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VIETNAMESE GERMAN UNIVERSITY
Water Technology reuse and management

TOPIC:

Effect of organic solute adsorption on biological nitrogen removal in biologically active granular activated carbon filtration for drinking water treatment – A modeling study.



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Abstract

Pilot-scale investigations have a hard time quantifying the difference between adsorption and biodegradation of organics, as well as the potential impact of adsorption of easily degradable organics on nitrogen removal. Modeling provides an organized and more precise analysis of potential outcomes in a bGAC setup. The biodegradation of organics, nitrification, and denitrification processes in water treatment can be modeled using activated sludge models (ASM).

Simultaneous biodegradation and adsorption in granular activated carbon (GAC) columns is a complicated treatment process, consisting of two potential mechanisms for contaminant removal, two distinct phases GAC and liquid. A detailed mathematical model may contribute to a better understanding of the process, assist in planning pilot studies, and serve as a useful tool in design and operation. In this study, an enhanced Activated Sludge Model No. 1 in which nitrification and denitrification are modelled as two-step processes combining with the adsorption kinetic numerical model that differentiates between the adsorption and biodegradation capability of COD was developed and validated. The modeling software AQUASIM is used to differentiate the adsorption and biodegradation quantities of a biological activated carbon (BAC) fixed bed column.

The mechanisms considered in this model are adsorption, biodegradation, diffusion. Simulations were performed to evaluate the effects of the major parameters on the adsorption and biodegradation performances for the removal of dissolved organic carbon. This research developed a numerical model to simulate both adsorption and biodegradation quantities of a BGAC column under a steady-state condition, so as to predict the effluent concentration, biomass profiles and the residual capacity of adsorption. There will be an examination of how well the ASM1 kinetic parameters apply to real-world scenarios and how sensitively the model parameters characterizing the contributions of adsorption and biodegradation can be predicted. This work in modeling integrated biodegradation/adsorption processes aimed to theorize the effects of organic solute adsorption on biological nitrogen elimination.

The results of the simulation show that the processes of biodegradation and adsorption occur simultaneously during the initial time period. Later on, adsorption dominates biodegradation until equilibrium is reached. Moreover, the subsequent active heterotroph biomass concentration is so low that heterotrophic ammonification does not take place. An increased NO_3 content in the effluent also indicated that NO_3 was being generated by autotrophic aerobic, but that no heterotrophic anaerobic consumption was occurring. This means that while nitrification can be observed, denitrification cannot. Because of this, the adsorption-biodegradation model is a useful tool for simulating the adsorption-biodegradation behaviors of organic compounds that occur in water as it passes through a GAC filter bed.

1 Chapter 1 - Introduction to the topic

1.1 Overall introduction

Increasing water use and waste production are two consequences of a growing population and rising levels of agricultural and industrial production. An unavoidable but challenging requirement for water supply systems is the development of clean water supply systems and the improvement of water quality to deliver safe, clean water to users. Consequences of a decline in raw water quality include negative effects on human health, significant financial losses for businesses, and a dampening of economic growth. Saigon River water quality is presently declining as a result of rising levels of pollution, especially organic pollution, ammonia, manganese, iron, and so on. It is essential to investigate raw water pretreatment technologies and to support the existing treatment system in addition to replacing and improving the entire system.

There has been a rise in the use of biological reactors for treating wastewater and drinking water. These reactors use granular particles coated with a biofilm of microorganisms to process the water or wastewater (Forster et al., 1986; Denac and Dunn, 1988; Livingstone and Chase, 1989; Fan et al., 1990; Mendez and Lema, 1992). One of the earliest systems for removing organic contaminants from wastewaters, fixed-bed reactors are still widely employed because to their simple mechanical construction, low energy requirements, and low operating costs (Atiqullah et al., 1990; Mendez and Lema, 1992). The microorganisms immobilized in a thin film may exhibit adsorptive properties of the solid support packing material. According to studies by Andrews and Tien (1981) and Tien and Wang (1982), a potential approach for eliminating soluble organic contaminants from wastewaters is the combination of biological degradation with adsorption in a single unit. The modeling of bioreactors requires an understanding of their hydrodynamics as well as the overall substrate consumption rate.

PAC and GAC have been widely used in water treatment plants to remove organic compounds that cause an unpleasant taste and odor (AWWA Committee Report, 1977). When PAC is applied in such a way that it flows with the water through the treatment units, it tends to equilibrate with the concentration of organics in the water treatment plant effluent. GAC at the adsorber inlet, on the other hand, tends to equilibrate with the concentration in the water before it comes into contact with the carbon, whereas GAC at the adsorber outlet tends to equilibrate with the organics in the effluent. As a result, GAC tends to equilibrate at higher concentrations than PAC. More PAC than GAC is often needed to achieve the desired removal because a substantially lower loading, or mass of organic material adsorbed per mass of carbon, may be achieved at low equilibrium concentration versus high equilibrium concentration. In general, the same types of compounds should adsorb on PAC as they do on GAC. When PAC is applied in such a way that it comes into contact with water for a short period of time, it is very unlikely to support biological activity. In water treatment, removing adsorbable, biodegradable organics via microbial activity rather than adsorption improves the GAC bed's ability to remove adsorbable, nonbiodegradable organics.

The research was directed toward additional development and refinement of mathematical models of simultaneous adsorption and biodegradation in granular activated carbon (GAC) columns used in the treatment of low concentrations of organic chemicals.

This research developed a numerical model to simulate both adsorption and biodegradation quantities of a BAC column under a steady-state condition in fixed bed reactors, so as to predict the effluent concentration, biomass profiles and the residual capacity of adsorption. The basic assumptions of this model are that (1) the granules used in BAC are spherical in shape, and the biofilm is homogeneous and the density of the biofilm is constant; (2) desorption after the saturation of the GAC is taken into consideration; (3) there is no competition or inhibition between two substrates.

The model consists of three sets of biofilm reactor compartments that are linked to three fully mixed reactors. The input loadings for the first of the biofilm reactor series' three compartments must be specified. Assumptions were used as input for the initial biofilm reactor compartments in order to reduce the complexity of the model. Presumably, the influent

contains 80% of the rapidly biodegradable substrate and 20% of the slowly biodegradable substrate. The purpose of this study was to develop a numerical model to predict the effluent concentration, biomass profiles, and the residual capacity of adsorption by simulating the adsorption and biodegradation quantities of a BGAC column under a steady-state condition. The sensitivity of the model parameters characterizing the contributions of adsorption and biodegradation to prediction will be investigated, as will the applicability of the ASM₁ kinetic parameters to real-world scenarios.

1.2 Overview of Mass transfer and reaction terms

1.2.1 Mass transfer in biological processes

Transformations (e.g., substrate use) and transport are the two universal types of processes happening in biofilm systems (e.g., diffusion). These two kinds of processes are interdependent: Utilization of substrates within the biofilm generates gradients that promote diffusive mass transport, while diffusive mass transport provides substrates that can be utilized. Substrate gradients are the result of substrate use and diffusion. Due to the exposure of microorganisms to varying substrate concentrations, the rates of microbial development fluctuate depending on the location within the biofilm. In addition, gradients can establish distinct microbial niches in various biofilm regions. For instance, oxygen may not reach the substratum, allowing stable anaerobic microenvironments to exist in the deep parts of a biofilm.

Transfer between the biofilm and the bulk liquid is an additional important class of processes. The transfer processes consist of the exchange of dissolved chemicals across the mass-transfer boundary layer, the attachment of planktonic cells from the bulk liquid to the biofilm, and the detachment of particulate components from the biofilm to the bulk liquid. They are the mathematical boundary conditions for the mass-balance equations in each compartment. Multiple transformation, transport, and transfer processes coexist for each component. The component's concentration relies on how all operations "add up." The mass balance, which is the core of any mathematical biofilm model, is used to total up the effects of all processes.

For any given time and location within the compartment, a component's total mass is always referred to as "accumulation" in a general mass balance. In order to begin mathematical modeling, it is necessary to create mathematical expressions for all terms within brackets. The typical procedures and their rate expressions are discussed below.

$$\begin{aligned} &\{Net\ rate\ of\ accumulation\} \\ &= \{Sum\ of\ all\ rates\ of\ transfer\ and\ transport\} \\ &+ \{Sum\ of\ all\ rates\ of\ transformation\} \end{aligned}$$

a. Transformation processes

In most cases, transformation processes take the form of biochemical reactions that result in the production or consumption of one or more components. Abiotic chemical reactions, such as the adsorption of a solute onto the biomass or the precipitation of a mineral solid, can also be a part of the transformation process. When modeling, the processes of transformation are typically described mathematically using rate expressions, which express the change in amount over the period of time. Rittmann and McCarty (2001) and Grady et al. provide more in-depth descriptions of rate expressions that are utilized in the general modeling of biological processes (1999). The Monod equation for a single limiting substrate is a model that is utilized rather frequently for the purpose of understanding the process of microbial biomass synthesis.

$$\mu = \mu_{max} \frac{S}{K_S + S} \quad (\text{eq. 1.1})$$

where μ is the specific growth rate (T⁻¹), μ_{max} the maximum specific growth rate (T⁻¹), S is the concentration of the rate-limiting substrate (M_SL⁻³), and K_S is the concentration (M_SL⁻³) giving one-half the maximum rate

The specific growth rate can be described with a multiplicative-Monod expression (Bae and Rittmann 1996).

$$\mu = \mu_{max} \frac{S_1}{K_{S1}+S_1} \frac{S_2}{K_{S2}+S_2} \quad (\text{eq. 1.2})$$

It is possible to represent the effect of an inhibitory component by adding a specific term that describes the influence of the concentration of the inhibitor on the specific growth rate.

$$\mu = \mu_{max} \frac{S}{K_S+S} \frac{K_I}{K_I+I} \quad (\text{eq. 1.3})$$

where I is the concentration of the inhibitor ($M_I L^{-3}$) and K_I is the concentration ($M_I L^{-3}$) of the inhibitor giving 50% inhibition of the rate.

b. Transport processes

Biofilm models frequently consider advection, molecular diffusion, and turbulent dispersion as transport processes.

For dissolved substances: Molecular diffusion is typically the major transport method for dissolved components inside the biofilm compartment. The majority of the time, the diffusion coefficient of a component in the liquid phase of a biofilm is lower than in the bulk liquid compartment. Outside of the biofilm, the primary transport processes are advection and turbulent dispersion. It is reasonable to define advection as the product of fluid velocity and component concentration. Near the surface of a biofilm, spatial gradients of component concentration are typically not ignorable. They can also be theoretically estimated by the continuity and momentum equations for the fluid, however they are typically approximated with empirical mass-transfer equations for the interface between the biofilm and the bulk liquid.

For particulate components: Due to bacterial growth or decay and extracellular polymeric substances (EPS) synthesis, the biofilm's solid matrix expands or contracts, resulting in the transport of particle components. Transport of the biofilm's particulate components is facilitated by the expansion or contraction of the biofilm's solid matrix as a result of bacterial growth or decay and EPS generation. These components' motion can be depicted in a variety of ways. Continuum-based biofilm models involve either an advective flux (e.g., Rittmann and Manem 1992; Dockery and Klapper 2001; Eberl et al. 2001), a diffusive flux, or both types of fluxes (Wanner and Reichert 1996).

c. Transfer processes

The transfer of mass of dissolved or particulate components between two compartments is referred to as transfer. At the interface between the compartments, a continuity requirement must be met for the component concentration C and the particular mass flux j . Mass transfer between the bulk liquid and the biofilm is a particularly significant process, as the bulk liquid is the source of substrates in the majority of biofilm systems. Transporting the substrate to the biofilm is necessary for its consumption, and substrate utilization is essential for the biofilm's formation and maintenance. Typically, a concentration gradient across the mass-transfer boundary layer drives transport (MTBL).

The film theory established by Nernst, the simplest and most widely used boundary-layer model, characterizes mass transfer over the MTBL as molecular diffusion across an effective diffusion layer of thickness L_L . The mass transfer coefficient is then given by $k_C = D/L_L$ (D : Diffusion coefficient of substrate). For slow flow velocities or low turbulence, L_L is large (high mass-transfer resistance), causing k_C to be small; for fast flow velocities or high turbulence, L_L is small (low resistance), causing k_C to be large. If the mass-transfer resistance in the boundary layer is extremely low, the boundary layer can be ignored and the component concentration in the bulk liquid C_B will be equal to that in the biofilm surface, C_{LF} . Typically, the mass transfer coefficient k_C and L_L are computed using experimental correlations (e.g., Perry and Green 1999).

Detachment and attachment represent the exchange of particle components between the biofilm solid matrix and the bulk liquid. Detachment is the movement of cells and other particle components from the solid matrix of the biofilm into the bulk liquid. Sloughing is the process that occurs when huge chunks of biomass are abruptly separated from the solid matrix.

Erosion refers to detachment involving only single cells or very tiny particles. Attachment is the deposition and adherence of suspended cells and other particles to the biofilm solid matrix.

Attachment is not expressly incorporated in many models. In other instances, this simplicity is appropriate because detachment is the predominant process. When this is not the case, however, the simulated detachment process must represent the net transfer of particle mass from the biofilm to the bulk liquid, encompassing implicitly both attachment and detachment processes.

1.2.2 Mass transfer in adsorption processes

According to the general mass transfer equation

$$\begin{aligned} & \text{Mass transfer rate} \\ & = \text{mass transfer coefficient} \times \text{area available for mass transfer} \times \text{driving force} \end{aligned}$$

The exterior surface area influences the rate of mass transfer during adsorption significantly. In the case of porous adsorbents, external and internal mass transfer must be distinguished.

a. External surface area

External mass transfer refers to the transfer of mass through the hydrodynamic boundary layer surrounding the adsorbent particle. The area available for mass transfer in the mass transfer equation can be approximated by the external adsorbent surface area when the boundary layer is very thin.

Internal mass transfer is facilitated by intraparticle diffusion mechanisms. If the internal mass transfer is characterized approximatively by a mass transfer equation according to the above equation (linear driving force method), the exterior adsorbent surface area also provides the area available for mass transfer.

In mass transfer equations, the available surface area for mass transfer is frequently expressed as a volume-related surface area – for example, a surface area related to the adsorber volume, V_R ,

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$$\alpha_{VR} = \frac{A_S}{V_R} = \frac{3(1-\varepsilon_B)}{r_P} \quad (\text{eq. 1.4})$$

If the particles can be assumed to be spherical, the average radius is $r_P = \sqrt[3]{\frac{3m_{A,P}}{4\pi\rho_P}}$

Where $m_{A,P}$: The average mass of a single adsorbent particle; ρ_P : the particle density.

b. Internal surface area

Typically, the interior surface area of porous adsorbents greatly exceeds the outward surface area. Specifically, designed adsorbents have exceptionally large interior surface areas. Consequently, the interior surface area provides the vast majority of the absorption capacity. Therefore, the interior surface area of an adsorbent is a crucial quality.

The dimension of the pore system is connected to the size of the interior surface area. Extremely microporous adsorbents used for water purification have substantial interior surface areas.

1.3 Research gap

As a means of reducing the cost of regeneration and extending the life of granular activated carbon (GAC) beds in water and wastewater treatments, the biological activated carbon (BAC) technique is frequently employed. The impact of adsorption of easily degradable organics on nitrogen removal is difficult to quantify in pilot-scale research, as is the distinction between adsorption and biodegradation of organics. For the sake of modeling and optimization, researchers and operators have been working to clarify each mechanism. By simulating potential outcomes in a bGAC setup, we can get a more thorough and systematic understanding of the system's potential behavior. Activated sludge models (ASM) are widely used in the wastewater treatment industry to simulate the biodegradation of organics, nitrification, and denitrification processes.

The superiority of GAC over sand in encouraging microbial activity was also shown in the denitrification studies conducted by Jeris et al. (1974). It was found in this investigation that growth on sand particles was insignificant. After only two weeks of operation, however, they found that nitrates had been effectively removed from the system thanks to the use of freshly activated carbon.

Filter beds will become colonized by microorganisms, mostly bacteria, due to the fact that they adsorb to GAC. They absorb nutrients from the GAC and dissolved nutrients, allowing them to expand to large populations.

Traditionally, activated sludge models consider nitrification as a single step process (Henze et al., 2000). However, several two-step nitrification models have been developed in the recent years (Hellings et al., 1999, Moussa et al., 2005, Wett and Rauch, 2003, Pambrun et al., 2006, Volcke, 2006, Jones et al., 2007, Kampschreur et al., 2007, Van Hulle et al., 2007, Sin and Vanrolleghem, 2006, Kaelin et al., 2009). Sin et al. provide a review of these two-step nitrification models (2008). These models differ considerably from one another. The substrate taken into account is the primary distinction with regard to AOB. Most of the models consider Total Ammonia Nitrogen as the substrate for AOB. Only the models proposed by Hellings et al., 1999, Volcke, 2006 and Van Hulle et al. (2007) considered that free ammonia is the real substrate and the growth rate of AOB depends on FA concentration.

Because adsorption and biodegradation happen at the same time in biologically active GAC columns, predicting how much nitrogen will be removed is challenging. However, under real-world operating settings, where time-varying influent concentrations and various substrates are met, mathematical modeling is required to acquire an understanding of this treatment process. There are a number of different models that have been created (Andrews and Tien 1981, Benedek 1980, Tien 1980, Ying and Weber 1979), and DiGiano (1981) provides a summary of their key characteristics. In addition, maximizing the GAC service life extension by starting biodegradation as soon as possible after startup is recommended by Erlanson (1997). In this work, the models include simplifying assumptions regarding mass transport resistances, microbial kinetics, and biofilm thickness in order to facilitate solution. This study will involve the integration of an enhanced version of the ASM1 model into AQUASIM 2.1g, which will include a 2-step nitrification process and a basic adsorption model for soluble organics. It is planned to study how well the ASM1 kinetic parameters apply to real-world scenarios and how sensitively the model parameters measuring the roles of adsorption and biodegradation behave.

1.4 Research method

Research literature review:

- Characterization and microbiological transformation of organic water constituents (Chemical oxygen demand, COD) and nitrogen compounds ($\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$) in water treatment.
- Introduction to the theory and methods of mathematical modeling of biological processes in (waste)water treatment.
- Introduction to the mathematical description of adsorption processes, i.e. adsorption equilibrium and adsorption kinetics.
- Introduction to fixed-bed process parameters.

Modeling simulation/ development:

- Development of a simple biokinetic model which is able to describe biodegradation of COD and 2-step nitrification as well as denitrification based on ASM1. Integration of a simple adsorption model for COD.
- Representation of a bGAC filter in the modeling software AQUASIM 2.1. The developed biokinetic model has to be combined with an appropriate representation of fixed-bed mass transport processes.

Methods of data processing:

-
- Obtained kinetic parameters from the literature on similar biofilm systems..
 - Sensitivity analysis of kinetic model parameters and discussion of uncertainty regarding the differentiation of adsorptive and biological COD removal and its impact on simulated biological removal of nitrogen.

Modeling biological systems mathematically is a well-established method for assessing and enhancing the efficacy of microorganism-based processes. Tools like this have been extensively used for improving scalability and productivity. As a result, the objectives of this study are to identify the kinetic and stoichiometric parameters that have the most significant influence on the model and to estimate the values of these parameters with the help of a review of the relevant prior research. The model will still have to take into consideration two different substrates: an organic substrate for the heterotrophs, and ammonium substrate for the nitrifiers.

Last but not least, an uncertainty analysis is carried out in order to determine the amount to which the influential parameters that were previously discovered are accountable for the observed variation in the model findings.



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2 Chapter 2 - Theoretical basics

2.1 Introduction to the water quality parameters

There are five groups of organic chemicals found in drinking water, each of which has been designated by the EPA (1978c). The water treatment industry must take into account the unique characteristics of each classification.

