Modelling chemical and biological clogging of permeable reactive barrier when treating acidic groundwater

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1 Abstract

Acid sulphate soils are commonly occurring in Australia and are dormant unless exposed to oxygen.. Pyrite is abundant in these soils which oxidises to form sulphuric acid. This poses environmental issues and threatens surrounding infrastructure [1, 8]. A solution to this oxidisation are permeable reactive barriers (PRB). These are a passive method to neutralise acid groundwater. However, PRBs very easily become clogged due to biological and chemical components, which greatly reduces its efficacy.

Mathematically, the clogging of the PRB can be modelled using a partial differential equation for hydraulic head. As a part of this PDE, an equation for the reduction in porosity due to bacteria and chemical clogging is required. The reduction in porosity due to biological clogging is especially important to this project. It requires an equation for the growth of bacteria and the currently used equation is the Logistic equation [4,7]. It was the goal of this report to compare the Gompertz equation and investigate if it could be used to model the hydraulic head.

Overall, the Gompertz equation holds many similar characteristics to the Logistic equation. A plot comparing the two models was created and they are very similar in shape. Also, a part of the solution to the PDE of hydraulic head could be found using the Gompertz equation and compared to the Logistic equation. They were very similar which shows promise. But a complete solution to hydraulic head using the Gompertz equation could not be found, as it can for the Logistic equation. This could be due to missing data and therefore, parameter values could not be found for the Gompertz equation. So a complete comparison and evaluation on the Gompertz equation could not be made.

2 Introduction

Acid sulphate soils (ASS) are naturally occurring sediments commonly found in Australia, occupying over 200,000 km^2 of land. Acidic groundwater resulting from the oxidation of pyrite (FeS_2) in ASS is a major environmental problem in coastal regions of Australia and many countries around the world [1]. When exposed to air during groundwater lowering due to flood mitigation drains or upon excavation (e.g. coal mining), FeS_2 can rapidly oxidise to form sulphuric acid, which pose high risk to surrounding infrastructure [4]. AI solubility is also increased in the soil, risking the surrounding aquatic flora and fauna.

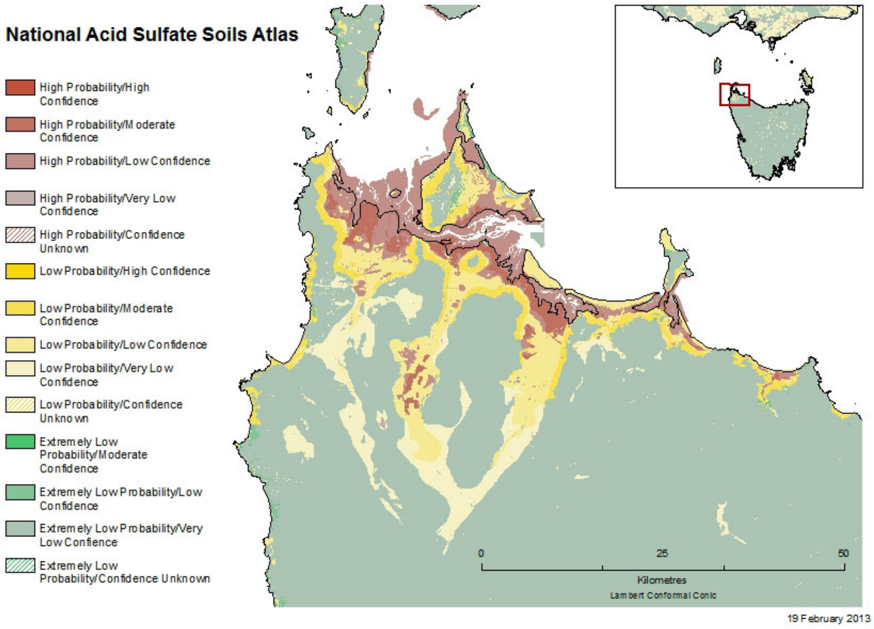

Figure 1: Location of ASS soils in Tasmania north western Tasmania [9]

Figure 1 shows the presence of ASS in northwestern Tasmania. It can be seen it is concentrated along the coastline and becomes less common inland.

