquad \text{III-24}$$

where

P_1 = the concentration of organic phosphorus, mg-P/L

α_2 = phosphorus content of algae, mg P/mg-A

ρ = algal respiration rate, day^{-1}

A = algal biomass concentration, mg-A/L

β_4 = organic phosphorus decay rate, temperature dependent, day^{-1}

σ_5 = organic phorphorus settling rate, temperature dependent, day^{-1}