- Class I: organic compounds that alter the water's taste, odor, and/or color;
- Class II: synthetic organic chemicals found in source waters due to upstream discharges or runoff;
- Class III: organic compounds (precursors) that react with disinfectants to produce "disinfection by-products";
- Class IV: organic compounds that are the disinfection by-products themselves;
- Class V: natural (non-Class III) organic compounds of little direct toxicological importance

In this study, the characteristics of raw water source are divided into three categories: (i) Physical Features; (ii) Chemical Features; (iii) Biological Features. The physical properties of sewage are related to the physical characteristics. The chemical properties are associated with the chemical constituents of sewage. The biological properties are associated with the biological constituents of sewage. Table 2-1 lists the physical properties, chemical and biological constituents, and sources of sewage.

Table 2-1: Physical, Chemical and Biological Characteristics of Sewage and their Sources (Sources: Ravi Kumar)

No.	Characteristic	Sources
1.	Physical properties	
	i. Color	Domestics and industrial wastes, natural decay of organic materials
	ii. Odour	Decomposing waste water, industrial wastes
	iii. Solids	Domestic water supply, domestic and industrial wastes, soil erosion, Inflow infiltration
	iv. Temperature	Domestics and industrial wastes
2.	Chemical constituents	
	a. Organic	
	i. Carbohydrates	Domestic, commercial and industrial wastes
	ii. Fats, oils and grease	Domestic, commercial and industrial wastes
	iii. Pesticides	Agricultural wastes
	iv. Phenols	Industrial wastes
	v. Proteins	Domestic and commercial wastes
	vi. Surfactants	Domestic and industrial wastes
	vii. Others	Natural decay of organic materials
	b. Inorganic	
	i. Alkalinity	Domestic wastes, domestic water supply, groundwater infiltration
	ii. Chlorides	Domestic wastes, domestic water supply, groundwater infiltration, water softeners

No.	Characteristic	Sources
	iii. Heavy metals	Industrial wastes
	iv. Nitrogen	Domestic and agricultural wastes
	v. pH	Industrial wastes
	vi. Phosphorous	Domestic and industrial wastes, natural runoff
	vii. Sulphur	domestic water supply, domestic and industrial wastes
	viii. Toxic compounds	industrial wastes
c.	Gases	
	i. Hydrogen Sulphide	Decomposition of domestic wastes
	ii. Methane	Decomposition of domestic wastes
	iii. Oxygen	Domestic water supply, surface water infiltration
3.	Biological constituents	
	i. Animals	Open watercourses and treatment plants
	ii. Plants	Open watercourses and treatment plants
	iii. Protista	Domestic wastes, treatment plants
	iv. Viruses	Domestic wastes

Considering the raw water supply for public drinking water, the most important parameters for this study are those listed below.

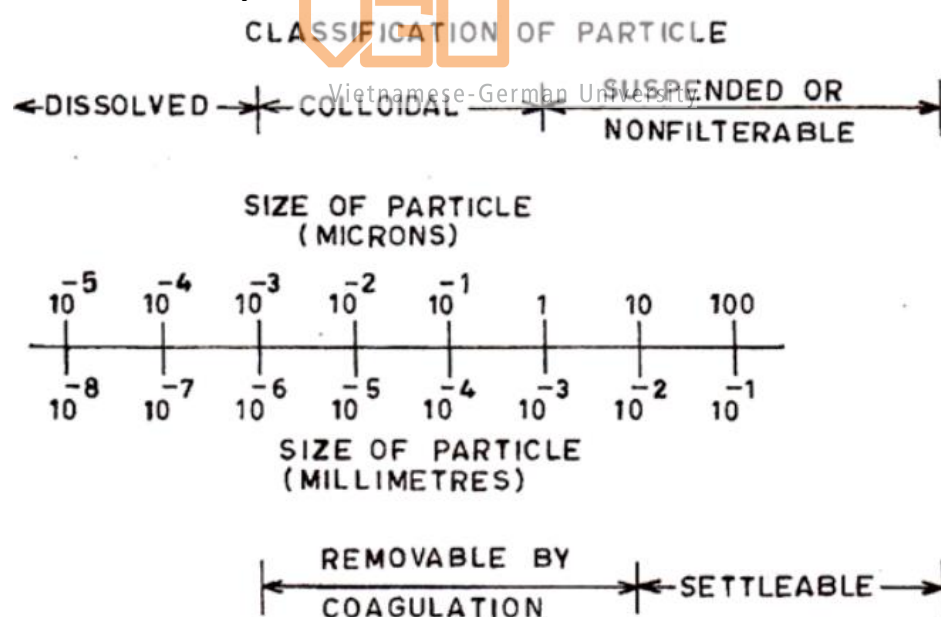


Figure 2-1: Classification and size range of solids found in sewage

2.1.1 Total Solids content - turbidity

Typically, sewage contains a substantial amount of organic materials. However, the amount of organic matter in sewage is dependent on its composition and state. In sewage, organic matter may exist as dissolved compounds, colloidal matter, suspended or sedimented matter.

Suspended solids are those that are held in suspension in liquid, and these may be further categorized as follows: (a) Settleable solids are those that settle out if sewage is left undisturbed

for roughly two hours; and (b) Non-settleable solids are those that do not settle down by normal detention, but may be captured by specific laboratory filters.

Colloidal solids are finely dispersed materials in suspension that cannot be removed by settling or filtration, but are often eliminated by biological oxidation or coagulation, followed by sedimentation. Dissolved solids are those that remain dissolved in sewage, similar to how salt dissolves in water.

Each category of solids found in sewage can be further categorized as:

- (a) Organic or volatile solids: account for approximately 45% of the total solids and can be divided into the three groups below: (i) Carbohydrates, including cellulose, cotton and wool fiber, starch, and sugar, among others. (ii) Fats, oils, and grease from kitchens, laundries, garages, stores, gas stations, etc. (iii) Nitrogenous molecules include proteins and their breakdown products, animal and vegetable wastes, urea, amines, amino acids, fatty acids, hydrocarbons, and alcohol, among others.
- (b) Inorganic or non-volatile or fixed solids: account for the remaining 55% of total solids, and include minerals and salts such as sand, gravel, grit, clay, and other detritus, dissolved salts, chlorides, sulphates, etc.

2.1.2 Nitrogen contents

Depending on the degree of decomposition or oxidation of nitrogenous organic materials, the following types of nitrogen emerge in sewage: Albuminoid nitrogen or albuminoid ammonia; Ammonia nitrogen or free nitrogen; Nitrites or Nitrite nitrogen; and Nitrates or Nitrate nitrogen.

- (a) Albuminoid nitrogen or albuminoid ammonia: represents the amount of nitrogenous organic stuff in sewage that has not been degraded.
- (b) Ammonia nitrogen or free ammonia: arises from bacterial breakdown of nitrogen-containing organic materials. Depending on the pH value of the sewage, it occurs as either ammonium ion (NH_4^+) or ammonia (NH_3), in line with the following equilibrium reaction: $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$. When $\text{pH} > 7$, the equilibrium is shifted to the left, so ammonia exists, whereas ammonium ion exists when $\text{pH} < 7$. The relative proportion of ammonia in sewage can be used to determine its age. Significant levels of ammonia nitrogen or free ammonia are indicative of stale or aged sewage. In an aerobic environment, bacteria are able to convert ammonia to nitrites and nitrates.
- (c) Nitrites are a sign of partially oxidized or degraded nitrogenous organic matters in sewage. The presence of nitrites in sewage indicates that organic nitrogen is being broken down or oxidized. Consequently, nitrites represent the intermediate step of conversion of sewage's nitrogenous organic matter into a stable form. The presence of nitrites indicates past pollution during the stabilization process. Nitrite concentrations in sewage rarely surpass 1 mg/l. Nitrites are nonetheless unstable and easily oxidized to nitrate, making them rather inconsequential in investigations of sewage and water contamination.
- (d) Nitrates are the end products of the decomposition (or oxidation) of nitrogenous organic materials found in sewage. As a result, the presence of nitrates suggests that sewage contains the most stable and fully oxidized form of nitrogenous organic matter, indicating that the sewage has been adequately oxidized and treated. Increase in the proportion of nitrates during the sewage treatment process acts as a guide for monitoring the treatment's progress. Nitrate concentrations in sewage can range from 0 to 20 mg/l as nitrogen.

2.1.3 Dissolved Oxygen

Dissolved oxygen (DO) is the amount of dissolved oxygen contained in sewage. The presence of dissolved oxygen in untreated sewage is indicative of its freshness. However, oxygen has a low solubility in water. For the respiration of aerobic microorganisms and all other aerobic life forms present in sewage, dissolved oxygen is necessary. Thus, it is important for sewage to have dissolved oxygen. Fresh sewage quickly loses its dissolved oxygen content

due to aerobic degradation. When the total amount of dissolved oxygen is depleted, aerobic decomposition ceases and anaerobic decomposition begins, leading to the production of offensive odors. Therefore, the presence of dissolved oxygen in sewage is also desirable, since it prevents the formation of offensive odors. Before sewage is treated, its dissolved oxygen level must be determined so that the appropriate treatment procedure may be chosen.

2.1.4 Biological characteristics

The biological features of sewage rely on the types of organisms present. Protista, viruses, plants, and animals are the most common types of creatures discovered in sewage.

In this study, bacteria are the primary contributors to the biological processes. Based on their oxygen needs, bacteria are categorised as: (i) aerobic bacteria, (ii) anaerobic bacteria; and (iii) facultative bacteria. These organisms require free oxygen for existence; therefore, if they are present in sewage, they will consume dissolved oxygen from the waste. Anaerobic bacteria are those that thrive in the absence of free oxygen, deriving the oxygen they require from the oxygen radical of organic molecules and mineral compounds such as nitrites (NO_2), nitrates (NO_3), sulphates (SO_4). Facultative bacteria are those which can survive and flourish with or without free oxygen.

Bacteria are divided into three groups based on the temperatures at which they can survive and thrive: (i) Psychrophilic bacteria, which can do so between 10° and 20°C ; (ii) Mesophilic bacteria, which can do so between 20° and 40°C ; and (iii) Thermophilic bacteria, which can do so between 40° and 65°C .

2.2 Basics of microbiological carbon and nitrogen removal

Nitrificants oxidize ammonium and produce oxygen, while aerobic heterotrophs oxidize an organic substrate. The growth and substrate usage of the heterotrophs can be regulated by the concentrations of the organic substrate, oxygen, or both when heterotrophs and nitrifiers coexist in a biofilm (a frequent condition). Similar to how ammonium, oxygen, or both can regulate nitrifier development and substrate usage. Even if oxygen is not a limiting factor for either kind of microbe, the model will still need to account for two substrates: organic substrate for the heterotrophs and ammonium for the nitrifiers (Wagner; Eberl; et al. 2006)

Separate aerobic and anaerobic phases, often carried out in various bioreactors or by varying aeration intervals, are important to the conventional biological process employed in wastewater treatment for nitrogen removal (Metcalf and Eddy, 1991). The availability of organic carbon and ammonia are linked to the water's carbon to nitrogen (C/N) ratio. When the carbon-to-nitrogen ratio in a biofilter is high, heterotrophic bacteria are able to outcompete nitrifiers for oxygen and space. Autotrophic bacteria can only outcompete Heterotrophs when the C/N ratio is low (Michaud, Blancheton et al. 2006). The nitrification rate is dependent on the critical C/N ratio, which varies from system to system and is linked to the properties of the organic carbon that is readily available (Michaud, Blancheton et al. 2006).

Nitrification and denitrification rely heavily on the activities of ammonia-oxidizing bacteria or archaea (AOB/AOA), nitrite-oxidizing bacteria (NOB), and heterotrophic and autotrophic denitrifiers. Almost completely, biological processes are responsible for nitrogen removal. Typically, nitrogen is eliminated by converting ammonia to nitrate in the presence of abundant oxygen (Nitrification). In the absence of molecular oxygen, nitrate gets denitrified to nitrite and then nitrogen gas (anoxic condition). The processes of nitrification and BOD removal can occur in the same reactor, or in a separate reactor entirely. Nitrification was found to be possible at very reduced oxygen concentrations. Nitrification could occur at oxygen concentrations as low as 0.3 mg/l . Denitrification was also discovered to take place in the presence of oxygen with oxygen concentrations as high as 1.5 mg/l . This was explained in two different ways. The first is that denitrifying organisms are partially aerobic, meaning that they can survive, thrive, and denitrify in the presence of a relatively small amount of dissolved oxygen. The second theory proposes that the process is associated with oxygen diffusion restrictions in the biological floc as a whole. In other words, the nitrification process is carried out by the outer portions of the flocs, which are aerobic even at low amounts of dissolved oxygen. Conversely, oxygen transmission limits keep the inner part of the floc anoxic.

Nitrification and denitrification happened at the same time, therefore scientists used the term "SND" to describe it ("Simultaneous Nitrification and Denitrification")

Nitrification

Under aerobic circumstances, with dissolved oxygen concentrations of 1.0 mg/L or higher, nitrification can take place. A low growth rate is observed at dissolved oxygen (DO) concentrations below 0.5 mg/L. There are a number of conditions that must be met for nitrification to take place, including a high mean cell residence time (MCRT or Sludge Age), a low food to microbe ratio (F/M), and an adequate buffering capacity (alkalinity). An extended aeration tank with plug flow is recommended. The ambient temperature is also crucial.

The temperature plays a role in nitrification. Nitrification is most efficient at around 30°C. For optimal nitrification, keep the dissolved oxygen concentration at 2.0 mg/L or above. The pH of activated sludge mixed liquor is decreased when alkalinity is used during the nitrification process. Nitrification can be severely impeded by a pH below 6.5 or above 8.0. Acid is created during the nitrification process. Because of this acid generation, the pH of the biological population in the aeration tank can drop, which in turn can slow the reproduction of nitrifying bacteria. Both *Nitrosomonas* and *Nitrobacter* grow at pH levels between 7.5 and 8.5, but most treatment facilities can nitrify at pH levels as low as 6.5 to 7.0. When the pH falls below 6.0, nitrification is inhibited. Alkalinity, in the form of CaCO₃, is used at a rate of 7.1 mg/L for each mg/L of ammonia nitrogen oxidized during the nitrification reaction. Buffering effectiveness is dependent on alkalinity levels between 50 and 100 mg/L.

Biological conversion of ammonia to nitrate typically takes place in suspended growth reactors (i.e. biological nitrification). Single-stage and two-stage processes are both examples of biological nitrification. The primary effluent of a single-stage treatment plant has a BOD₅/TKN (Total Kjeldahl Nitrogen) ratio larger than 5, as nitrification and carbonaceous oxidation (BOD removal) take place in the same basin.

Both heterotrophic and nitrifying bacteria live in the same environments. Heterotrophs' ability to secrete EPS can be helpful to nitrifiers because it helps keep the biofilm structure stable. The nitrifying microorganisms are shielded from detachment and dehydration. When there are no other organic carbon sources available, the heterotrophs can rely on the soluble microbial metabolites created by the nitrifiers and dead cells to proliferate (Rittmann, 2001). Competition for oxygen can occur, however, if the biofilm's oxygen diffusion rate is slower than the bacteria's consumption rate. Heterotrophs are more effective competitors than autotrophs and can inhibit nitrification due to their faster growth rates and lower oxygen requirement for growth. Several factors determine whether the mutualistic or competitive nature of the inter-guild interaction between heterotrophs and nitrifiers predominates in a specific system. Organic carbon: ammonia nitrogen (C/N) ratio, biofilm structure, oxygen and space availability, and specific loading rate of degradable carbon also play an important role.

Increased carbon input can reduce nitrification in a biofilm by increasing competition for oxygen. There is evidence that a higher C/N ratio can boost denitrification while simultaneously decreasing nitrification efficiency. This has potential benefits in a variety of systems but could potentially have drawbacks in others. Denitrification in the nitrifying unit of a WWTP can reduce nitrate production, which in turn can make the pre-denitrification stage anaerobic and cause a negative feedback loop that can shut off nitrification.

Nitrification kinetics considers what influences the microbial synthesis of nitrifying bacteria and how those rates might be altered. The availability of ammonium or nitrite, respectively, limits the development of ammonium oxidizer and nitrite oxidizer. The dynamics of nitrifying bacteria development, as described by the most used Monod equation, are given by Equation (Lawrence K. Wang et al., 2009)

$$\mu_n = \mu_{n,max} \frac{S}{K_S + S}$$

In aerobic conditions, ammonium-oxidizing bacteria are responsible for the conversion of ammonium to nitrite. This acidifying process can be mitigated to some extent in the presence of bicarbonate in wastewater. To produce nitrite, two moles of bicarbonate are required for

every mole of ammonium. This is critical for the nitrification process because a lack of alkalinity can cause a drop in pH and stop the reaction completely. Nitrification does not occur at pH levels lower than 6.5. The substrate for ammonium oxidizers is NH_3 rather than NH_4^+ , and the inhibitor is HNO_2 rather than nitrite. The pH of the solution has a significant impact on the $\text{HNO}_2\text{-NO}_2^-$ equilibrium. At concentrations greater than 0.2 mg HNO_2/L , total nitrification is inhibited. If there is enough oxygen and the conditions are favorable, nitrite-oxidizing bacteria carry out the second phase of nitrification (Paredes et al., 2007).

The primary requirement for regulating partial nitrification is the accumulation of stable nitrite in a nitrification reactor. Various methods and procedures, such as regulating the reactor's temperature, hydraulic retention time, pH, dissolved oxygen, and free ammonia concentration, have been used to accomplish this (see Tab. 2.2), Paredes et al (2007).

Table 2-2: Effect of the pH, temperature, free ammonia and nitrous on the nitrification process, (Paredes, Kuschik et al. 2007)

Factor	Effect	References
Temperature		
T > 15°C	Ammonium oxidizers grow faster than nitrite oxidizers	L. G. J. M. van Dongen, M. S. M. Jetten, M. C. M. van Loosdrech, 2001.
T = 25°C	Ammonium oxidizers can out-compete nitrite oxidizers	L. G. J. M. van Dongen, M. S. M. Jetten, M. C. M. van Loosdrech, 2001.
pH		
7.0 - 8.0	Optimum range for nitrification	P. Antoniou et al., 1990; G. L. Jones et al., 1982; H. A. Painter et al., 1983.
7.9 - 8.2	Optimum range for ammonium oxidizers (<i>Nitrosomas</i>).	J. E. Alleman et al., 1984
7.2 - 7.6	Optimum range for nitrite oxidizers (<i>Nitrobacter</i>)	J. E. Alleman et al., 1984
Free NH_3 (mg/l)		
150	Inhibition of ammonium and nitrite oxidizers.	A. C. Anthonisen et al., 1976
1.0 - 7.0	Inhibition of ammonium oxidizers and nitrite accumulation.	C. Anthonisen et al., 1976; U. Abeling et al, 1992.

The growth rates of ammonium oxidizers and nitrite oxidizers are sensitive to temperature in distinct ways.

The ammonium oxidizers may be able to outperform the nitrite oxidizers, but only at temperatures above 25 °C. There is no difference between the sludge retention time and the hydraulic retention time. It is the growth rate of the bacteria involved, not the concentration of the influent, that determines the effluent concentration. Because of the high temperatures and lack of sludge retention, the dilution rate is adjusted so that the ammonium oxidizers can proliferate quickly enough to remain in the reactor, while the nitrite oxidizers are washed out.

Since nitrite oxidizers proliferate more rapidly than ammonium oxidizers in the low pH range, pH plays a significant role in the system. With respect to the optimal pH ranges for nitrification (see Tab. 2), three distinct effects of the pH on the nitrifying bacteria have been observed. Nutritional effects related to alkalinity and inorganic carbon species, as well as inhibition via free ammonia and free nitrous acid, all play a role in the activation and deactivation of nitrifying bacteria (Paredes et al., 2007)

Nitrous acid and free ammonia both block ammonium and nitrite oxidizers, but nitrite oxidizers are more sensitive to free ammonia than ammonium oxidizers (see Tab. 2). However, the concentration of free ammonia required to block nitrite oxidation rises over time.