Permeable reactive barriers (PRBs) are a passive method used to neutralize groundwater acidity induced by pyrite oxidation in ASS terrain [3,4]. PRBs are alkaline materials (e.g. crushed recycled concrete, ash, blast-furnace slag and calcitic limestone $CaCO_3$), which are used as an underground filter to eradicate the contaminants through chemical and/or biological processes [5,6]. However, the biogeochemical clogging of PRBs reduces their lifespan and efficacy. The modelling of the biogeochemical clogging is important as it can target the area in the PRB that needs replacement. This could save money as only the clogged areas of the PRB will be replaced. It could also increase the effectiveness as we will better understand how clogging occurs and at what rate.

To understand this clogging mathematically, the Logistic equation forms a basis for developing the equation. It is the goal of this report to investigate if the Gompertz equation could be used to model the phenomena.

2.1 On Site and Laboratory Experiments

Experiments on site in Shoalhaven and laboratory experiments have been conducted to get data on the clogging of the PRBs. The Shoalhaven site is a flood plain that had a PRB made of concrete aggregate installed in 2006. To observe the efficacy of this PRB, a column experiment was conducted at the Shoalhaven site [4, 7].

Furthermore, a laboratory experiment to simulate the columns onsite at Shoalhaven was conducted to simulate how bacteria and chemical precipitates travel through the real life PRB [7].

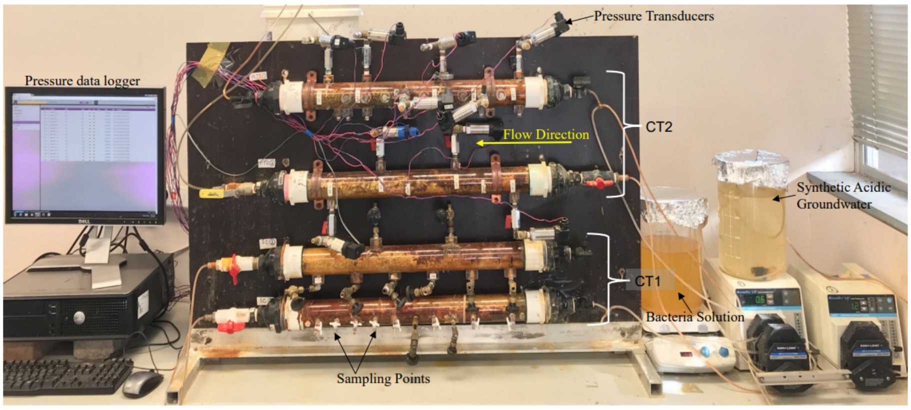

Figure 2: Setup of Laboratory Experiment [7]

From figure 2, CT1 examines the effects of acid neutralising due to chemical precipitates only and CT2 examines the clogging effects from both the chemical and biological components [7]. Zones were also set up based off influent and effluent flow of water, and chemicals and biological components were measured at each point. The zones are labelled with SP1-SP6 and are shown in figure 3.

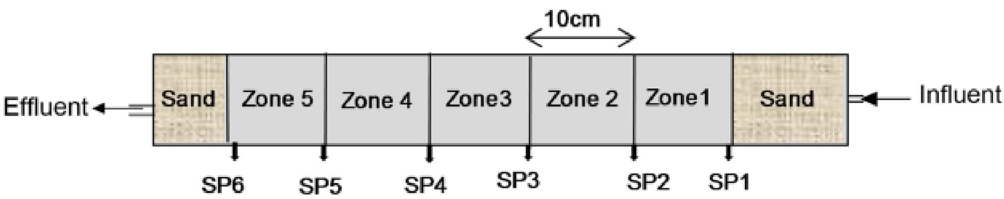

Figure 3: Influent and Effluent Flow [7]

3 Background

3.1 Biological modelling:

Using mathematical modelling to understand bacteria growth and population in general is a concept that has been researched since the late 18th century.