When it comes to nitrification, alkalinity is also crucial. A molar ratio of 1:1 of NH_4^+ to NO_2^- is optimal if a later Anammox procedure for nitrogen removal is desired. The alkalinity of the wastewater can be managed to do this. Using a molar ratio of 1:1 between ammonium and bicarbonate results in conversion of approx. 50% of ammonium to nitrite and the rest remains as ammonium due to the high rate of bicarbonate consumption in the oxidation of 1 mole of ammonia to nitrite and the reaction's completion at a pH lower than 6.5. Denitrification via the nitrite route, on the other hand, necessitates either the complete oxidation of ammonium to nitrite or an intermittent anaerobic stage achieved through the suspension of aeration and the introduction of a carbon source into the reactor. Since denitrification results in the production of bicarbonate, this second choice has the advantage that it does not necessitate high alkalinity levels.

Changing the amount of oxygen in the reactor is another strategy for boosting nitrite buildup. Nitrite buildup occurred in biofilm systems because of the low dissolved oxygen concentration. If the ammonium oxygen ratio is less than 3.4 (theoretical requirement), then oxygen is the limiting factor, and nitrite will accumulate, as was observed by Tanaka et al.

2.3 Basics of GAC adsorption, adsorption equilibrium and adsorption kinetics

2.3.1 Activated Carbons

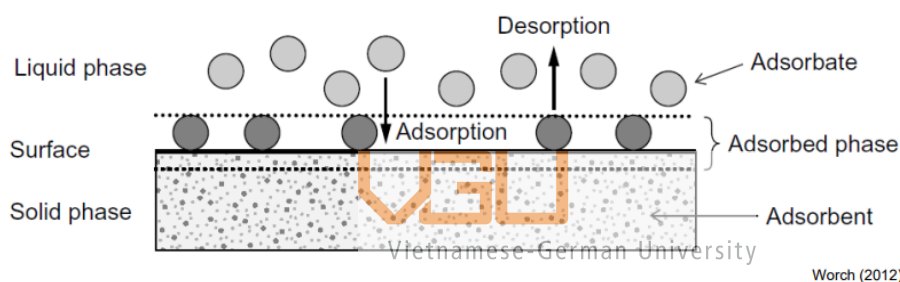


Figure 2-2: Activated carbon served as adsorption medium (Worch, 2012)

Activated carbons are applied in two different forms, as granular activated carbon (GAC) with particle sizes in the range of 0.5 to 4 mm and powdered activated carbon (PAC) with particle sizes $<40 \mu\text{m}$. The different particle sizes are related to different application techniques: slurry reactors for PAC application and fixed-bed adsorbers for GAC.

Activated carbons show a broad variety of internal surface areas ranging from some hundreds m^2/g to more than a thousand m^2/g depending on the raw material and the activation process used. Activated carbon for water treatment should not have pores that are too fine so that larger molecules are also allowed to enter the pore system and to adsorb onto the inner surface. Internal surface areas of activated carbons applied for water treatment are typically in the range of 800–1,000 m^2/g .

Activated carbons are able to adsorb a multiplicity of organic substances mainly by weak intermolecular interactions (van der Waals forces), in particular dispersion forces. In the case of aromatic adsorbates, π -interactions or electrostatic interactions between surface oxide groups and ionic adsorbates might superimpose these attraction forces. Activated carbons are the preferred adsorbents in all water treatment processes where organic pollutants need to be eliminated due to their high adsorption capabilities. Aside from background dissolved organic matter (DOM), activated carbon is also effective in removing trace pollutants (micropollutants).

The following list includes some broad trends in the adsorption of activated carbon.

- + The adsorption increases with increasing internal surface (increasing micropore volume) of the adsorbent.

- + The adsorption increases with increasing molecule size of the adsorbates as long as no size exclusion hinders the adsorbate molecules from entering the pore system.
- + The adsorption decreases with increasing temperature because (physical) adsorption is an exothermic process.
- + The adsorbability of organic substances onto activated carbon increases with decreasing polarity (solubility, hydrophilicity) of the adsorbate.
- + Aromatic compounds are better adsorbed than aliphatic compounds of comparable size.
- + Organic ions (e.g. phenolates or protonated amines) are not adsorbed as strongly as the corresponding neutral compounds (pH dependence of the adsorption of weak acids and bases).

2.3.2 Adsorption equilibrium

Mechanisms of mass transfer: There are four distinct stages to the adsorption procedure:

- (a) The adsorbate is moved from the bulk liquid phase to the hydrodynamic boundary layer surrounding the adsorbent particle.
- (b) "Film diffusion" or "external diffusion," which is transport across the boundary layer to the adsorbent's outer surface.
- (c) Transportation into the interior of the adsorbent particle ("intraparticle diffusion" or "internal diffusion") occurs via diffusion in the pore liquid ("pore diffusion") and/or diffusion in the adsorbed state along the internal surface ("internal diffusion") (surface diffusion)
- (d) The final adsorption sites' energetic interaction with the adsorbate molecules.

It is commonly believed that film and/or intraparticle diffusion control the overall rate of the adsorption process and that the first and fourth steps are extremely fast. The kinetic model often only takes into account a single intraparticle diffusion mechanism, which is often believed to be the dominant one. Adsorption processes from aqueous solutions onto porous adsorbents can typically be characterized using a surface diffusion approach, which accounts for the intraparticle diffusion that occurs throughout the process. The mass transfer within the adsorbent particle takes place normally by pore diffusion and surface diffusion in parallel, but their portions are difficult to separate. Therefore, often only one intraparticle diffusion mechanism is assumed as predominant and considered in the kinetic model. In most adsorption processes from aqueous solutions onto porous adsorbents, the intraparticle diffusion can be described successfully by a surface diffusion approach.

Each adsorption equilibrium state is uniquely defined by the variables adsorbate concentration, adsorbed amount (also referred to as adsorbent loading), and temperature. For a single-solute system, the equilibrium relationship can be described in its general form as:

$$q_{eq} = f(c_{eq}, T)$$

where c_{eq} is the adsorbate concentration in the state of equilibrium, q_{eq} is the adsorbed amount (adsorbent loading) in the state of equilibrium, and T is the temperature.

It is common practice to keep the temperature constant and to express the equilibrium relationship in the form of an adsorption isotherm

$$q_{eq} = f(c_{eq}), T = \text{constant}.$$

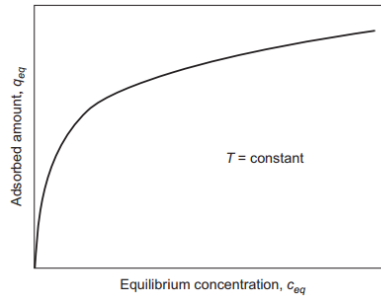


Figure 2-3: Adsorption Isotherm

Typically, an appropriate isotherm equation is used to represent the obtained data after an experimental determination of the dependency of the adsorbed amount on the equilibrium concentration is made at constant temperature. It is essential to characterize the data by a mathematical equation in order to use equilibrium data to more complicated adsorption models (such as kinetic models and breakthrough curve models).

To determine equilibrium data, the bottle-point method is usually applied. In this method, a set of bottles is used to determine a larger number of isotherm points in parallel. A minimum number of 8 to 10 is recommended to get enough data points for the subsequent isotherm fitting. Each bottle is filled with the adsorbate solution of known volume, V_L , and known initial concentration, c_0 . After adding a defined adsorbent mass, m_A , the solution is shaken or stirred until the state of equilibrium is reached (Figure 3.2). The time needed to establish equilibrium can range from a few hours to a few weeks. The adsorbent particle diameter, in particular, has a significant impact on the needed equilibration time, in addition to the kind of adsorbent and adsorbate.

After the equilibrium is established, the residual (equilibrium) concentration, c_{eq} , has to be measured. Then, the adsorbed amount, q_{eq} , can be calculated by using the material balance equation for the batch adsorption process. Under the condition that other elimination processes (e.g. degradation, evaporation, adsorption onto the bottle walls) can be excluded and only adsorption onto the adsorbent particles takes place, the **mass** Δm^l removed from the liquid phase must be **the same** as the **mass adsorbed** onto the adsorbent, Δm^a

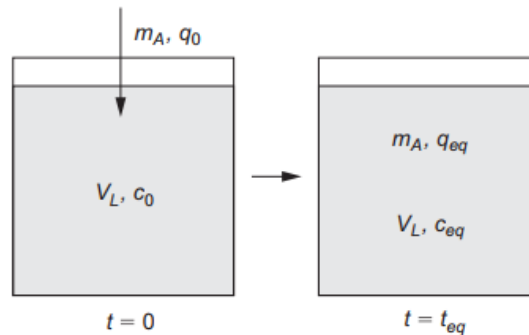


Figure 2-4: Experimental determination of adsorption equilibrium data.

or explicitly with the starting and end values (subscripts 0 and eq):

$$m_0^l - m_{eq}^l = m_{eq}^a - m_0^a \quad (\text{eq. 2.1})$$

With the definitions of the mass concentration, c , and the adsorbent loading, q ,

$$c = \frac{m^l}{V_L} \quad (\text{eq. 2.2})$$

$$q = \frac{m^a}{m_A} \quad (\text{eq. 2.3})$$

the material balance (eq. (3.4)) can be written in the form $V_L(c_0 - c_{eq}) = m_A(q_{eq} - q_0)$

Because fresh (i.e. not preloaded) adsorbent is usually used in equilibrium measurements ($q_0 = 0$), the balance equation reduces to

$$q_{eq} = \frac{V_L}{m_A} (c_0 - c_{eq}) \quad (\text{eq. 2.4})$$

Thus, if the adsorbent dose (m_A/V_L) is known and the concentration difference has been measured, the equilibrium loading corresponding to the equilibrium concentration can be calculated from eq. (2.4). In this way, one isotherm point is found. To get more points of the isotherm, the adsorbent dose or the initial concentration has to be varied.

2.3.3 Adsorption kinetics

The mass transfer from the solution to the adsorption sites within the adsorbent particles is constrained by mass transfer resistances that determine the time required to reach the state of equilibrium. The time progress of the adsorption process is referred to as adsorption kinetics. The rate of adsorption is usually limited by diffusion processes toward the external adsorbent surface and within the porous adsorbent particles. The mass transfer parameters, together with the equilibrium data, are essential input data for determination of the required contact times in slurry reactors as well as for fixed-bed adsorber design.

The progress of the adsorption process can be characterized by four consecutive steps:

- a. Transport of the adsorbate from the bulk liquid phase to the hydrodynamic boundary layer localized around the adsorbent particle.
- b. Transport through the boundary layer to the external surface of the adsorbent, termed "**film diffusion**" or "external diffusion"
- c. Transport into the interior of the adsorbent particle (termed "**intraparticle diffusion**" or "internal diffusion") by diffusion in the pore liquid (pore diffusion) and/or by diffusion in the adsorbed state along the internal surface (surface diffusion)
- d. Energetic interaction between the adsorbate molecules and the final adsorption sites.

An organic compound's equilibrium concentration (C_{eq}) in solution and its adsorption concentration (C_s) on activated carbon's surface are plotted on an adsorption isotherm (surface concentration, q). Activated carbon's adsorption capacity for a wide range of organics can be predicted using equilibrium models. The thermodynamic properties of the solvents, adsorbents, and adsorbates are necessary for using such models.

Diffusion mechanisms toward the external adsorbent surface and within the porous adsorbent particles often limit the rate of adsorption. Research into adsorption kinetics is required for identifying the rate-limiting mass transfer mechanisms and assessing the typical mass transfer parameters.

As a result of a kinetic experiment, the kinetic curve is found in the form $c = f(t)$. Where c is the concentration and t is the time.

During the adsorption process, the concentration decreases from the initial value, c_0 , to the equilibrium concentration, c_{eq} . Since for each time during the experiment the material balance equation

$$\bar{q}(t) = \frac{V_L}{m_A} [c_0 - c(t)] \quad (\text{eq. 2.5})$$

The kinetic curve can also be expressed as $\bar{q} = f(t)$

where q is the mean solid-phase concentration (adsorbed amount)

The experimentally determined kinetic curve provides the data for a fitting procedure with a kinetic model, where the respective mass transfer coefficients are the fitting parameters

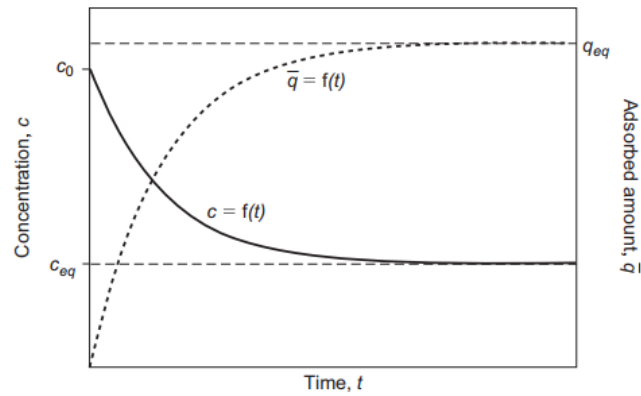


Figure 2-5: Kinetic curves. Progress of concentration and adsorbent loading with time

Kinetic experiments are often carried out in a manner that the film diffusion becomes very fast and therefore does not need to be considered in the mathematical model. Such an experimental approach simplifies considerably the determination of the desired mass transfer coefficients of the internal diffusion processes. The requirements of this approach have to be considered in the choice of the reactor for kinetic experiments.

Mass transfer models

In general, a kinetic model includes mass transfer equations, equilibrium relationships, and the material balance for the reactor applied

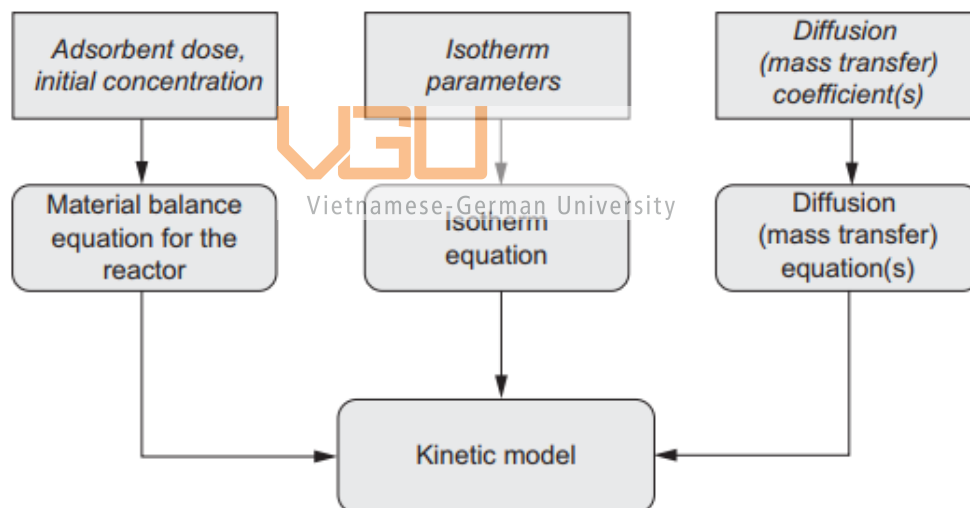


Figure 2-6: Modelling of adsorption kinetics. Model constituents and input data (Worch 2021)

The common assumptions in kinetic models are as follows: (a) the temperature is assumed to be constant, (b) the bulk solution is assumed to be completely mixed, (c) the mass transfer into and within the adsorbent can be described as diffusion processes, (d) the attachment of the adsorbate onto the adsorbent surface is much faster than the diffusion processes, and (e) the adsorbent is assumed to be spherical and isotropic.

An important aspect to be considered is that adsorption kinetics is not independent of the adsorption equilibrium. Therefore, kinetic models can be applied only if the required equilibrium parameters are known. If necessary, an isotherm has to be measured prior to the kinetic experiment.

The differential material balance for a batch system reads

$$m_A \frac{d\bar{q}}{dt} = -V_L \frac{dc}{dt} \quad (\text{eq. 2.6})$$

Where: m_A is the adsorbent mass, and V_L is the liquid volume in the reactor. This equation links the change of the mean adsorbent loading with time to the change of the liquid-phase

concentration with time. Integration of eq. (5.4) with the initial conditions $c(t = 0) = c_0$ and $\bar{q}(t = 0) = 0$ leads to the material balance equation in the form

$$\bar{q}(t) = \frac{V_L}{m_A} [c_0 - c(t)] \quad (\text{eq. 2.7})$$

Determination of model parameters

In order to simplify the model, the dispersion is neglected and the internal diffusion is assumed to be dominated by only one mechanism. In this case, the number of considered mechanisms, and therefore also the number of the needed coefficients, is reduced to the half in comparison to a model that includes all possible mechanisms

Table 2-3: Breakthrough curve (BTC) models with different assumptions about the dominating mass transfer processes, (Worch 2021)

Model	Mass transfer mechanisms			
	Dispersion	Film Diffusion	Pore Diffusion	Surface Diffusion
Dispersed-flow, pore and surface diffusion model	x	x	x	x
Dispersed-flow, pore diffusion model	x	x	x	x
Dispersed-flow, homogenous surface diffusion model	x	x		x
Plug-flow, pore and surface diffusion model		x	x	x
Plug-flow, pore diffusion model		x	x	
Plug-flow, homogeneous surface diffusion model		x		x
Linear driving force model			x	x

Under the assumption that the adsorbate uptake follows a first-order rate law, the adsorption kinetics can be described by

$$\frac{dq}{dt} = k_1(q_{eq} - q) \quad (\text{eq. 2.8})$$

where k_1 is the first-order rate constant. Integration with the condition $q = 0$ at $t = 0$ gives

$$\ln \frac{(q_{eq} - q)}{q_{eq}} = -k_1 t \quad (\text{eq. 2.9})$$

The frequently mentioned alternative equation $\ln(q_{eq} - q) = \ln q_{eq} - k_1 t$ (eq. 2.10)

A fixed-bed adsorber requires both time and space for the adsorption process to take place. Until equilibrium is broken, the adsorbate from the percolating solution will continue to be accumulated by each adsorbent particle in the bed. However, because adsorption kinetics are slow, the loaded and unloaded adsorbent layers do not have a distinct separation. In its place, the mass transfer zone (MTZ) or adsorption zone is where the equilibration occurs. Profiles of concentration and adsorption onto adsorbents are typical in this MTZ. For a given time in single-solute adsorption, three unique regions of the adsorbent bed can be identified.

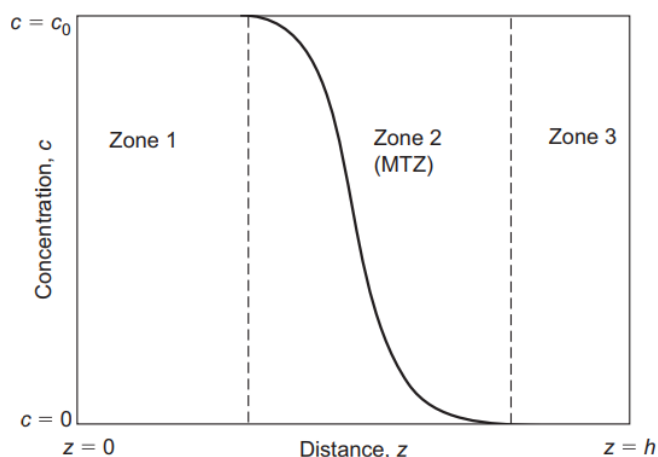


Figure 2-7: Concentration profile during single – solute adsorption in a fixed – bed adsorber of bed height, (Worch 2021)

Zone		Adsorbed amount	Inlet concentration	Adsorption capacity		Concentration in the liquid phase
Zone 1	between the adsorber inlet and the MTZ	$q = 0$	$c = c_0$	No more mass transfer	$q_0 = c_0$	$c_L = c_0$, constant
Zone 2 - MTZ		$q = 0$	$c = c_0$	Occur mass transfer	$q_0 = q_0(c_0)$	$C = 0$
Zone 3						$C = 0$

When the MTZ reaches the end of the adsorber, the adsorbate is first produced in the adsorber outlet. This period is known as breakthrough time, t_b . After the breakthrough time, the concentration in the adsorber outlet increases due to the progress of adsorption in the MTZ and the related decrease of the remaining adsorbent capacity. If the entire MTZ has left the adsorber, the outlet concentration equals c_0 . At this point, all adsorbent particles in the fixed bed are saturated to the equilibrium loading, and no more adsorbate uptake takes place. The related time is referred to as saturation time, t_s .