To begin modelling the bacterial growth through the PRB, it is first important to gain an idea of the stages of bacterial growth. Typically a growth curve is used to illustrate:

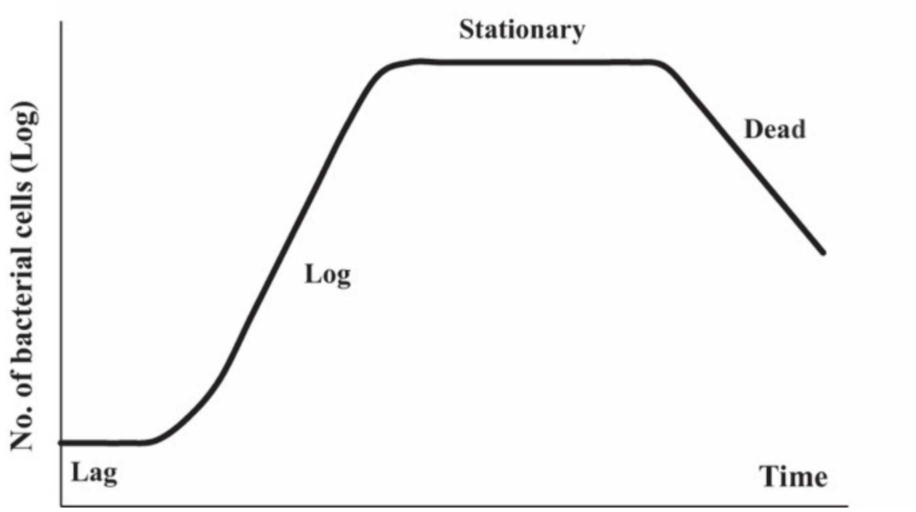

Figure 4: Graph of Typical Bacteria Growth [12]

Note that a log scale is used to properly show the curve. The first phase is the lag phase which occurs after the bacteria is first introduced. The log phase occurs when the bacteria begin to grow at an exponential rate. The stationary phase occurs when the bacteria has run out of nutrients and can no longer grow. This is followed by the death phase when the bacteria are no longer viable.

3.2 Clogging of the PRB

Clogging in the PRB occurs due to the chemical precipitate buildup, from the oxidation of Pyrite. Further, the bacteria *Acidithiobacillus ferrooxidans* accelerates the oxidisation of Pyrite. This is a common bacteria found in acid sulphate soils and pyritic soils and therefore, it can enter the PRB and cause the chemical precipitates to clog the medium. This is why it is important to also consider the biological effects when considering this problem.

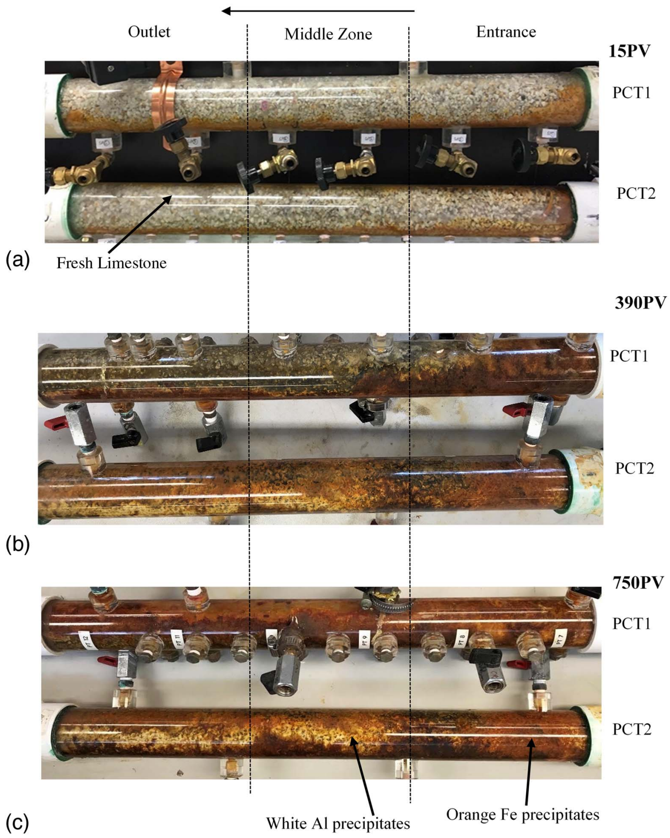

Figure 5: Clogging of the PRB over time [7]