The concentration versus time curve, which is measurable at the adsorber outlet, is referred to as the breakthrough curve (BTC). The BTC is a mirror of the MTZ and is therefore affected by the same factors, in particular adsorption rate and shape of the equilibrium curve

The governing equation for the adsorption kinetic model i based on mass balance for the contaminant.

Desorption

If the loaded adsorbent is brought into contact with a liquid from which the adsorbate is adsorbed to a lesser extent than from the original aqueous solution, desorption into the liquid phase is possible. Thus, the respective isotherm is shifted to lower adsorbent loadings than the original isotherm. The operating time of an adsorption unit is limited by the capacity of the adsorbent. When the adsorbent capacity is exhausted, the adsorbent has to be removed from the reactor and has to be replaced by fresh or regenerated adsorbent material

The restoration of the adsorption capacity of activated carbons, in particular GAC, is typically carried out by reactivation. Although the terms “regeneration” and “reactivation” are sometimes used synonymously, it is necessary to distinguish between them because they describe different processes. The term “regeneration” describes the removal of the adsorbed substances from the adsorbent surface by desorption without irreversible transformation of

the adsorbent surface. In the case of fixed-bed adsorption, the desorption process can also be carried out directly in the adsorber. If the desorbed adsorbate concentration is measured at the column outlet, typical elution curves are obtained. Because the adsorbent bed's void volume is still filled with adsorbate solution after the adsorption stage, a throughput volume equal to the void volume is required to replace the original adsorbate solution with the desorption liquid. As a result, the effluent concentration is constant and equal to the adsorbate feed concentration at first. If the desorbate reaches the adsorber outlet, the concentration rises sharply and reaches a peak. The desorbed amount decreases with increasing time, and thus the concentration decreases as well. The shape of the elution curve and the maximum concentration are affected by a variety of factors, including the equilibrium conditions, desorption rate, and flow velocity. Because concentration decreases with increasing throughput after the maximum, an optimum throughput in terms of desorbate concentration and degree of regeneration must be found.

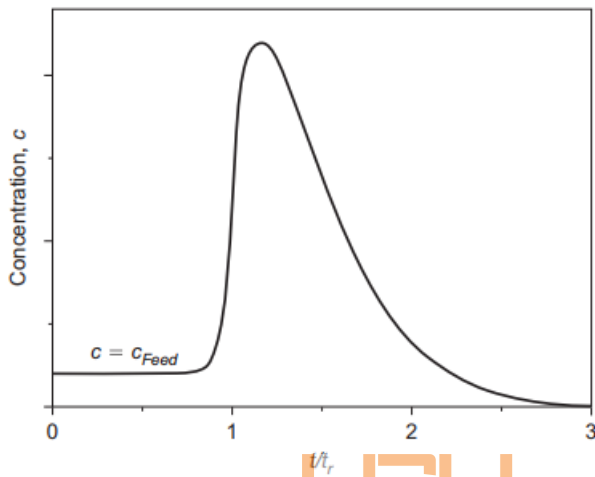


Figure 2-8: Typical elution curve as can be found for fixed bed desorption, Worch, 2021.

The desorption rate is expressed by the mass transfer equation

$$\rho_B \frac{\partial \bar{q}}{\partial t} = -k_{des}(c_{eq} - c) \quad (\text{eq. 2.11})$$

where k_{des} is the desorption rate constant, c_{eq} is the concentration of the desorbed component in equilibrium with the actual adsorbent loading, and c is the concentration of the desorbed component in the liquid phase. The isotherm completes the set of equations that must be solved in order to describe the elution curve. Under the assumption that the equilibrium will be established spontaneously at all points of the column, a simplified model can be derived (equilibrium model, Chinn and King 1999).

2.4 Biologically activated carbon systems (bGAC)

2.4.1 Biomass in biofilm

A biofilm is a community of microbes and other particles bound together in a gel by extracellular polymeric molecules (EPS). Although biofilms are composed of water on the inside, their solid state is their most distinguishing physical feature. Typically, a biofilm will have one side in contact with liquid and one side attached to a solid surface (known as the substratum).

In many cases, the biofilm itself is separated from the bulk liquid by a boundary layer that facilitates mass transfer. Accordingly, the four regions of a biofilm depicted in Figure 2.9 are the substratum, the biofilm itself, the border layer, and the bulk liquid outside the biofilm.

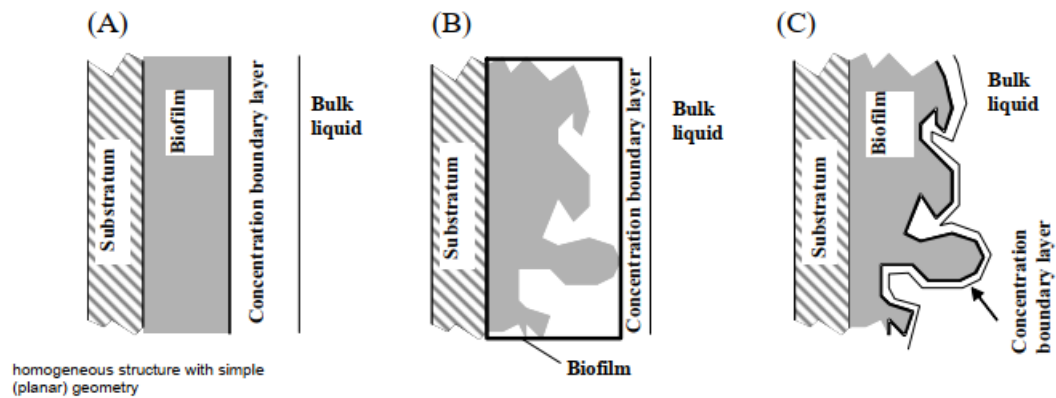


Figure 2-9: Examples of biofilm compartments modeled as a homogeneous structure with simple (planar) geometry (A), a heterogeneous structure with a geometrically simple (planar) biofilm compartment, but with irregularly shaped water pores and channels considered as part of the biofilm compartment (B), or a homogeneous structure where the irregular geometry of the biofilm compartment is strictly defined as the space occupied by the particulate components (C), (Wanner, 2006).

The biofilm compartment contains various types of liquids and solids. Although liquids make up the majority of the mass of a biofilm, solids are the focus of modeling because they give the biofilm its reactive and structural properties. Active cells, organic and inorganic particles, and EPS are among the solids. A biofilm's liquid contains water that is found inside the cells, is closely associated with the outside of the solids, or is more or less free in the spaces between the solids. A model may separate the solid and water components, or it may treat everything inside the biofilm as a single solid-like component broadly defined as "biomass."

The biofilm compartment is often covered by a **bulk-liquid compartment**. This compartment can be very large as compared to the biofilm, such as for a biofilm growing on the sediment of a lake, or it can be a thin layer of water, as in a trickling filter, soil, or dental plaque. Dissolved and particulate components can exchange between the biofilm and the bulk liquid. For example, the bulk liquid usually supplies nutrients utilized by the microorganisms in the biofilm, while pieces of biofilm solids detach from the biofilm compartment and move to the bulk-liquid compartment.

2.4.2 GAC as biofilm carrier and adsorbent

The most popular adsorbents used in water purification are activated carbons made from carbonaceous material either chemical activation or gas activation. Wood, wood charcoal, peat, lignite and lignite coke, hard coal and coke, bituminous coal, petrol coke, and residual materials like coconut shells, sawdust, or plastic residuals are among the most often used raw materials.

Powdered activated carbon (PAC) and granular activated carbon (GAC) are two forms of activated carbon utilized in slurry reactors and fixed-bed adsorbers, respectively. In the latter, water passes over a GAC filter bed, where organic compounds are adsorbed. Over time, a biofilm forms on the adsorbent particles because microorganisms in the raw water for drinking water treatment accumulate and develop there. After being exposed to biological activity, the GAC filter changes into a biologically active GAC (bGAC) filter, which serves not only as an adsorber but also as a bioreactor with additional organic adsorption and biodegradation. In addition, microorganisms capable of oxidizing ammonia do so during bGAC-filtration. It is possible for denitrification processes to occur simultaneously within the biofilm since the biofilm is not always fully oxygenated due to diffusion effects. The latter require both readily biodegradable and adsorbable organics that are both readily biodegradable and adsorbable by heterotrophic bacteria.

Weber (1977) claims that GAC is superior to other media for stimulating microbial activity because it increases contact time between the substrate and the microorganisms, concentrates the substrate through adsorption, and enriches the oxygen concentration at the surface through sorption. Even though the GAC bed is a great place for microbes to thrive, studies

haven't yet determined which organic materials decompose at what rates. In addition to the substrate's availability, its concentration is also significant. Naturally, many organics of concern are present in drinking water at such low concentrations that opportunities for microbial action may be quite limited unless adsorption occurs first; however, as stated before, adsorption may prevent biodegradation if the substrate becomes inaccessible to the microorganism. Much of the current focus on how microbes influence GAC efficiency originates from European studies and practices.

According to Hutchinson and Ridgway (1977), GAC beds have been implemented in numerous English waterworks to decrease residual organics. As proof of the significance of microbial action in the removal of organics, it was pointed out that the GAC beds were still functioning after several years of use.

Brodthmann et al. (1980) studied the long-term operation (180 days) of full-scale GAC beds at the Jefferson Parish Water Treatment Plant, located on the lower Mississippi River, and found that a relatively steady-state removal of organic precursors to chloroform production was reached after roughly 60 days of operation. The influent concentration of these precursors fluctuated by a factor of two, but their elimination converged on a steady-state level of about 50%, indicating that biological activity was responsible. There is no evidence to support the claim that particular organic compounds are removed by microorganisms but are resistant to GAC treatment. However, if performance is evaluated based on the amount of total organics removed (TOC, UV absorbance, potassium permanganate demand), it appears that the service life of a GAC bed can be prolonged by microbial action.

The superiority of GAC over sand in encouraging microbial activity was also shown in the denitrification studies conducted by Jeris et al. (1974). It was found in this investigation that growth on sand particles was insignificant. After only two weeks of operation, however, they found that nitrates had been effectively removed from the system thanks to the use of freshly activated carbon.

Filter beds will become colonized by microorganisms, mostly bacteria, due to the fact that they adsorb to GAC. They absorb nutrients from the GAC and dissolved nutrients, allowing them to expand to large populations.

Since adsorption occurs at the adsorbent's surface, its surface area is a crucial quality element in determining the efficiency of the adsorption process. When compared to extremely porous, synthetic adsorbents, natural adsorbents often have substantially lower surface areas. Activated carbons and other specialized polymeric adsorbents have the highest surface areas. Large interior surfaces provided by the pore walls are necessary for a material to have a high surface area. Engineered adsorbents have substantially bigger interior surfaces compared to their particle exteriors. A higher internal surface generally corresponds to a larger pore system and finer pores. However, for rapid adsorbate transport to the adsorption sites, a certain percentage of bigger pores is required.

Depending on the starting material and the activation method, the interior surface area of activated carbons can range from the hundreds of m^2/g to over a thousand m^2/g . Larger molecules should be able to enter the pore system and adsorb onto the inner surface of the activated carbon used in water purification, hence the pores should not be too fine. A typical range for the internal surface areas of activated carbons used in water treatment is 800-1,000 m^2/g .

Activated carbons can adsorb a wide variety of organic compounds due to their strong dispersion forces and weak intermolecular interactions (van der Waals forces). It is possible for additional attractive forces, such as π -interactions for aromatic adsorbates or electrostatic interactions between surface oxide groups and ionic adsorbates, to act on top of these. Because of their superior adsorption capacity, activated carbons are widely used as adsorbents in all methods of water purification that aim to eliminate organic contaminants. Activated carbon is effective at filtering out both the dissolved organic matter (DOM) in the water supply and the micropollutants.

It is possible for microorganisms in raw waters to colonize the adsorbent particles of a fixed-bed adsorption system. This is typical of GAC adsorbents used in the purification of

drinking water. Due to its rough surface and adsorption capabilities, activated carbon is ideal for microbial accumulation. The GAC filter acts as an adsorber and bioreactor in these setups, degrading NOM fractions and micropollutants to aid in net organic removal. The graph shows the difference between a typical DOC BTC for a GAC adsorber with biological activity and a BTC for an inactive adsorbent. Because of mass loss caused by NOM fraction degradation, the steady-state concentration of BTC is reduced. Since the biologically active carbon filter also eliminates biodegradable micropollutants, the steady-state concentration is based on the amount of NOM fractions that are biodegradable, the rate at which they degrade, and the amount of time the bed is in contact with air. In contrast to NOM, the steady-state concentration can be zero if degradation occurs quickly enough. Nonbiodegradable micropollutants may be indirectly affected by biological activities. Adsorption of nonbiodegradable micropollutants is enhanced when competition from NOM fractions is reduced due to biodegradation. The effect of biological NOM reduction is weak under normal settings because NOM consists mostly of bigger molecules that are not or very slowly degradable.

However, NOM degradation can be sped up through preozonation. After being ozonated, the NOM molecules can be taken up by microbes and oxidized with greater efficiency. Because of this, NOM decomposition is improved as a result of a higher biomass concentration within the adsorbent bed. Because of this, the concentration at the adsorber's exit should decrease at steady state. When ozonation is followed by the use of GAC, the technique is called biological activated carbon (BAC) or biologically enhanced activated carbon (Worch, 2021).

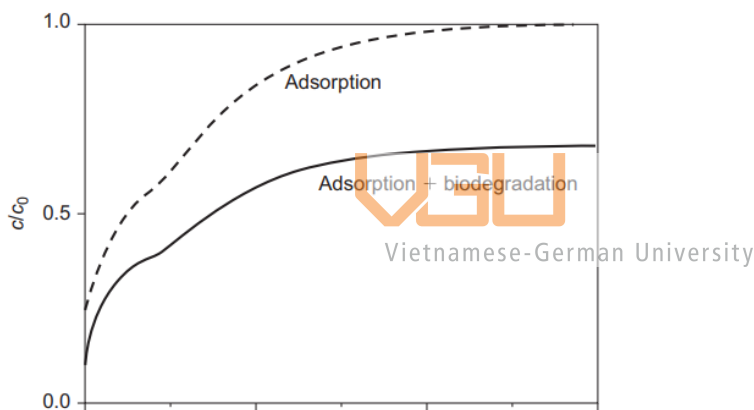


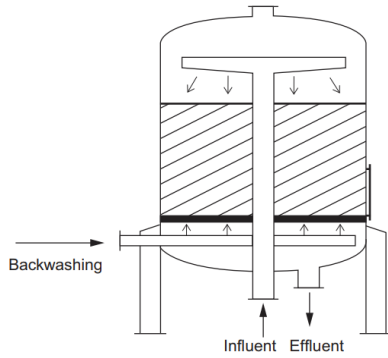
Figure 2-10: NOM breakthrough behavior in the case of adsorption with and without biodegradation (schematic), (Worch, 2021)

2.4.3 Filter bed and filter operation parameters

In fixed-bed adsorption models, several different process parameters are used to characterize the adsorbent bed and the flow conditions within the bed.

Parameters		Equation	Note
Bed density	ρ_B	$\rho_B = \frac{m_A}{V_R} = \frac{m_A}{V_A + V_L}$	m_A : Adsorbent mass V_R : Adsorber volume V_A : adsorbent volume V_L : Liquid-filled void volume
Particle density	ρ_P	$\rho_P = \frac{m_A}{V_A}$	

Parameters		Equation	Note
Bed porosity	ε_B	$\varepsilon_B = \frac{V_L}{V_R} = \frac{V_R - V_A}{V_R} = 1 - \frac{V_A}{V_R} = 1 - \frac{\rho_B}{\rho_P}$	
Adsorber volume	V_R	$V_R = A_R \times h$	A_R : cross-sectional area h : the height of the adsorber
Absorbent mass	m_A	$m_A = V_R \rho_B = A_R h \rho_B$	
Absorbent Volume	V_A	$V_A = Z_T \frac{4 \pi r_P^3}{3}$	Z_T : the total number of the (spherical) adsorbent particles in the adsorbent bed
the total number of the adsorbent particles	Z_T	$Z_T = m_A Z_{SP}$	Z_{SP} : the average number of particles per gram adsorbent
The equivalent radius adsorbent particles	r_P	$r_P = \sqrt[3]{\frac{3}{4 \pi \rho_P Z_{SP}}}$	
The total surface area in the adsorbent bed	A_S	$A_S = \frac{3 V_A}{r_P}$	
		$\alpha_{VR} = \frac{A_S}{V_R} = \frac{3 V_A}{V_R r_P} = \frac{3}{r_P} (1 - \varepsilon_B)$	
Flow/ Filter velocity	v_F	$v_F = \frac{V}{A_R}$	V : Volumetric flow rate
Effective flow velocity	u_F	$u_F = \frac{V}{A_R \varepsilon_B} = \frac{v_F}{\varepsilon_B}$	
Empty bed contact time	EBCT	$EBCT = \frac{h}{v_F} = \frac{h A_R}{V} = \frac{V_R}{V}$	The residence time for an empty reactor
Effective residence time	t_R	$t_R = \frac{h}{u_F} = \frac{h A_R \varepsilon_B}{V} = \frac{V_R \varepsilon_B}{V} = EBCT \varepsilon_B$	
The number of bed volumes fed to the adsorber	BV	$BV = \frac{V_{Feed}}{V_R} = \frac{V t}{V_R} = \frac{t}{EBCT}$	
Specific throughput	V_{sp}	$V_{sp} = \frac{V_{Feed}}{m_A} = \frac{V t}{m_A} = \frac{V t}{V_R \rho_B} = \frac{t}{EBCT \rho_B} = \frac{BV}{\rho_B}$	



Parameter	Symbol	Unit	Typical values
Bed height	h	m	2 - 4
Cross sectional area	A_R	m ²	5 - 30
Filter Velocity	v_F	m/h	5 - 20
Empty bed contact time	$EBCT$	min	5 - 30
Effective contact time	t_R	min	2 - 10
Particle diameter	d_P	mm	0.5 - 4
Bed volume	V_R	m ³	10 - 50
Bed porosity	ϵ_B	-	0.35 - 0.45

Figure 2-11: Typical fixed-bed adsorbers in water treatment: pressure GAC filter made of corrosion-resistant steel

2.5 The short introduction to modelling according to Petersen matrix notation

Mathematical modelling has an important and continued role to play in the design and operation of engineered biological systems (EBS), where the inherently complex interaction between biotic and abiotic components may result in unpredictable and undesirable process behaviour requiring operator intervention or advanced control architecture.

Over the last four decades (circa 1980 onwards), much focus has been on the development and extension of classical models based on first-principles theory and engineering knowledge. Notably, the work of several research groups coalesced around a unified mechanistic model with the aim to represent, i.e. simulate, the dynamics of the activated sludge treatment process. This reference model, the Activated Sludge Model No. 1 (ASM1), initiated a highly productive period in wastewater engineering, where mathematical modelling became a distinct and important field within the bioprocess engineering community.

The use of a structural matrix for deriving a system of equations representing biochemical reactions was first proposed by E.E. Petersen and employed in the development of a mathematical model of activated sludge systems by the IAWPRC (now International Water Association, IWA) Task Group on *Mathematical Modelling for Design and Operation of Biological Wastewater Treatment*. The conversion rates for each state variable can be simply calculated by the column-wise summation of the product of stoichiometric terms and process rates

$$R = \rho^T \cdot \Lambda = \sum_{j=1}^n \rho_j v_{i,j}, i = 1, \dots, m,$$

Where Λ is the matrix of $m \times n$ stoichiometric terms and ρ is a vector of n process specific kinetic rates.

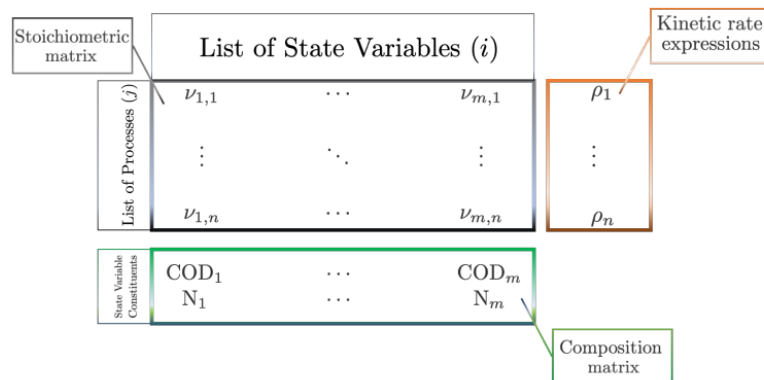


Figure 2-12 A general schematic of the Gujer/Petersen matrix.

We use $n_{i,j}$ to represent stoichiometric coefficients, r_j for process rates and indicate the two commonly used constituents in biological treatment models, Chemical Oxygen Demand (COD) and Nitrogen (Ni), (Wade 2020).

This highly structured matrix formulation for constructing biochemical reaction models was adopted as standard within the engineering community, leading to a general framework for modelling the activated sludge process, specifically related to nitrogen removal (ASM1). Naturally, this led to a number of bespoke simulation softwares to provide engineers with the tools to rapidly develop and interrogate the models through process simulation, often in a modular way (e.g., Biowin, STOAT, GPS-X, SIMBA, AQUASIM).

The model is far from perfect but its flexibility and structure means it is suitable as a tool to be used at the design stage of AD plant development, for qualitative scenario testing, or for benchmarking control schemes. As with the ASMs, modifications to the model have been implemented based on process requirements, such as operating mode.

2.5.1 Theory of biological processes in (waste) water treatment:

Heterotrophic bacteria are growing in an aerobic environment by consumption of a soluble substrate for carbon and energy. In simple concept, two fundamental processes occur: the biomass increases by cell growth and decreases by decay. In addition, oxygen utilization and substrate removal also occur that they derived from biomass growth and decay. Therefore these are not considered to be fundamental, just are coupled to them through the system stoichiometry.

In order to make the simplest model, this situation must focus on the concentration of three components: biomass, substrate and dissolved oxygen. The removal of these three components is incorporated in the two fundamental processes in Table 2.4

Table 2-4: Peterson Matrix of the mathematical model. Processes considered: growth and decay of bacteria.

Component \rightarrow i	1	2	3	
Process \downarrow j	X_B	S_S	S_O	Process Rate, p_j [ML ⁻³ T ⁻¹]
1 Growth	1	$-\frac{1}{Y}$	$-\frac{1-Y}{Y}$	$\frac{\mu S_S}{K_S + S_S} X_B$
2 Decay	-1		-1	$b X_B$
Observed conversion Rates ML⁻³T⁻¹	$r_i = \sum_j r_{ij} = \sum_j v_{ij} \rho_j$			Kinetic Parameters: Maximum specific growth rate: μ
Stoichiometric Parameters: True growth yield: Y	Biomass [M(COD) L ⁻³]	Substrate [M(COD) L ⁻³]	Oxygen [M(-COD) L ⁻³]	Half velocity constant: K_S Specific decay rate: b

Initially, the setting up the matrix start with the identification of the components involving the model. In this scenario these are **biomass, substrate and dissolved oxygen**. The index i is assigned to each component. For this simple model, i ranges from 1 to 3 for the three compounds including X represents for insoluble constituents and B stands for biomass, S specify for individual components and S stands for substrate and O for Oxygen.

The second step is developed to identify the biological processes occurring in the system. In this example, there are two processes considered: aerobic growth of biomass and its loss by decay. These processes are shown in the leftside column of the matrix. The index j is assigned to each process, $j=1$. The kinetic expressions which are used based on the simple Monod-Herbert model are recorded in the rightside column of the matrix in the appropriate row. To be more specific, according to Monod equation, p_1 means that growth of biomass is proportional to biomass concentration in a first order manner and to substrate concentration in a mixed

order manner. The expression p_2 defines the biomass decay is first order regarding biomass concentration.

The stoichiometric coefficient, v_{ij} , are included in the matrix which define the mass relationships between the elements in the each process. It is (+1) in the case generation of biomass, [-1/Y] due to expense of soluble substrate and $[-(1-Y)/Y]$ represent the consumption of oxygen for the metabolic process. These coefficients are significantly simplified by using in unity units. For example, it would be expressed as equivalent amounts of chemical oxygen demand (COD); oxygen is displayed as negative oxygen demand. In addition, the negative sign in the matrix is considered as consumption and the positive sign as production. All stoichiometric coefficients are identify in the left conner of the table.

Use in mass balance

Many different processes have an effect on the concentration of a component. The basic expression for a mass balance within the defined system boundary is:

$$\text{Input} - \text{Output} + \text{Reaction} = \text{Accumulation}$$

Transport terms of the system being modelled include the input and output terms. Calculation of the system reaction term r_i is defined by suming the products of the stoichimetric coefficients v_{ij} and the process rate expression p_j for the component i in the mass balance:

$$r_i = \sum_j r_{ij} = \sum_j v_{ij} p_j$$

$$\text{The rate of reaction, } r, \text{ for biomass } X_B \text{ would be: } r_{X_B} = \frac{\mu S_S}{K_S + S_S} X_B - b X_B$$

$$\text{The rate of reaction, } r, \text{ for biomass } S_S \text{ would be } r_{S_S} = -\frac{1}{Y} \frac{\mu S_S}{K_S + S_S} X_B$$

The rate of reaction, r , for dissolved oxygen S_o would be

$$r_{S_o} = -\left(\frac{1-Y}{Y}\right) \frac{\mu S_S}{K_S + S_S} X_B - b X_B$$

To create the mass balance for each component within a given system boundary (e.g. a completely mixed reactor), the conversion rate would be combined with the appropriate advective flow terms for the particular system. These terms have not been shown here because the purpose of the example was to demonstrate how the matrix is used to define the fundamental reactions regardless of the system configuration. It should be emphasized, however, that the modelling of a particular physical system requires definition of the system boundary with the associated advective terms.

Another benefit of the matrix is that continuity may be checked by moving across the matrix, provided consistent units have been used because then the sum of the stoichiometric coefficients must be zero. This can be demonstrated by considering the decay process. Recalling that oxygen is negative COD so that its coefficient must be multiplied by -1, all COD lost from the biomass because of decay must be balanced by oxygen utilization. Similarly, for the growth process, the substrate COD lost from solution due to growth minus the amount converted into new cells must equal the oxygen used for cell synthesis.

2.5.2 Mathematical Modelling Of Biological Processes

The development of a mathematical model acquires from making a balance of conflicting needs. Firstly, the fundamental processes occurring within the system must be considered in the way which is appropriate with knowledge about the system. In addition, it should be put a reasonable effort on the solution of the model equations. The more the number of processes, the more difficult solutions become. Moreover, the process rate expressions are simulated closely reality, they are likely to be more complicated. In many cases, the simulation should focus on the major events and select the simplest rate expressions as long as mimic well the results of those events. When the environmental conditions are changed, the process rate equations are turned on and off as the concept of switching functions.

In order to setting up the model for development of activated sludge theory, the measure of the concentration of organic material in wastewater must be consistent. Three measures

have raised acceptance and are widely used: Biochemical Oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). According to (Henze;, Gujer; et al. 2000), COD is considered as the dominant measure since it alone supplies a link between electron equivalents in the organic substrate, the biomass and the oxygen utilized. Furthermore, by using COD mass balance can be made. As a consequence, the concentrations of all organic matters are in COD units in the simulated model.

There are many ways to make a category of the organic matters. In these it can be identified by biodegradability.

- + Non – biodegradable organic matter, may be divided into two fractions, depending on their physical state, including: solule and particulate. Inert soluble organic matter, S_I , passes through the system at the same concentration that it comes in. Inert suspended organic matter, X_I , is removed from the system through sludge wastage.
- + Biodegradable organic matter classifies into two fractions: slowly biodegradable matters, X_S and readily biodegradable matters, S_S . Although there are some slowly biodegradable matter, X_S , may actually be soluble, it is treated as if it were particulate, whereas the readily biodegradable matter, S_S is treated as if it were soluble. Heterotrophic bacteria may use the readily biodegradable material, consisting of the simple molecules, for growth of new biomass. The electrons associated with that portion are transferred to the exogenous electron acceptors (oxygen or nitrate). Conversely, the slowly biodegradable material, including the relatively comples molecules, must be carried on extracellularly and converted into readily biodegradable substrate before it can be used. It is made an assumption that no energy utilization is used for the conversion of slowly biodegradable substrate into the readily biodegradable form (called hydrolysis) and therefore it does not require utilization of electron acceptor. The specific rate of hydrolysis of slowly biodegradable substrate is usually remarkably lower than the specific rate of utilization of readily biodegradable sustrate, so that it becomes the rate limiting factor in the growth of biomass when X_S alone is present as substrate. Moreover, the rate of hydrolysis is lower under anoxic conditions (only nitrate available as the electron acceptor) than under aerobic conditions and is completely stopped under anaerobic conditions (neither nitrate nor oxygen are present) (Van Haandel et al., 1981).
- + Heterotrophic biomass is produced by growth on readily biodegradable substrate under either aersonic or anoxic conditions, but is assumed to stop under anaerobic conditions. By combination of a lot of mechanisms including endogenous metabolism, death, predation and lysis, decay process leads to conversion of biomass into slowly biodegradable substrate X_S and partilulate products X_P which are impossible to further biological attack and lastly biomass is lost (Dold et al., 1980). The nature of the electron acceptors have an influence on the conversion of the resultant slowly biodegradable substrate to a form that can be used for regrowth of new cells, whereas this seems not to affect a rate of the decay process of biomass.

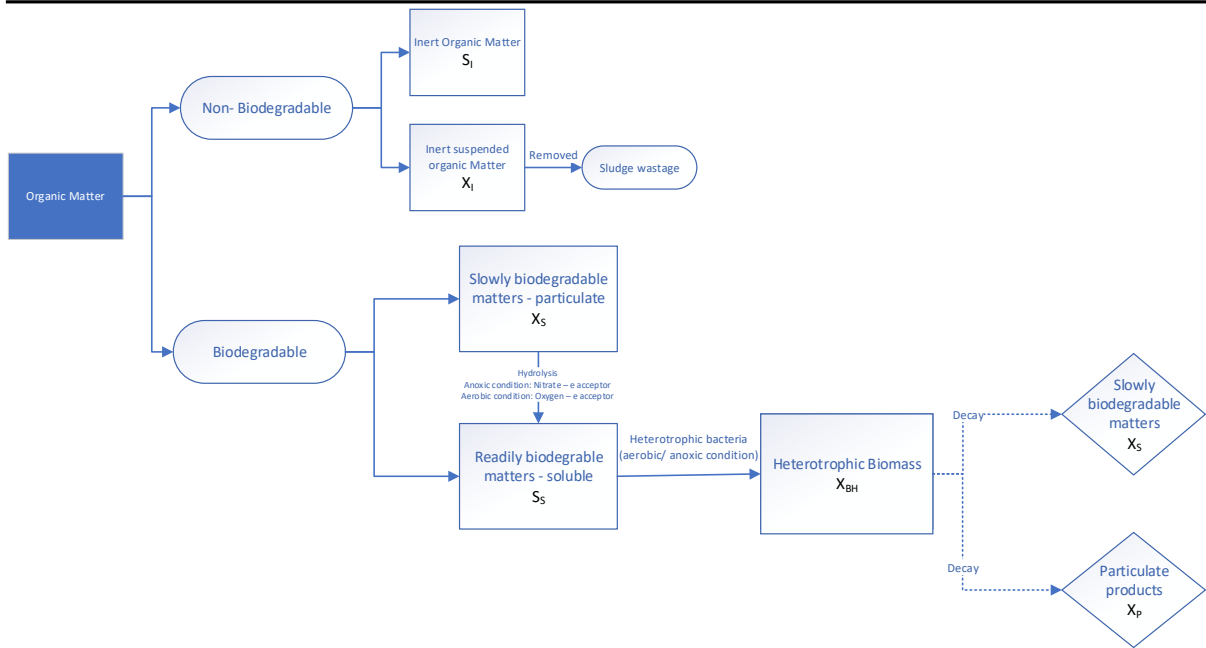


Figure 2-13: Diagram of the organic matters conversion process

Like carbonogenous matter, nitrogenous matter in wastewater can be classified into two groups: non-biodegradable and biodegradable, each with further subdivisions. In terms of the non-biodegradable fraction, the particulate portion is associated with the non-biodegradable particulate COD, the soluble portion which is usually small is not involved into the model. The biodegradable nitrogenous matter may be classified into: Ammonia (including the free compound and its salts) - S_{NH} ; soluble biodegradable organic nitrogen - S_{ND} ; Particulate biodegradable organic nitrogen - X_{ND} . Addition to the hydrolysis of slowly biodegradable organic matter, particulate organic nitrogen is also hydrolysed to soluble biodegradable organic nitrogen. The heterotrophic bacteria utilizes the soluble organic nitrogen and convert it into ammonia nitrogen. The ammonia nitrogen serves as a nitrogen supply for the synthesis of heterotrophic biomass and as the energy supply for growth of autotrophic nitrifying bacteria. As a result, it is assumed that the autotrophic conversion of ammonia nitrogen to nitrate nitrogen in the presence of oxygen only requires one step. Under anoxic conditions, the nitrate generated may act as an electron acceptor for heterotrophic bacteria, producing nitrogen gas. Finally, the release of particulate organic nitrogen during cell decay of either autotrophic or heterotrophic biomass allows it to reenter the cycle.

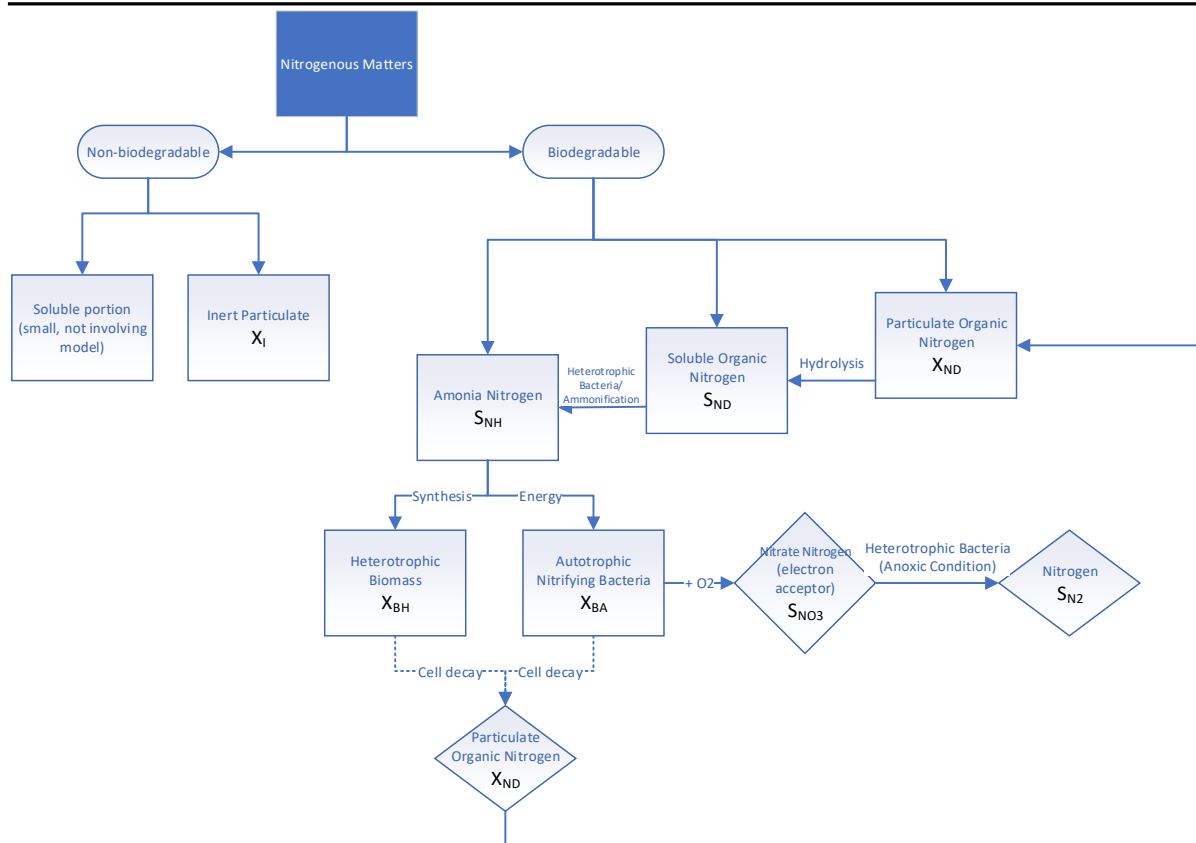


Figure 2-14: Diagram of the organic nitrogen matters conversion process

2.6 Literature review about existing bGAC models

Enhanced Activated Sludge Model No. 1 with two-step nitrification and denitrification processes is presented (Ostacey, Cristea et al. 2011). The two-stage modeling approach is used to represent the dynamics of nitrite and nitrate nitrogen concentrations under aerobic and anoxic conditions. Nitrite nitrogen accumulation may be accurately predicted, which enhances the description of the system's steady state and dynamic behavior.

In order to reduce the cost of regeneration and extend the life span of granular activated carbon (GAC) beds, the biological activated carbon (BAC) technique has been widely used in water and wastewater treatments. For the sake of modeling and optimization, researchers and operators have been trying to analyze each mechanism. Hozalski et al. (1995) found that the removal effectiveness for biodegradation was relatively constant between 4 and 20 minutes of empty-bed contact time (EBCT). According to Melin and deggard (2000), the optimum EBCT lasts about 20 minutes. Using EBCT for a longer period of time did not considerably improve removal efficiency. According to Rittmann et al. (2002), dissolved organic carbon (DOC) removal in pilot filters treating ozonated groundwater was unaffected by EBCT longer than 3.5min. When using an ozone-BAC procedure to treat raw waters, the optimum EBCT reported by Li et al. (2006) was 15 minutes.

In the open literature, some mathematical models for packed-bed biological reactors have been suggested. Based on the similarities between catalytic reactors and biofilm reactors, Rodrigues et al. (1983) created a model of a biofilm reactor that accounts for the resistance of the exterior liquid layer to mass transfer inside plug-flow and continuous-stirred tank reactors. To account for the influences of diffusional resistance inside the biofilm and back mixing of the bulk liquid in the reactor for zero-order and first-order kinetics, Beg and Hassan (1985) proposed a biofilm model for packed-bed reactors. Hassan and Beg (1987) took into account additional reaction kinetics of practical value in their biofilm model. The theoretical model for a packed-bed biological loop reactor developed by Atiqullah et al. (1990) took into account the impacts of axial and recycling backmixing.

Andrews and Tien (1981) and Tien and Wang (1982) indicated that combining biological degradation with adsorption in a single unit was a viable strategy for eliminating soluble

organic contaminants from wastewaters. The modeling of bioreactors requires an understanding of their hydrodynamics as well as the overall substrate consumption rate. In order to quantify the levels of adsorption and biodegradation, Chang and Rittmann (1987) created a mathematical model. Significantly, it shows how substrates diffuse through a biofilm, get digested by microorganisms, and then reach the GAC surface. Dispersion, convection, biodegradation, and adsorption were all proposed as mechanisms in a theoretical model of a BAC column by Sakoda et al. (1996). The most important simplification presupposes that the concentration of substrate at the biofilm/GAC contact is the same as that in the bulk solution. However, this model is not suitable for the situation with thick biofilm since it assumes there is no concentration reduction within the biofilm.