Figure 5 shows the clogging of the PRB in the laboratory experiment. The images are ordered according to PV (pore volume) which acts as dimensionless time. Therefore, image c) shows the buildup over time. The figure shows what is the Aluminium (white) precipitate and the Iron (orange) precipitate.

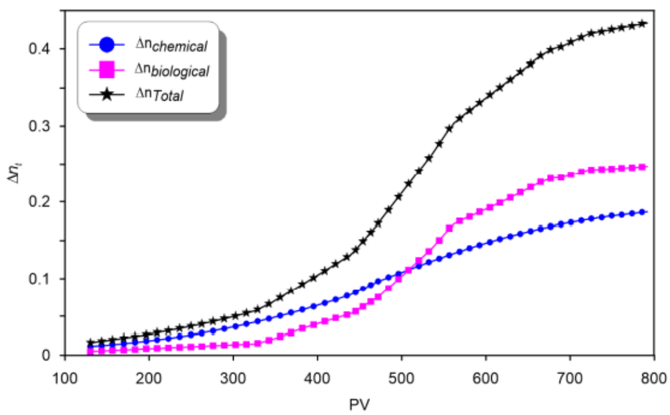

Figure 6: Biological, Chemical and Total Clogging [7]

Figure 6 shows the clogging from biological and chemical effects. It can be seen the biological effects follow a sigmoid shape, as expected, and the chemical effects are approximately linear. As time goes on and we would expect to see clogging occur, it appears the biological effects have a higher impact on the clogging of the medium. Therefore, the scope of this report was decided to focus on the biological modelling.

3.3 Equations for Reduction in Porosity

To understand how chemical and biological components affect clogging, equations to model the reduction in porosity are used. Clogged materials are known to affect the porosity of a material, as the porosity is the measure of void space in a material. The equations are:

- Reduction of porosity due to biological growth:

$$n_{t_b} = \frac{X_S}{\rho_c}, \tag{1}$$

  ρ_c is solid phase biomass density, X_s is the solid phase concentration of bacterial cells.

- Reduction of porosity due to chemical precipitation:

$$n_{t_c} = \sum_{k=1}^{N_m} M_k R_k t, \tag{2}$$

  where M_k is molar volume of a mineral, R_k is reaction rate for the mineral and N_m is number of minerals.

- Total reduction in porosity is:

$$\triangle n_t = n_{t_b} + n_{t_c}, \tag{3}$$

In equation (1), ρ is a constant and X_s can be expressed using bacteria growth equations. Such models and equations will be explored in Section 3.

4 Mathematical models

4.1 Logistic Equation Derivation

The most commonly used equation for X_S in equation 1 is the Logistic equation using Monod Kinetics. Jacques Monod developed an equation to model the growth of bacteria and is now known as Monod kinetics:

$$\mu = \frac{S\mu_{max}}{K_S + S}, \tag{4}$$

We know the net growth is equal:

$$\mu_{net} = \mu_g - k, \tag{5}$$

where μ_{net} is net growth, μ_g is total growth and k is the death of the bacteria. In this case, we ignore k. Therefore, $\mu_{net} = \mu_g$.

Further, using Monod kinetics:

$$\begin{aligned} \mu_{net} &= \frac{S\mu_{max}}{K_S + S} \\ \mu_{net}X &= \frac{S\mu_{max}}{K_S + S}X \\ \mu_g X &= \frac{S\mu_{max}}{K_S + S}X \end{aligned}$$

$\mu_{net}X$ is the cell increase rate differential equation, therefore:

$$\begin{aligned} \frac{dX}{dt} &= \mu_{net}X \\ \frac{dX}{dt} &= \mu_g X \\ \frac{1}{X}\frac{dX}{dt} &= \mu_g \end{aligned}$$

From here, a logistic approach can be used to calculate an expression for the population of bacteria (X). Logistic equations find an expression for growth in terms of unused carrying capacity. In this case:

$$\begin{aligned} \mu_g &= k\left(1 - \frac{X}{X_\infty}\right) \\ \frac{1}{X}\frac{dX}{dt} &= k\left(1 - \frac{X}{X_\infty}\right) \end{aligned}$$

Where k is the carrying capacity and X_∞ is the maximum population.

Solving this differential equation leads to a solution for X:

$$\begin{aligned}
\frac{1}{X}\frac{dX}{dt} &= k\left(1-\frac{X}{X_\infty}\right)\\
\frac{1}{X}\frac{dX}{dt} &= k\left(\frac{X_\infty - X}{X_\infty}\right)\\
\frac{1}{X(X_\infty - X)}\frac{dX}{dt} &= \frac{k}{X_\infty}\\
\left(\frac{1}{XX_\infty}+\frac{1}{X_\infty(X_\infty - X)}\right)\frac{dX}{dt} &= \frac{k}{X_\infty}\\
\left(\frac{1}{X}+\frac{1}{(X_\infty - X)}\right)dX &= kdt\\
\ln(X)-\ln(X_\infty - X) &= kt+c\\
\ln\left(\frac{X}{X_\infty - X}\right) &= kt+c
\end{aligned}$$

Using initial conditions, when t = 0, X = X_0:

$$\ln\left(\frac{X_0}{X_\infty - X_0}\right) = c$$

Using this value for c and rearranging to find an expression for X:

$$\begin{aligned}
\ln\left(\frac{X}{X_\infty - X}\right) &= kt + \ln\left(\frac{X_0}{X_\infty - X_0}\right)\\
\frac{X}{X_\infty - X} &= e^{kt}\frac{X_0}{X_\infty - X_0}\\
X &= \frac{X_0e^{kt}}{X_\infty - X_0}(X_\infty - X)\\
X + \frac{X_0e^{kt}X}{X_\infty - X_0} &= \frac{X_0e^{kt}X_\infty}{X_\infty - X_0}\\
X\left(1+\frac{X_0e^{kt}}{X_\infty - X_0}\right) &= \frac{X_0e^{kt}X_\infty}{X_\infty - X_0}\\
X\left(\frac{X_\infty - X_0 + X_0e^{kt}}{X_\infty - X_0}\right) &= \frac{X_0e^{kt}X_\infty}{X_\infty - X_0}
\end{aligned}$$

$$X = \frac{X_0 e^{kt} X_\infty}{X_\infty - X_0 + X_0 e^{kt}}$$
$$X = \frac{X_0 e^{kt}}{1 - \frac{X_0}{X_\infty} + \frac{X_0 e^{kt}}{X_\infty}}$$

$$X_s = \frac{X_0 e^{kt}}{1 - \frac{X_0}{X_\infty}(1 - e^{kt})}, \tag{6}$$

This is the equation for cell growth using the logistic equation.

4.2 Gompertz Equation

The Gompertz equation is a popular model to describe population growth. It is sigmoid, similar to the logistic equation, and describes growth being slowest at the start and end of a time period. However, it differs from the logistic model as it does not approach asymptotes symmetrically. The upper limit asymptote is approached more gradually than the lower limit.

The Gompertz equation, in its original form is:

$$f(t) = ae^{-be^{-ct}}, \tag{7}$$

Where, a is the upper asymptope, b translates the graph along the x axis and c is the growth rate. Results from using this model are included in the results section.

Due to the popularity of the Gompertz model, there have been numerous reparametrizations of the model. Larry Norton used a reparaemtrized Gompertz model to model the growth of cancer cells and has been found to model populations [11].