Table 2-5: Some of the representative BAC models

Reactor Type	Mechanisms considered	Kinetic condition				Mas transport description	Solution method	Ref.
		Substrate in bulk phase	Substrate in biofilm	Biofilm amount	Substrate in GAC			
Complex mixing	A, B	Non-steady monod	Monod	Non-steady	Non-equilibrium	1, 2, 3, 4, 5	Analytical	Chang and Rittmann (1987)
Column	A, B, C, D	Non-steady no biodegradation	n.a.	Non-steady	Equilibrium	1	Analytical	Sakoda et al. (1996)
Column	A, B	Uniform Monod	Monod	Non-steady	n.a ^c	1	Analytical	Walker and Weatherley (1997)
Column	A, B, C	Non-steady no biodegradation	Monod	Steady	Non-equilibrium	1, 5	Analytical	Abumaizar et al. (1997)
Column	B, C, D	Non-steady monod	Monod	Non-steady	n.a ^c	1, 2, 3	Numerical	Hozalski and Bouwer (2001)
Column	A, B, C, D	Non-steady no biodegradation	Monod	Non-steady	Non-equilibrium	1, 2, 3, 4, 5	Numerical	Badriyha et al. (2003)

A = adsorption, B = Biodegradation, C = Convection, D = Dispersion
 1 = bulk phase, 2 = interface between bulk phase and biofilm, 3 = biofilm, 4 = interface between biofilm and GAC, 5 = GAC
^c Not analyzed in the article.

Table 2-6: Typical parameter values at neutral pH (Brown, Gelman, et al. 1991)

Symbol	Unit	Value at 20°C	Value at 10°C
Stoichiometric parameters			
Y_A	g cell COD formed (gN oxidized) ⁻¹	0.24	0.24
Y_H	g cell COD formed (gN oxidized) ⁻¹	0.67	0.67
f_P	dimensionless	0.08	0.08
i_{XB}	gN (gCOD) ⁻¹ in biomass	0.086	0.086
i_{XE}	gN (gCOD) ⁻¹ in endogenous mass	0.06	0.06
Kinetic parameters			
μ_H	day ⁻¹	6.0	3.0
K_S	gCOD m ⁻³	20.0	20.0
K_{OH}	gO ₂ m ⁻³	0.2	0.2
K_{NO}	gNO ₃ -N m ⁻³	0.5	0.5
b_H	day ⁻¹	0.62	0.2
η_g	dimensionless	0.8	0.8
η_h		0.4	0.4

Symbol	Unit	Value at 20°C	Value at 10°C
K_h	g slowly biodegradable COD (g cell COD . day) ⁻¹	3.0	1.0
K_x	g slowly biodegradable COD (g cell COD) ⁻¹	0.03	0.01
μ_A	day ⁻¹	0.8	0.3
K_{NH}	gNH ₃ -N m ⁻³	1.0	1.0
K_{OA}	gO ₂ m ⁻³	0.4	0.1
k_a	m ³ . COD (g.day) ⁻¹	0.08	0.04

Table 2-7: Typical characteristics of settled domestic sewage, (Brown; Gelman; et al. 1991)

Symbol	Unit	Denmark	Switzerland	Hungary
S _S	g COD m ⁻³	125	70	100
S _I	g COD m ⁻³	40	25	30
X _S	g COD m ⁻³	250	100	150
X _I	g COD m ⁻³	100	25	70
S _{ND}	g N m ⁻³	8	5	10
X _{ND}	g N m ⁻³	10	10	15
S _{NH}	g NH ₃ -N m ⁻³	30	10	30
S _{NI}	g N m ⁻³	2	2	3
S _{NO}	g NO ₃ -N m ⁻³	0.5	1	1



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3 Chapter 3 - Model development

3.1 Introduction about AQUASIM and its advantages

An application for identifying and simulating aquatic systems is called AQUASIM. The simulation, identifiability analysis, parameter estimate, and uncertainty analysis are the four tasks it completes. The mathematical methods used are comparable, therefore identifiability and uncertainty analyses are combined to provide sensitivity analysis (Reichert 1998).

AQUASIM's initial objective is to give the user the ability to run model simulations. Such simulations show if specific model assumptions are compatible with measurable data by comparing computed outcomes with measured data. An indication that additional significant processes may need to be taken into account or that changes to the way processes are formulated are necessary is the existence of persistent differences between calculations and measurements. The user can quickly alter the model's structure and parameter values using AQUASIM (Reichert 1998).

The second duty for AQUASIM is to carry out sensitivity tests in relation to a group of chosen variables. The user can use this tool to determine the linear sensitivity functions of any arbitrary variable with regard to any of the analysis's parameters. These sensitivity functions aid in evaluating the model parameters' identifiability (identifiability analysis). Additionally, the derivatives computed in sensitivity analyses enable the user to compute the linear error propagation formula's estimation of the uncertainty in any variable. The identification of significant sources of uncertainty is made easier through the calculation of each parameter's contribution to the overall uncertainty (uncertainty analysis) (Reichert 1998).

The automatic parameter estimate of a given model structure using measurable data is AQUASIM's third significant task. This is crucial for getting accurate parameter estimates, but it's also a necessary condition for effectively contrasting various models. A single parameter estimate procedure can be created by combining various calculations, each of which describes a single experiment with the potential for multiple target variables, as well as generic and experiment-specific model parameters. For statistical evaluation of the model's suitability, the parameter estimation technique minimizes the quantitative measure of the deviation between model calculations and measurements (Reichert 1998).

Generally, the computer program AQUASIM was used to model biofilter experiments. These biofilters degraded Ammonium Nitrogen commonly found in raw water sources. Apparent steady state data from the biofilter experiments and supporting fixed bed experiments were used to estimate kinetic parameters for ammonia degradation. AQUASIM can be used to calculate substrate removal in biofilm reactors for any specified user of microbial system. It can also calculate the biofilm thickness development over time. However, its major limitation is considering the spatial variation gradients of substrate and microorganisms by the biofilm only in perpendicular direction of the substratum.

3.2 Components In Mathematical Models

ASM1 is the most widely accepted biological wastewater treatment model (Henze, 1987). It is mainly used for municipal activated sludge wastewater treatment plants and it describes the removal of organic carbon and ammonium nitrogen. The model is based on eight biological processes that describe the growth and decay of heterotrophic and autotrophic bacteria that are involved in the AS processes. Activated Sludge Model - ASM1 (Henze, Gujer, et al. 2000) consists of a set of variables that are calculated using constants provided in the literature.

The model was built on the same principles used in the activated sludge model 1 (ASM1) described in Henze et al. (2000). The rate expressions of all growth processes were described using Monod's rate equations. All bacterial species were assumed to undergo decay. The rate equation describing the synthesis of microbial biomass was expressed as a first-order process. The stoichiometric matrix and rate expressions are shown (supplementary data)

The modelling approach and components considered in the new model, denoted by the acronym ASM-Ad, are derived from the ASM1.

The chemical oxygen demand (COD) is divided into three groups: biodegradable COD, non-biodegradable COD and the active biomass (Henze et al., 2000). The total nitrogen is divided into ammonia nitrogen (S_{NH}) and organically bound nitrogen. As in ASM, microbial growth was made the keystone. Electron donor (substrate) removal and electron acceptor (oxygen or nitrogen oxides) use were linked to the appropriate microbial growth rates through stoichiometry. Organic substrate and biomass were expressed in terms of chemical oxygen demand (COD), because this parameter most clearly defines the relationship between electron donor and electron acceptor use.

Table 3.1 contains the names and symbols for the components incorporated into ASM-Ad. The symbols for the components have been formulated following the ASM#1 convention. The variables X and S indicate particulate and soluble components, respectively, with subscripts being used to define their nature. For example, O represents oxygen; S represents substrate; and BH, BA1, and BA2 represent heterotrophic biomass, AOB, and NOB, respectively. The components are the columns in the ASM-Ad matrix. The model's components are displayed across the top of the Table 3.3. Considered the very minimum for modeling an activated sludge system capable of carbon oxidation, nitrification, and denitrification, and adsorption processes, these 17 components are presented.

Table 3-1: ASM-Ad components

No.	Component	Description	Unit
1.	S_I	Inert soluble organic matter	gCOD/m ³
2.	S_S	Readily biodegradable substrate	gCOD/m ³
3.	X_I	Inert particulate organic matter	gCOD/m ³
4.	X_S	Slowly biodegradable substrate	gCOD/m ³
5.	X_{BH}	Active heterotrophic biomass	gCOD/m ³
6.	X_{AOB}	Active AOB biomass	gCOD/m ³
7.	X_{NOB}	Active NOB biomass	gCOD/m ³
8.	X_P	Particulate products arising from biomass decay	gCOD/m ³
9.	S_O	Dissolved oxygen	gCOD/m ³
10.	S_{NO_2}	Nitrite nitrogen	gN/m ³
11.	S_{NO_3}	Nitrate nitrogen	gN/m ³
12.	S_{N_2}	Molecular nitrogen	gN/m ³
13.	S_{NH}	Ammonia nitrogen	gN/m ³
14.	S_{ND}	Soluble biodegradable organic nitrogen	gN/m ³
15.	X_{ND}	Particulate biodegradable organic nitrogen Debris from biomass death and lysis	gN/m ³
16.	S_{alk}	Alkalinity	mol/l
17.	q	Adsorbed phase concentration	mg/g

For **the adsorption processes**, to simplify the system, consider only one liquid phase state variable S

COD mass change in the liquid phase = COD mass change in the adsorbed phase

$$\frac{dS}{dt} \cdot V_{mixed\ reactor} = \frac{dq}{dt} \cdot m_{GAC}$$

$$\frac{dS}{dt} \cdot V_{mixed\ reactor} = \frac{dq}{dt} \cdot V_R \cdot \rho_{bulk}$$
$$\frac{dq}{dt} = \frac{V_{mixed\ reactor}}{V_R \cdot \rho_{bulk}} \cdot \frac{dS}{dt}$$

With ρ_{bulk} being the bulk density of the GAC in the considered filter compartment.

This means that the change of 1mg/g of q in the adsorbed phase results from a concentration change of S in the pore water zone of $\frac{V_{mixed\ reactor}}{V_R \cdot \rho_{bulk}} \cdot 1 \frac{mg}{l}$. These are stoichiometric constants.



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Table 3-2: Summary of the relation between model parameters

Column	Component	Production Process	Removal Process	Stoichiometric
1.	S_I	None	None	No conversion
2.	S_S	Hydrolysis slowly biodegradable substrate X_S (under aerobic/ anoxic condition) with electron acceptor either Nitrate or Oxygen.	Growth of active heterotrophic biomass X_{BH} (under aerobic/ anoxic condition).	
3.	X_I	-	Sludge Wastage	No conversion
4.	X_S	Decay of Active heterotrophic biomass X_{BH} .	Hydrolysis/ Degradation of active heterotrophic biomass X_{BH} / active AOB biomass X_{AOB} / X_{NOB} (under aerobic/ anoxic condition).	
5.	X_{BH}	Growth on S_S (under aerobic/ anoxic, and stop under anaerobic)	Decay/ conversion into X_P / X_S	
6.	X_{AOB}	Growth on SNH (under aerobic).	Cell decay	
7.	X_{NOB}	Growth on S_{NO_2} (under aerobic).	Cell decay	
8.	X_P	Decomposition of X_{BH} X_{AOB} / X_{NOB}	Not eliminated	
9.	S_O	Supplied	Microbial decomposition \rightarrow results in slowly biodegradable substrate $X_S \rightarrow$ then recycled back into soluble substrate and utilised for further cell growth.	The 4.57 term: theoretical oxygen demand for aerobic growth of autotrophs associated with the oxidation of ammonia nitrogen to nitrate nitrogen.
10.	S_{NO_2}	Growth of nitrifying autotrophic bacteria (under aerobic)	Growth of Nitrite Oxidizing bacteria (under aerobic)	Factor 1.72 : the oxygen equivalence for anoxic growth of heterotrophic biomass associated with conversion of nitrite nitrogen to nitrate nitrogen.
11.	S_{NO_3}	Growth of Nitrite Oxidizing bacteria (under aerobic)	Degradation of heterotrophic biomass (under anoxic)	Factor 2.86 : the oxygen equivalence for anoxic growth of heterotrophic biomass associated with conversion of nitrate nitrogen to nitrogen gas.

Column	Component	Production Process	Removal Process	Stoichiometric
12.	S_{N_2}	Growth of heterotrophic biomass (under anoxic)	evapourate	
13.	S_{NH}	Ammonification of soluble biodegradable organic nitrogen S_{ND}	Synthesis for biomass growth	The $-1/Y_A$ term: Ammonia Nitrogen as a source for the aerobic growth of autotrophic biomass. The $-i_{XB}$ term: Nitrogen served as the growth of both heterotrophs and autotrophs
14.	S_{ND}	Hydrolysis of Particulate biodegradable organic nitrogen X_{ND}	Ammonification of soluble biodegradable organic nitrogen S_{ND}	
15.	X_{ND}	Decomposition (cell decay) of heterotrophic X_{BH} and autotrophic biomass X_{AOB}, X_{NOB} .	Hydrolysis	The $f_{P,iXP}$ term: associated with the inert particulate products.
16.	S_{alk}	Ammonification	-	
17.	q	Adsorbable substrates	Desorption	



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Table 3-3: Peterson Matrix of Mathematical model of ASM - Ad

#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
#	S _I	S _S	X _I	X _S	X _{BH}	X _{AOB}	X _{NOB}	X _P	S _O	S _{NO2}	S _{NO3}	S _{N2}	S _{NH}	S _{ND}	X _{ND}	S _{ALK}	q
	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gN/m ³	gN/m ³	gN/m ³	gN/m ³	g/m ³	gN/m ³		mg/g
1		$-\frac{1}{Y_H}$			1				$1 - \frac{1}{Y_H}$				$-i_{XB}$			$-i_{XB}/14$	
2		$-\frac{1}{Y_H}$			1					$(1 - \frac{1}{Y_H})/1,72$		$-(1 - \frac{1}{Y_H})/1,72$	$-i_{XB}$			$\left[\begin{array}{c} -i_{XB} \\ (1 - \frac{1}{Y_H}) \\ -\frac{1}{1,72} \end{array} \right]$	
3		$-\frac{1}{Y_H}$			1					$(1 - \frac{1}{Y_H})/2,86$		$-(1 - \frac{1}{Y_H})/2,86$	$-i_{XB}$			$\left[\begin{array}{c} -i_{XB} \\ (1 - \frac{1}{Y_H}) \\ -\frac{1}{2,86} \end{array} \right]$	
4				$1 - f_P$	-1			f_P							$i_{XB} - f_P$ $* i_{XP}$		
5						1			$1 - \frac{3,43}{Y_{AOB}}$	$\frac{1}{Y_{AOB}}$			$-\frac{i_{XB}}{Y_{AOB}}$			$\left[\begin{array}{c} -1 \\ 1 - 7Y_{AOB} \\ -\frac{i_{XB}}{14} \end{array} \right]$	
6							1		$1 - \frac{1,14}{Y_{NOB}}$	$-\frac{1}{Y_{NOB}}$	$\frac{1}{Y_{NOB}}$		$-i_{XB}$			$-\frac{i_{XB}}{14}$	
7				$1 - f_P$		-1		f_P							$i_{XB} - f_P$ $* i_{XP}$		
8				$1 - f_P$			-1	f_P							$i_{XB} - f_P$ $* i_{XP}$		
9													1	-1		$-1/14$	



#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
#	S _I	S _S	X _I	X _S	X _{BH}	X _{AOB}	X _{NOB}	X _P	S _O	S _{NO2}	S _{NO3}	S _{N2}	S _{NH}	S _{ND}	X _{ND}	S _{ALK}	q
	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gCOD/m ³	gN/m ³	gN/m ³	gN/m ³	gN/m ³	g/m ³	gN/m ³		mg/g
10		1		-1													
11														1	-1		
12	1																$\frac{V_{mixed\ reactor}}{\frac{V_R}{3} \cdot \rho_{S}}$
13		1															$\frac{V_{mixed\ reactor}}{\frac{V_R}{3} \cdot \rho_{S}}$
14	$0.8 \frac{V_R \cdot \rho_S}{V_{mixed\ reactor}}$	$0.2 \frac{V_R \cdot \rho_S}{V_{mixed\ reactor}}$															1



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3.3 Processes in the models

The mathematical model is shown in Table 3.3 in a Peterson matrix representation in which the below-mentioned processes are numbered in the first column and defined mathematically in the last column. Table 3.4 lists the fundamental processes that are a part of the model on the left, and their rate expressions on the right. Growth of biomass, degradation of biomass, ammonification of organic nitrogen, and hydrolysis of particulate organics entrapped in the biofloc are the four main processes taken into account. Modeling the growth of heterotrophic biomass is simplified by assuming that only readily biodegradable matters is available as a substrate. By entrapping in the biofloc, slowly biodegradable material is supposed to be eliminated from suspension instantly. While there, it is transformed into a readily biodegradable substrate by chemical reactions. In the model, these events are referred to as hydrolysis, although in fact they are likely to be considerably more complex. The change of active biomass into inert particle products and slowly biodegradable substrate, which re-enters the cycle of hydrolysis, growth, etc., is considered to occur during decay.

Many of the processes from ASM#1 have been transferred into ASM-Ad with no changes at all. These include ammonification of soluble organic nitrogen, hydrolysis of particulate COD and particulate organic nitrogen, and aerobic heterotrophic development. Nitrification and denitrification are the most notable additions to ASM-Ad. In addition, ASM-Ad is taken into account the adsorption process.

There are two distinct microbial communities and two distinct process steps involved in nitrification. ASM-Ad includes two autotrophic nitrification processes.

The ASM-Ad deals with alkalinity shifts in the same way that ASM-1 does. Microbial growth and hydrolysis of organic nitrogen use and generate alkalinity, respectively. The consumption of alkalinity during nitrification is assigned to the AOB, NOB. Denitrification is responsible for the production of alkalinity because nitrate oxide is converted to nitric oxide and nitrite oxide is converted to nitrogen (gas).

Dynamic surface state variables are considered immobile within the reactor. Soluble components, for example, ammonium were implemented as volume state variables. Diffusion aspects of a biofilm were not included explicitly in the model however, it was shown to be manifested in the K_s values.

The concentration profiles of the dynamic surface state variables vs. depth in the reactor are required a priori for estimation of model parameters under dynamic conditions.

The following important model extensions to ASM-Ad were made.

(1) The autotrophic biomass that is now divided in two subcomponents: the ammonia-oxidizing bacteria (X_{AOB}) and the nitrite-oxidizing bacteria (X_{NOB}), according to the two-step nitrification approach - were implemented as **dynamic surface state variables** in units of gCOD/m (Prosser, 1989) (Hiatt and Grady 2008).

(2) Other new components of the new ASM1-Ad, derived from the two-step assumption, are the nitrate (S_{NO_3}) and nitrite nitrogen (S_{NO_2}) which were considered to be one single component in the ASM1 model.

(3) Another component introduced in the ASM1-Ad model is the molecular nitrogen (S_{N_2}) – Soluble components, for example, the inlet ammonia were implemented **as volume state variables**.

(4) For the adsorption process, the relationship between the change of S_i and S_s (unit e.g. mg/l) and the adsorbed phase COD concentration q , is implemented as **dynamic surface state variables** (unit e.g. mg/g), can be achieved by applying a mass balance (this example is for the aquasim biofilm reactor compartment: Adsorption is assumed to take place only from the pore water zone).