Final parameterised version is:

$$f(t) = X_0 e^{ln\left(\frac{X_\infty}{X_0}\right)(1-e^{-k_c t})}, \tag{8}$$

Values for X_0, X_∞ and k_c are provided in past study. To compare the suitability of this equation, a plot with the Logistic and Gompertz Equation across time was created.

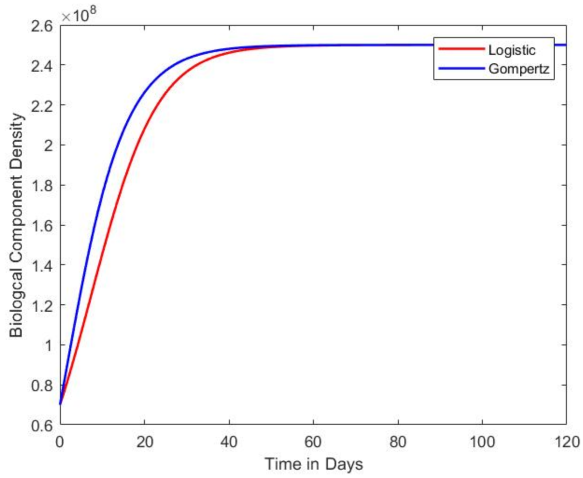

Figure 7: Comparison of the Logistic Equation and the Gompertz Equation

Figure 7 shows this comparison and it can be seen that they models have a similar shape. The Gompertz equation accelerates quicker but they both appear to reach the asymptote at similar times.

4.3 PDE for Transient Flow of Groundwater Through a Porous Media

To model the clogging of the PRB, a partial differential equation (PDE) modelling the flow of groundwater through a porous media can be used. The three dimensional expression of this is:

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right)+W=S_s\frac{\partial h}{\partial t}, \tag{9}$$

However, this is a very difficult PDE to solve. For this project, only the flow in one dimension will be considered:

$$\frac{\partial^2 h}{\partial x^2}=\frac{S_s}{K}\frac{\partial h}{\partial t}, \tag{10}$$

where h is hydraulic head, x is horizontal distance from the inlet, S_s is the storage of the material and t is time. K is an expression for hydraulic conductivity. Hydraulic conductivity is a measure of how easily water passes through the pores of a surface. What has been found to work, through past research [4,7], the normalized Kozeny-Carman equation has been used:

$$K=K_0\left[\frac{n_0-\triangle n_t}{n_0}\right]^3/\left[\frac{1-n_0+\triangle n_t}{1-n_0}\right]^2, \tag{11}$$

where, n_0 is initial porosity, $\triangle n_t$ is total reduction in porosity and K_0 is the initial hydraulic conductivity.

Using the chosen expression for hydraulic conductivity, the PDE for hydraulic head (equation (10)) can be written as:

$$\frac{\partial^2 h}{\partial x^2} = g(t)\frac{\partial h}{\partial t}, \tag{12}$$

where

$$g(t) = B\frac{(1-n_0+f(t))^2}{(n_0-f(t))^3}, \quad f(t) = \triangle n_t = n_{t_b} + n_{t_c}, \quad B = \frac{S_s n_0^3}{K_0(1-n_0)^2}.$$

This equation can be solved using separation of variables and the equation can be assumed to have the form of:

$$h(x,t) = [C_1 \sin(\lambda x) + C_2 \cos(\lambda x)] \exp\left(\int_0^t \frac{-\lambda^2}{g(\tau)} d\tau\right) \tag{13}$$

Using the Logistic Equation, an analytical solution could be found and plot for the hydraulic head created [7]:

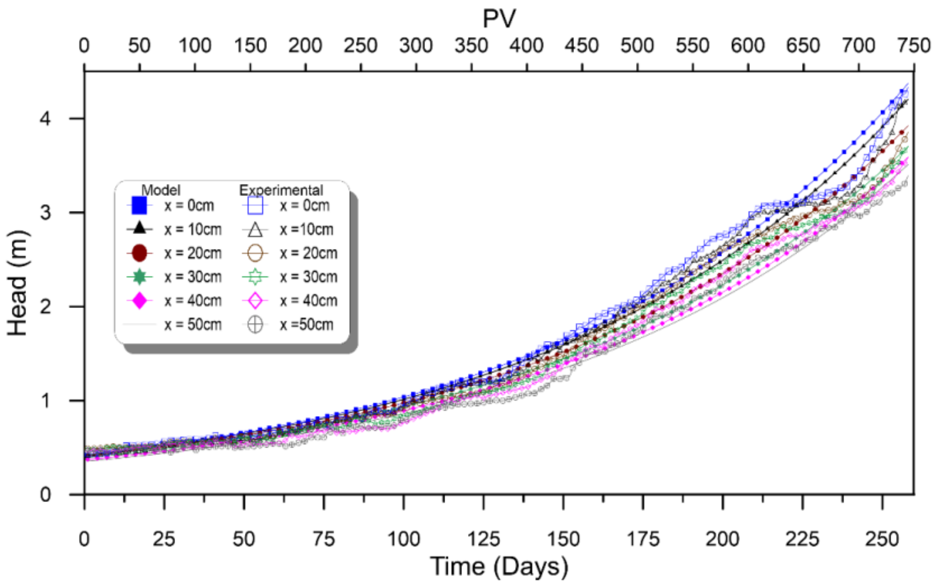

Figure 8: Plot of Solution of Hydraulic Head at Different Distances from Inlet [7]

It can be seen the model follows the experimental data closely until time reaches approximately 200 days. Then the experimental data begins to plateau and the model continues to increase. This is less noticeable for the points that are further from the inlet as they do not have as much bacteria and chemical precipitate buildup.

5 Results

It will be the goal of this report to test how the solution to the hydraulic head changes if the Gompertz equation is used instead of the Logistic equation. It is the goal to demonstrate the Gompertz equation is also a good fit. Using equation (12), $f(t)$ requires the expression for reduction in porosity from the biological component. Therefore, it will change based of which equation for biological growth is used. $f(t)$ is used in $g(t)$. Using equation (13), $g(t)$ is used in the intgeral. Therefore, this is the part of the model that will change depending on if Gompertz or Logistic is used. However, it should be noted the values for S_s, n_0, K_0 and λ could not be determined for this project so arbitrary values were chosen. This will not affect the ability to compare the integrals as the same values will be chosen for both.

Using the Logistic equation:

- $n_{t_b} = \frac{X_0 e^{kt}}{1-\frac{X_0}{X_\infty}(1-e^{kt})}$ (from equation (6))

- Therefore:

$$g(t) = B\frac{(1-n_0+f(t))^2}{(n_0-f(t))^3}, \quad f(t) = \triangle n_t = \frac{X_0 e^{kt}}{\rho_c(1-\frac{X_0}{X_\infty}(1-e^{kt}))} + n_{t_c}, \quad B = \frac{S_s n_0^3}{K_0(1-n_0)^2}$$

Using the Gompertz equation:

- For the Gompertz Equation, n_{t_b} will equal:
  $n_{t_b} = \frac{X_0 e^{ln\left(\frac{X_\infty}{X_0}\right)(1-e^{-k_c t})}}{\rho_c}$

- Therefore:

$$g(t) = B\frac{(1-n_0+f(t))^2}{(n_0-f(t))^3}, \quad f(t) = \triangle n_t = \frac{X_0 e^{ln\left(\frac{X_\infty}{X_0}\right)(1-e^{-k_c t})}}{\rho_c} + n_{t_c}, \quad B = \frac{S_s n_0^3}{K_0(1-n_0)^2}$$

The integral to be solved is:
$\int_0^t \frac{-\lambda^2}{g(\tau)} d\tau$
where $g(\tau)$ changes depending upon the model used.