In general, the ASM-Ad processes are listed in Table 3.4, with their respective rate equations. The names of the biological process rate equations are abbreviated as P1 to P14, which correspond to their row numbers in the ASM- Admatrix. Table 3.4 contains the ASM-

Ad matrix, which shows the stoichiometric relationship between the different components and the process rate equations. The mathematical model considered 14 processes in which 8 were biological, characterized by growth and decay of the microorganisms, 1 was ammonification of soluble organic nitrogen, 2 were hydrolysis, and 3 were adsorption desorption; these processes are defined as follows.

Table 3-4: Peterson Matrix of Mathematical Process model of ASM - Ad

		Processes	Processes rate equation ρ_j
1.	P1	Aerobic growth of heterotrophs	$\mu_H * \frac{S_S}{K_S + S_S} \frac{S_O}{K_{OH} + S_O} X_H \frac{S_{NH}}{K_{NH_{het}} + S_{NH}}$
2.	P2	Anaerobic growth of heterotrophs on S_{NO2}	$\mu_H \eta_{NO2} * \frac{S_S}{K_S + S_S} \frac{K_{OH}}{K_{OH} + S_O} \frac{S_{NO2}}{K_{NO2,HB} + S_{NO2}} X_H \frac{S_{NH}}{K_{NH_{het}} + S_{NH}}$
3.	P3	Anaerobic growth of heterotrophs on S_{NO3}	$\mu_H \eta_{NO3} * \frac{S_S}{K_S + S_S} \frac{K_{OH}}{K_{OH} + S_O} \frac{S_{NO3}}{K_{NO3,HB} + S_{NO3}} X_H \frac{S_{NH}}{K_{NH_{het}} + S_{NH}}$
4.	P4	Decay of heterotrophs	$b_H X_H$
5.	P5	Aerobic growth of AOB	$\mu_{AOB} * \frac{S_{NH}}{K_{NH} + S_{NH}} \frac{S_O}{K_{OA} + S_O} X_{AOB}$
6.	P6	Aerobic growth of NOB	$\mu_{NOB} * \frac{S_{NO2}}{K_{NO2} + S_{NO2}} \frac{S_O}{K_{OA} + S_O} \frac{K_{NHI}}{K_{NHI} + S_{NH}} X_{NOB}$
7.	P7	Decay of AOB	$b_{AOB} X_{AOB}$
8.	P8	Decay of NOB	$b_{NOB} X_{NOB}$
9.	P9	Ammonification of soluble organic nitrogen	$K_a S_{ND} X_H$
10.	P10	Hydrolysis of organics	$K_h * \frac{X_S}{X_H} \left[\frac{S_O}{K_{OH} + S_O} + \eta_H \frac{K_{OH}}{K_{OH} + S_O} \frac{S_{NO2} + S_{NO3}}{K_{NOx} + S_{NO3} + S_{NO2}} \right] X_H$
11.	P11	Hydrolysis of entrapped organic nitrogen	$\left\{ K_h * \frac{X_S}{X_H} \left[\frac{S_O}{K_X + \frac{X_S}{X_H}} \left[\frac{S_O}{K_{OH} + S_O} + \eta_g \frac{K_{OH}}{K_{OH} + S_O} \frac{S_{NO2} + S_{NO3}}{K_{NOx} + S_{NO3} + S_{NO2}} \right] \right] X_H \right\} \left(\frac{X_{ND}}{X_S} \right)$
12.	P12	Adsorption of S_I	$k \cdot S_I \cdot \left(1 - \frac{q}{q_{eq}} \right)$
13.	P13	Adsorption of S_S	$k \cdot S_S \cdot \left(1 - \frac{q}{q_{eq}} \right)$
14.	P14	Desorption	$k_{des} \cdot (q - q_{eq})$

Description of the mathematical processes

The **heterotrophic bacteria** are modelled using **three growth processes** and **one decay process** that it is assumed to have the same impact in all environmental conditions. The growth processes are modelled using Monod kinetics.

Row 1 in Table 3.4 demonstrates that the first growth process is considered to take place in aerobic conditions, denoted **aerobic growth of heterotrophic biomass**, consumes soluble substrate and produces heterotrophic biomass. The heterotrophic biomass uses the readily biodegradable substrate for growth in the presence of oxygen. Since substrate and biomass utilize COD units and oxygen is negative COD, continuity necessitates that the oxygen needs equal net COD elimination (soluble substrate removed minus cells formed). The concentrations of readily biodegradable substrate and DO determine heterotrophic biomass aerobic growth kinetics. The oxygen term is a switching function that stops aerobic development at low DO concentrations, therefore the saturation coefficient, K_{OH} , is minimal. Additionally, the heterotrophic growth processes also consume Ammonia nitrogen, it is necessary to add half saturation heterotroph coefficient $K_{NH,het}$ with the small value.

The other **two growth processes** occur in anoxic conditions. These two processes **represent** the **denitrification process** where in the absence of oxygen the heterotrophic bacteria use nitrate and nitrite as terminal electron acceptor. The substrate for growth is the same as in aerobic conditions, i.e. the readily biodegradable substrate

Row 2, 3 depicts the **anaerobic growth of heterotrophic biomass**. Denitrification in ASM-Ad was modeled using two process rate equations (P2 and P3) that represent anoxic heterotrophic growth with nitrate and nitrite as the terminal electron acceptor. As with aerobic development, it results in heterotrophic biomass at the loss of readily biodegradable substrate. Nitrate nitrogen and nitrite nitrogen is the terminal electron acceptor, and its elimination is proportional to the amount of readily biodegradable substrate removed minus the number of cells produced. Ammonia nitrogen is transformed into organic nitrogen in the biomass, as in aerobic growth. Analogous to the expression for aerobic growth is the expression for anaerobic growth. In practice, the effect of biodegradable substrate on the rate is identical, including the value of the saturation coefficient, K_S . It is known, however, that the maximum rate of substrate removal under anoxic conditions is often less than it is under aerobic conditions. There are two possible explanations for this: either μ_H is limited under anoxic conditions, or only a small proportion of the heterotrophic biomass may utilise nitrate as its terminal electron acceptor. There is currently no way to tell which of these possibilities is true. The best way to model this effect is to include an empirical coefficient, η_g , in the rate expression, with η_g less than 1.

Similar to how aerobic growth is dependent on the concentration of dissolved oxygen, anaerobic growth is dependent on the concentration of nitrate nitrogen. Further, the term $\frac{K_{OH}}{K_{OH}+S_O}$ is included to represent the fact that **oxygen inhibits anoxic growth**. Therefore, when aerobic growth slows, anaerobic growth speeds up since the coefficient K_{OH} in this expression is the same as in the expression for aerobic growth. Its major purpose, is as a switch.

Furthermore, in the absence of sufficient ammonia nitrogen, heterotrophic growth was limited by a saturation function $\frac{S_{NH}}{K_{NH,het}+S_{NH}}$, where $K_{NH,het}$ is the ammonia half-saturation coefficient for heterotrophic growth.

Similar to ASM#1, ASM-Ad uses a lumped parameter (η_{NO_2}, η_{NO_3}) to represent the variation in heterotrophic microorganism development between anoxic and aerobic environments. Given that nitrate reduction is the rate-limiting reaction in urban settings, the nitrogen transformation rate in ASM#1 was used as the basis for the lumped factor for growth with nitrate as electron acceptor (η_{NO_3} , process P3). The Ammonia nitrogen is taken into account in the Monod term process rate in the same consideration in the heterotrophic growth process.

The **nitrification process**, which is now modelled in two steps with nitrite nitrogen as an intermediate product, is represented by **two growth processes** and **two decay processes**, one for each type of biomass. Both growth processes take place in strict aerobic conditions. All the biomass in the system uses ammonia as nitrogen source for mass assimilation into their cell. Therefore, the ammonia concentration is decreased by each type of microorganisms present in the model. The ammonia concentration is significantly reduced by the ammonia oxidizing bacteria that also use ammonia as substrate for growth during the first

step of the nitrification process. Ammonia concentration only increases during the ammonification process of soluble organic nitrogen.

The **first step of the nitrification process** in **row 5** is accomplished by the ammonia oxidizing bacteria. The substrate for growth is free ammonia nitrogen (Suzuki et al., 1974) and the end product is nitrite nitrogen. Row 5 of the table depicts the aerobic growth of autotrophic biomass. Nitrifiers take their metabolic energy from soluble ammonia nitrogen, leading to an increase in autotrophic cell mass and the production of nitrite nitrogen. The biomass also accumulates a trace amount of ammonia. The quantity of ammonia nitrogen oxidized is directly proportional to the quantity of oxygen consumed. The dependence of the autotrophic specific growth rate on the soluble concentrations of ammonia nitrogen and oxygen, the latter serving as a switching function, is expressed by means of a double saturation function. The saturation K_{NH} and K_{OA} coefficients are both low. While it is well-known that the pH of the wastewater in which autotrophic biomass is growing has an effect on the growth of the organisms, this dependence was not accounted for in the rate equation due to the difficulties of properly determining the pH in a bioreactor. Instead, the alkalinity should be used to figure out pH issues

The **nitrite nitrogen** is further synthesized to nitrate nitrogen by the nitrite oxidizing bacteria (X_{NOB}), described in **row 6**.

The approach adopted for modelling **decay of the heterotrophic biomass** is basically the death-regeneration concept of Dold et al. (1980) and is depicted in **row 4** of Table 3.4. There it can be seen that the adopted rate expression is quite simple, example first order with respect to the heterotrophic biomass concentration. The rate coefficient, however, is different in both concept and magnitude from the usual decay coefficient. In this case, decay acts to convert biomass to a combination of particulate products and slowly biodegradable substrate. No loss of COD is involved in this split and no electron acceptor is utilized. Furthermore, decay continues at a constant rate regardless of the environmental conditions (i.e. b_H is not a function of the type of electron acceptor or its concentration). The slowly biodegradable substrate formed is then hydrolysed, as depicted in **row 7**, releasing an equivalent amount of readily biodegradable COD. If conditions are aerobic, that substrate will be used to form new cells with concomitant oxygen uptake. If conditions are anoxic, cell growth will occur at the expense of nitrate nitrogen. If neither oxygen nor nitrate nitrogen are available, no conversion occurs and slowly biodegradable substrate will accumulate. Only when aerobic or anoxic conditions are resumed will it be converted and used.

The ammonification of soluble organic nitrogen (**row 9**), hydrolysis of entrapped organics (**row 10**) and entrapped organic nitrogen (**row 11**) are modelled in the same way as for the ASM1. The equivalent for the nitrite oxidation is the term 1.14. For the denitrification process the nitrate oxygen equivalent is 2.86 g O₂/NO₃-N and for the nitrite the value is equal to 1.72 g O₂/NO₂-N. These theoretical values mean that 1.72 g of COD is needed to reduce 1 g of NO₂-N and 2.86 g of COD to reduce 1 g of NO₃-N.

For **the adsorption processes**, to simplify the system, consider only one liquid phase state variable S. The influent is assumed to contain 80% of the rapidly biodegradable substrate, 20% of the slowly biodegradable substrate.

COD mass change in the liquid phase = COD mass change in the adsorbed phase

$$\frac{dS}{dt} \cdot V_{mixed\ reactor} = \frac{dq}{dt} \cdot m_{GAC}$$

$$\frac{dS}{dt} \cdot V_{mixed\ reactor} = \frac{dq}{dt} \cdot V_R \cdot \rho_{bulk}$$

$$\frac{dq}{dt} = \frac{V_{mixed\ reactor}}{V_R \cdot \rho_{bulk}} \cdot \frac{dS}{dt}$$

With ρ_{bulk} being the bulk density of the GAC in the considered filter compartment.

This means that the change of 1mg/g of q in the adsorbed phase results from a concentration change of S in the pore water zone of $\frac{V_{\text{mixed reactor}}}{V_R \cdot \rho_{\text{bulk}}} \cdot 1 \frac{\text{mg}}{\text{l}}$. These are stoichiometric constants.

The liquid phase concentration of each adsorbable state variable defines its adsorption rate, whereas the adsorptive driving force (represented by $1 - \frac{q}{q_{eq}}$) decreases with increasing adsorptive saturation (represented by $\frac{q}{q_{eq}}$). By implementing it this way, the ratios of the liquid phase adsorbable state variables are kind of included (if one state variable is present only in a very small concentration, then its adsorption rate is very small). In addition, both state variables can adsorb until q equals q_{eq} . The kinetic reaction model delivers:

$$\frac{dq}{dt} = k \cdot S_S \left(1 - \frac{q}{q_{eq}}\right) \text{ and } \frac{dq}{dt} = k \cdot S_I \left(1 - \frac{q}{q_{eq}}\right)$$

Adsorption takes place only when $q_{eq} > q$, but when $q > q_{eq}$ desorption occurs. The constant variable k_{des} represents the desorption rate constant and should be significantly smaller than the adsorption rate constant under consideration that a small change in q leads to a big change in liquid phase concentrations. A fractionation for the desorption will be assumed as 0.8 for S_I and 0.2 for S_S (appropriate proportion compared to its fraction in the influent).

The kinetic constant k will be fitted and can be implemented in Aquasim as a constant variable. $q_{eq} \left(\frac{\text{mg}}{\text{g}}\right)$ being the equilibrium adsorbed phase concentration, can be implemented as a **formula variable**

$$q_{eq} = K \times (S_S + S_I)^n$$

Table 3-5: Stoichiometric kinetic and rate expression of the adsorption process.

	Process	S_I	S_S	q	Rate expression
12	Adsorption of S_I	1		$\frac{V_{\text{mixed reactor}}}{3} \cdot \frac{\rho_{\text{S}}}{1000 \text{mg}} \cdot \frac{\text{mg}}{\text{g}}$	$\text{if } q_{eq} > q \text{ then } k \cdot S_I \cdot \left(1 - \frac{q}{q_{eq}}\right) \text{ else } 0 \text{ endif}$
13	Adsorption of S_S		1	$\frac{V_{\text{mixed,reactor}}}{3} \cdot \frac{\rho_{\text{S}}}{1000 \text{mg}} \cdot \frac{\text{mg}}{\text{g}}$	$\text{if } q_{eq} > q \text{ then } k \cdot S_S \cdot \left(1 - \frac{q}{q_{eq}}\right) \text{ else } 0 \text{ endif}$
14	Desorption	$0.8 \cdot \frac{V_R \cdot \rho_{\text{S}}}{V_{\text{mixed reactor}} \cdot 1000 \frac{\text{mg}}{\text{g}}}$	$0.2 \cdot \frac{V_R \cdot \rho_{\text{S}}}{V_{\text{mixed reactor}} \cdot 1000 \frac{\text{mg}}{\text{g}}}$	1	$\text{if } q > q_{eq} \text{ then } k_{\text{des}} \cdot (q - q_{eq}) \text{ else } 0 \text{ endif}$

3.4 Reactor configuration

To model the inherently nonlinear biofilm system, a computer program (AQUASIM) was used (Wanner and Morgenroth 2004). The biofilm model described by (Reichert 1998) is implemented into AQUASIM as a biofilm reactor compartment (BRC). The model is set up with 3 series of biofilm reactor compartments which will be connected to the three fully mixed reactor. It is necessary to define the input loadings for the first of the three biofilm reactor compartments in a series.

On the outer surface of GAC particles, a biofilm was anticipated to exist. The substrate spread through the biofilm and was decomposed according to the kinetics of Monod. Consideration was also given to the biofilm's growth and decomposition in response to substrate deterioration, endogenous decay, and hydrodynamic shearing. Substrate movement

in the liquid phase was regulated by plug flow, and the transport resistance of the liquid film between the liquid phase and biofilm is neglected. The model was used to the treatment of 20-100 ug/L concentrations of organic compounds. These levels are common for drinking water treatment.

In columns packed with sorptive media, surface-attached microorganisms have access to two possible substrate sources: the liquid phase and the sorbed phase. Previously adsorbed chemicals can diffuse to the GAC's outer surface, desorb, and become accessible to microorganisms. Speitel et al. (1987) studied the capability of the model to simultaneously estimate effluent concentration and the biodegradation rate of sorbed substrate (bioregeneration) at specified positions within the GAC column.

A computational model was created to estimate the adsorption and biodegradation quantities of a BAC column under steady-state conditions in order to predict the effluent concentration, biomass profiles, and the residual adsorption capacity. (1) the granules utilized in BAC are spherical, and the biofilm is homogeneous with a constant density; (2) the concentration of particulate matter in the influent is negligible; and (3) the boundary layer resistance of dissolved variables is disregarded. Fixed-bed reactors were one of the earliest systems utilized for the removal of organic contaminants from wastewaters, and due to their simple mechanical construction, low energy requirements, and low operating costs, they are still widely employed.

The approaches were considered. In the first, the GAC external surface was separated into two portions, one with microbial growth and one without microbial growth. The intent was to construct within one model a biodegradation model for the first portion and an adsorption model for the second portion.

In order to simplify the model, assumptions were used as input for the initial biofilm reactor compartments. The influent is assumed to contain 80% of the rapidly biodegradable substrate, 20% of the slowly biodegradable substrate, and the remaining ingredients given in Table 3.6. The input for the other compartments of the biofilm reactor will be automatically defined by advective linkages, while the input for the compartments of the mixed reactor will be automatically defined by diffusive linkages.

Table 3-6: Influent concentration in the simulation

No.	Component	Description	State	Value	Standard Deviation	Unit
1.	$S_{I,in}$	Initial inert soluble organic concentration	Constant Variable	1	1	gCOD/m ³
2.	$S_{S,in}$	Initial readily biodegradable substrate concentration	Constant Variable	3	1	gCOD/m ³
3.	$S_{NH,in}$	Initial N-NH ₃ concentration	Constant Variable	0.5	1	gN/m ³
4.	$S_{NO_2,in}$	Initial N-NO ₂ concentration	Constant Variable	0.005	1	gN/m ³
5.	$S_{NO_3,in}$	Initial N-NO ₃ concentration	Constant Variable	1	1	gN/m ³
6.	$S_{O,in}$	Initial dissolved oxygen concentration	Constant Variable	5	1	gCOD/m ³

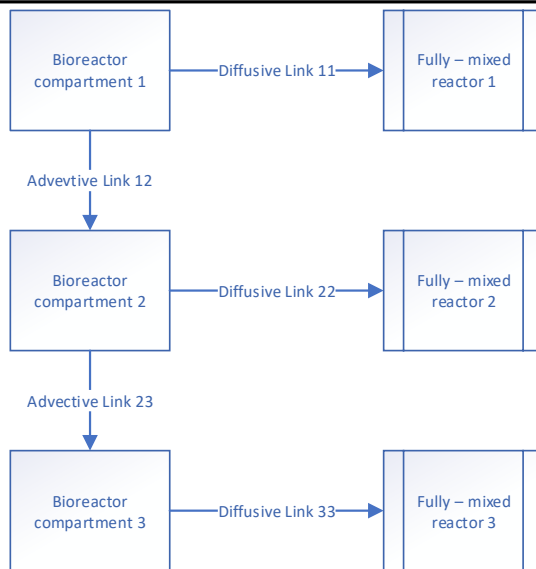


Figure 3-1: The proposed reactors in the simulation

3.4.1 Determination the Granular Activated Carbon's operational parameters

The biofilm compartment of AQUASIM software was used for modeling. The reactor was defined as the confined type with total adsorbent volume (Volume of GAC) equal to 0.001 m³. This value was determined by the reactor volume and empty bed volume of the GAC used. The value of ρ_S stands for a density of GAC and is regarded as a **constant variable** in all reactor compartments. Only the liquid phase was considered in the pore volume and the biofilm matrix was defined as rigid, that is, without diffusive transport of solids. Table 3.7 summarizes the relevant operational parameters for the modeled experimental based on the typical parameters suggested in Table 2.12.

Table 3-7: The operational parameters of the model.