MATLAB was used to analytically solve the integrals and plot to compare. The plot comparing the integrals is shown in figure 9:

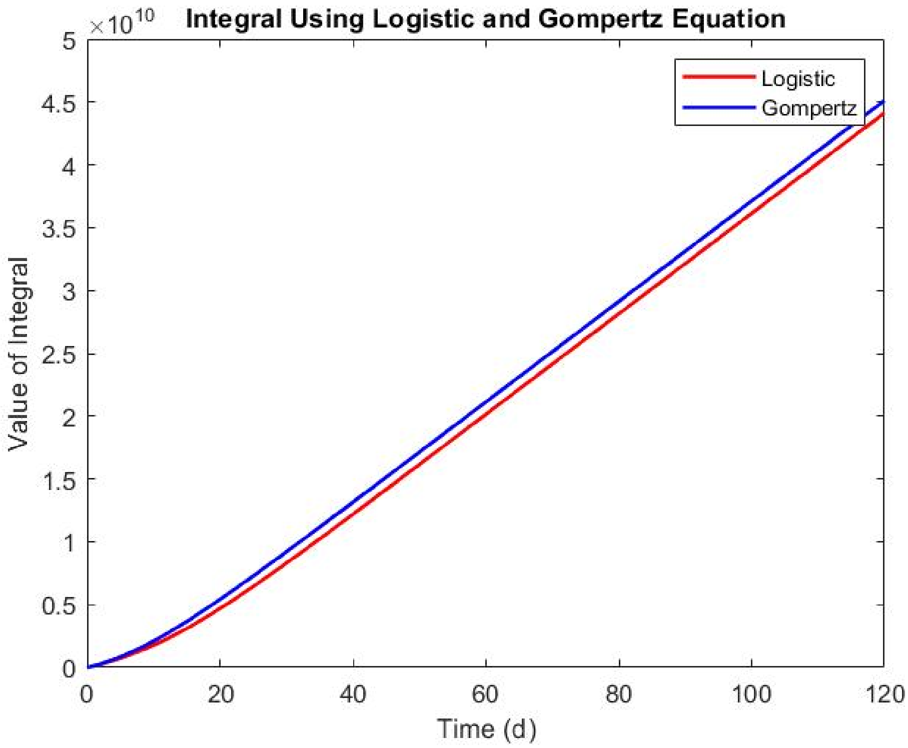

Figure 9: Comparison of Integral Using Gompertz and Logisitic Equation

They appear to have a very similar shape, with the Gompertz model being slightly higher valued than the Logistic equation. This is promising for the evidence that the Gompertz model will be a good fit to model the hydraulic head.

From figure 9, the scale of the integral is very large (10^{10}). To be used the solution for hydraulic head (equation 13), the exponential of this integral must be taken. This proves problematic on such a large scale and is computationally infinite. Therefore, for this project a solution for hydraulic head using the Gompertz equation could not be obtained. However, the integrals that needed to be compared appear to be similar and this is a promising start. This means, the Gompertz equation could be a viable fit to model the hydraulic head but the scale of the integral needs to be much smaller to test it.

6 Conclusion and Future Action

The aim of this report was to find further understand the biological and chemical clogging of PRB and to find a mathematical equation for bacteria growth that could model this clogging. Overall, the Gompertz equation shows the possibility that it will model the phenomena well because it displays similar characteristics to the Logistic equation, which has been shown to work well. However, a final evaluation on how it works in the hydraulic head equation is required and was not included in this report.

Some future action for this project is to find the true values of the unknown parameters and create a plot of the hydraulic head using Gompertz. This would be useful as the true reliability of the Gompertz equation could be evaluated. I could also investigate simpler population models that could mean the integral can be analytically computed or investigate other parametrizations of the Gompertz model.

Also, some research can be done to find a way to model the hydraulic head as it begins to plateau. This plateauing can be seen in figure 8 and the equation for hydraulic head no longer fits as well. Also, if the experimental data could be acquired, some statistical techniques could be used to analyse the data and create a model.

7 References

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