Parameter		Unit	Value	Formula
Surface loading rate		m ³ /m ² .d		
Empty bed contact time	EBCT	min	30	
Porosity	ε_B	-	0.46	
Influent pH	-	-	6.0	
Media size	d	m	0.0004	
GAC density	ρ_S	g/m ³	440000	
Bacterial density	ρ	gCOD/m ³	25000	
Absorbent mass	m_A	g	440	$m_A = V_R \rho_B = A_R h \rho_B$
Flowrate	Q_{in}	m ³ /d	0.048	$Q_{in} = \frac{V_R}{EBCT}$
Cross-sectinal area	A_R			$A_R = \frac{V_R}{h}$
The adsorbent surface area	A_{GAC}	m ²	2.7	$A_S = V_R \frac{3}{r_p} (1 - \varepsilon_B)$ $r_p = d/2$

Parameter	Unit	Value	Formula	
			$A_{GAC} = \frac{3 \times \frac{V_R}{3} \times (1 - \epsilon_{packed})}{\frac{d_{GAC}}{2}}$ $= \frac{0.001 \text{ m}^3 \times 0.54}{0.0002}$ $= 2.7 \text{ m}^2$ <p>(divided V_R by 3 consistent with setting up 3 biofilm reactors)</p>	
Absorbent volume	V_R	m^3	0.001	$V_R = A_R \times h$
Depth	h	m	-	$h = \frac{V_R}{A_R}$

3.4.2 Initial operation parameters for biofilm reactor compartment

Each BRC was chosen in AQUASIM to be **confined**, its biofilm matrix to be **rigid**, and its pore volume to be composed entirely of **liquid**. AQUASIM determined biofilm area using the geometric mean of the sieve sizes for each filter medium as the particle radius.

There are three distinct regions within a biofilm: the bulk volume, the biofilm matrix, and the pore volume. While the program will use the initial conditions specified for state variables and the variable biofilm thickness, the initial conditions for other types of variables are ignored. An extra **program variable**, **LF**, is defined to account for **biofilm thickness**.

For **the biofilm reactor compartments**, the reactor volume is the space between the GAC grains in the filter bed can be calculated by the packed porosity of the filter bed.

$$V_{R,BFR} = \frac{V_R}{3} \times \epsilon_{packed} = \frac{0.001 \text{ m}^3}{3} \times 0.46 = 0.153 \times 10^{-3} \text{ m}^3$$

Regarding the influent *concentrations of the particulate state variables* in the biofilm reactor compartments, it is simply assumed that they equal **zero**, implying that there are only dissolved components in the influent. It is, however, critical to define initial conditions for the particulate state variables in the biofilm matrix and to assume low initial biomass concentrations. Furthermore, The dominant transport process for dissolved components inside the biofilm compartment usually is molecular diffusion and The effective diffusion coefficient tends to be inversely proportional to the biomass density. The **diffusion coefficients (D_s)** are required to determine the properties of the dissolved components. In order to calculate the predict the distribution of microbial species within the biofilm or to calculate the expected biofilm thickness at steady state, then microbial growth and detachment processes are essential.

Table 3-8: Model parameters in biofilm reactor compartments


Model Parameter in biofilm reactor compartments	State	Unit	Value	
Number of reactors in series	-		3	
Pore Diffusivity	D_s	Formular Variable	m^2/d	2×10^{-5}
Bacterial Density	ρ	Formula Variable	gCOD/m^3	25000
Nitrogen Bacterial Density	ρ_N	Formula Variable	gN/m^3	2000

Model Parameter in biofilm reactor compartments		State	Unit	Value
Biofilm Thickness	LF	Program Variable	m	-
Detachment rate	k_{Det}	Constant Variable	1/ (m*d)	10000
Inflow	Q_{in}	Formula Variable	m ³ /d	0.048

Determination the surface detachment velocity:

Because of the potential for negative bulk volumes, it is also important to set the surface detachment velocity of the biofilm before running the model. If the biofilm is allowed to grow unchecked by limiting its surface detachment velocity, its volume will eventually exceed that of the biofilm reactor compartment. Wanner and Gujer (1986) propose a rate expression equal to $k_{Det} \times \rho \times LF$ to characterize the surface detachment velocity as a function of biofilm thickness. However, the unit of the surface detachment velocity in Aquasim (L/T) does not correspond with the equations from the literature, which use the unit M/(L²*T). The formula is modified to $k_{Det} \times LF$ in order to incorporate it into Aquasim. This means that the rate of detachment from the surface is a first-order rate law, independent of the density of bacteria. However, it was a failure.

Table 3-9: Different detachment rate expressions reported in the literature with corresponding biofilm dynamics under constant load conditions (based on Peyton and Characklis, 1993).

Resulting biofilm dynamics for constant loading	Reported detachment rate expression (ML⁻²T⁻¹)	Refs.
Unrestricted growth	 Vietnamese-German University	Kissel et al., 1984; Frunhen et al., 1991
Constant	Constant biofilm thickness defined	Wanner and Gujer, 1984
Constant	$k_{Det} X_f^2$	Trulear and Characklis, 1982; Bryers, 1984
Constant	$k_{Det} \rho_f L_f \tau^{0.58}$	Rittmann, 1982
Constant	$k_{Det} \rho_f L_f^2$	Wanner and Gujer, 1986
Constant	$L_f (k'_{Det} + k''_{Det} \mu)$	Speitel and DiGiano, 1987
Constant	$k_{Det} \rho_f L_f$	Kreikenbohm and Stephan, 1985; Chang and Rittmann, 1987; Rittmann, 1989
Dynamic variations with a constant average thickness over time	$\begin{cases} 0 & \text{during operation} \\ k_{Det} (L_f - L_{base\ thickness}) & \text{during backwashing} \end{cases}$	Morgenroth and Wilderer, 1999

$k_{Det}, k'_{Det}, k''_{Det}$ = detachment rate coefficients, X_f =biofilm areal mass density, ρ_f = biofilm volumetric mass density, L_f = biofilm thickness, $L_{base\ thickness}$ =biofilm thickness after backwashing, μ =specific growth rate, τ =shear stress

To solve the numerical problems and continue with the simulation, the surface detachment velocity expression $k_{Det} \times LF$ would be transformed into $k_{Det} \times LF^2$. The reason for this is because the second order expression provided a low detachment velocity for thin

biofilms but a high one for thick biofilms. There appears to be a steady state achieved here, with the biofilm thickness remaining constant (biofilm formation equals biofilm detachment). The kinetic constant in a second order equation takes the form $1/(L^*T)$.

Table 3-10: Initial condition in the biofilm reactor compartments.

Initial conditions inserted in the software	Location	Unit	Formula/ Value
Surface Detachment Velocity	ϑ_{Det}	Biofilm Reactor 1, 2, 3	m/d $K_{Det} * LF^2$
Biofilm Reactor Volume	$V_{R,BFR}$		m ³ 0.153*10 ⁻³
Activated Variables	<i>Substrates:</i> S_S, S_I, S_O	Biofilm Reactor 1, 2, 3	gCOD/m ³ -
	$S_{NO_2}, S_{NO_3}, S_{N_2}, S_{NH}, S_{ND}$	Biofilm Reactor 1, 2, 3	gN/m ³ -
	S_{alk}	Biofilm Reactor 1, 2, 3	Mol/l -
	<i>Biomass:</i> $X_I, X_S, X_{BH}, X_{AOB}, X_{NOB}, X_P, X_{ND}$	Biofilm Reactor 1, 2, 3	gCOD/m ³ -
Activated processes	Process 1 → Process 11	Biofilm Reactor 1, 2, 3	- -
Initial Condition	LF (Biofilm Matrix)	Biofilm Reactor 1, 2, 3	m 10 ⁻⁸
	$X_I, X_S, X_{BH}, X_{AOB}, X_{NOB}, X_P$	Biofilm Reactor 1, 2, 3	gCOD/m ³ 0.1ρ = 2500
	X_{ND}	Biofilm Reactor 1, 2, 3	gN/m ³ 0.1ρ _N = 200
Input (Variable: Loading)	$S_S: Q_{in} * S_{Sin}$	Biofilm Reactor 1	gCOD/d $Q_{in} * S_{Sin} = 0.144$
<i>Advective linkages will define the input for the other biofilm reactor compartments automatically</i>	$S_I: Q_{in} * S_{Iin}$	Biofilm Reactor 1	gCOD/d $Q_{in} * S_{Iin} = 0.048$
	$S_O: Q_{in} * S_{Oin}$	Biofilm Reactor 1	gCOD/d $Q_{in} * S_{Oin} = 0.24$
	$S_{NH}: Q_{in} * S_{NH,in}$	Biofilm Reactor 1	gN/d $Q_{in} * S_{NH,in} = 0.024$
	$S_{NO_2}: Q_{in} * S_{NO_2,in}$	Biofilm Reactor 1	gN/d $Q_{in} * S_{NO_2,in} = 0.00024$
	$S_{NO_3}: Q_{in} * S_{NO_3,in}$	Biofilm Reactor 1	gN/d $Q_{in} * S_{NO_3,in} = 0.048$
Density of particulate Variables	$X_I, X_S, X_{BH}, X_{AOB}, X_{NOB}, X_P$	Biofilm Reactor 1, 2, 3	gCOD/m ³ ρ = 25000
	X_{ND}	Biofilm Reactor 1, 2, 3	gN/m ³ ρ _N = 2000
Dissolved Variables's Pore Diffusivity	$S_S, S_I, S_O, S_{NO_2}, S_{NO_3}, S_{N_2}, S_{NH}, S_{ND}, S_{alk}$	Biofilm Reactor 1, 2, 3	m ² /d $D_S = 2 \times 10^{-5}$

The process of reactions of heterotrophs biomass (processes 1 to 4), autotroph biomass (processes 5 to 8), ammonification of soluble organic nitrogen (process 9), hydrolysis of organic (process 10), and hydrolysis of organic nitrogen (process 11) are taken into account in the three biofilm reactor compartments. It is assumed that there is no any adsorption process taken place here. Therefore, only process 1 to process 11 will be activated for modelling.

3.4.3 Initial operation parameters for mixed reactor compartment

Assuming that the fully mixed reactor compartments constitute a thin layer between the biofilm base and the GAC, it is essential to create another **constant variable** V_R that represents the total volume of the GAC filter divided by the number of biofilm reactor compartments.

For **the mixed reactor compartments**, the input will be specified by the diffusive linkages from each biofilm reactor compartment, thus input loadings are not necessary. In addition, **adsorbed phase concentration** q is activated as a state variable in the compartment and aside from S_i , S_s , and q , initial conditions for the state variable are not required to be defined (all have to be 0). The **volume of the mixed reactor compartments** simulates the space between the biofilm base and the grain outer layer of the GAC. This layer is responsible for adsorption onto the outside surface of the GAC particle. In order to establish the volume of the reactor, requires knowing the outer surface of the GAC grains in the corresponding filter bed section, and therefore it is necessary to **assume the thickness of this layer** ($LM = 10^{-9}$). Since this fictional layer was too thin, it is assumed that its volume is best represented by a cuboid to simplify the calculation.

$$A_{GAC} = \frac{3 \times \frac{V_R}{3} \times (1 - \varepsilon_{packed})}{\frac{d_{GAC}}{2}} = \frac{0.001 \text{ m}^3 \times 0.54}{0.0002} = 2.7 \text{ m}^2$$

$$V_{R,MR} = A_{GAC} \times LM = 2.7 \times 10^{-9} \text{ m}^3$$

The adsorption process rate is expressed using the adsorption kinetic rate constant, k , the constant variable, and q , the surface state variable. After determining the reactor volumes ($2.7 \times 10^{-9} \text{ m}^3$), k will be defined because this is affected by the reactor geometry. The Freundlich k and Freundlich n values were carefully studied in order to achieve a higher equilibrium adsorbed phase concentration, with $n = 0.25$ and $K = 20$ being chosen, respectively.

Table 3-11: Initial condition in the mixed reactor compartments.

Adsorption Parameters	process	State	Value	Unit
Adsorption kinetic rate constant	k	Constant Variable	10^7	1/h
Desorption kinetic rate constant	k_{des}	Constant Variable	1	1/h
Freundlich coefficient	K		20	(mg/g)/(mg/l) ⁿ
Freundlich exponent	n	-	0.25	-

The adsorption process of easily biodegradable substrates (Process 12), the adsorption process of soluble inert organic substrates (Process 13), and desorption (Process 14) will all be taken into account in the mixed reactor compartments.

3.5 Model Parametrization

The ASM-Ad parameters and default values are listed in Table 3.12. The ASM_Ad default parameters were established using ASM#1 default parameters (Grady et al., 1999). Values for new parameters were established on the basis of a combination of microbiological principles, literature reports.

The substrate concentration (in g/m³ or mg/l) that supports a growth rate of half the maximum is denoted by the half saturation constant, also known as the substrate saturation constant or substrate affinity constant.

Table 3-12: ASM – Ad parameter description and default values (at 20°C).

Description	Parameters	ASM - 1	ASM - Ad	Unit	Literature
Heterotrophic biomass					
Maximum specific growth rate, heterotrophs	μ_H	4	4	Day ⁻¹	0.6 – 13.2
Heterotrophic decay rate	b_H	0.3	0.3	Day ⁻¹	0.06 – 1.00
Half – saturation coefficient for heterotrophs growth	K_S	10	10	gCOD/m ³	5 - 225
Half – saturation coefficient for Oxygen, heterotrophs growth	K_{OH}	0.2	0.2	gO ₂ /m ³	0.01 – 0.2
Heterotrophic yield	Y_H	0.67	0.67	gCOD/gCOD	0.38 – 0.75
Half – saturation coefficient for Nitrate – nitrogen, heterotrophs	$K_{NO3,HB}$	0.5	0.5	gN/ m ³	0.1 -0.5
Half – saturation coefficient for Nitrite – nitrogen, heterotrophs	$K_{NO2,HB}$	0.5	0.5	gN/ m ³	0.1 -0.5
Half-saturation coefficient for Amonia, NH ₃ , heterotrophs	$K_{NH,het}$	-	0.05	gN/m ³	
Autotrophic biomass					
Maximum specific autotrophic growth rate	μ_A	0.5	-	Day ⁻¹	0.2 - 1
Maximum specific growth rate, AOB	μ_{AOB}	-	0.5	Day ⁻¹	0.5 – 2.21
Maximum specific growth rate, NOB	μ_{NOB}	-	0.68	Day ⁻¹	0.8 – 1.8
Anoxic growth rate correction factor	η_g	0.8	-	Dimensionless	0.6 - 1
Anoxic growth rate correction factor S _{NO2} , Process 2.	η_{NO2}	-	0.8	Dimensionless	0.6 - 1
Anoxic growth rate correction factor S _{NO3} , Process 3.	η_{NO3}	-	0.8	Dimensionless	0.6 - 1
Autotrophic decay rate	b_A	0.05	-	Day ⁻¹	0.05 – 0.2
AOB decay rate	b_{AOB}	-	0.05	Day ⁻¹	0.05 – 0.2
NOB decay rate	b_{NOB}	-	0.05	Day ⁻¹	0.05 – 0.2
Half – saturation coefficient for autotrophs	K_{NH}		1	gNH ₃ -N//m ³	

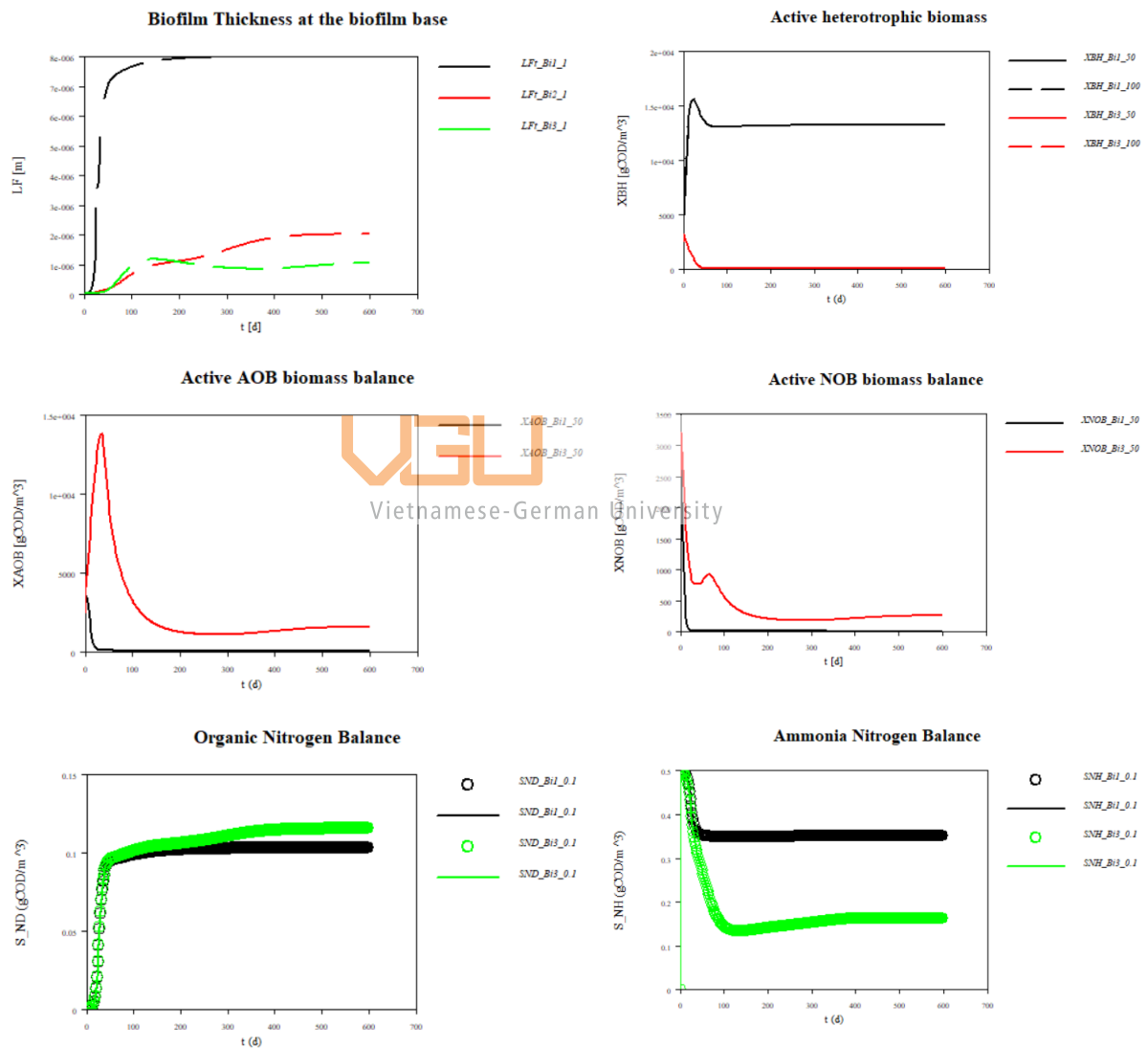
Description	Parameters	ASM - 1	ASM - Ad	Unit	Literature
Ammonia inhibition coefficient of nitrite oxidation	$K_{NH,I}$	-	5	gN/m ³	0.05
Half – saturation coefficient for Oxygen, autotrophs growth	K_{OA}	0.4	0.4	gO ₂ /m ³	0.4 - 2
Autotrophic yield	Y_A	0.24	-	g biomass COD formed/ g Nitrogen removed	0.07 – 0.28
AOB yield	Y_{AOB}	-	0.21	gCON/gN	0.07 – 0.28
NOB yield	Y_{NOB}	-	0.03	gCON/gN	0.11 – 0.21
Soluble organic nitrogen					
Ammonification rate coefficient	K_a	0.05	0.05	m ³ /(g biomass COD.d)	0.1608
Hydrolysis coefficient	K_h	3	3	gCOD/(g biomass COD.d)	2.208
Half – saturation coefficient for hydrolysis of slowly biodegradable substrate	K_x	0.1	0.1	gCOD/g biomass COD	0.15
Anoxic hydrolysis rate correction factor	η_g	0.8	0.8	dimensionless	0.4
Other parameters					
Fraction active biomass contributing to biomass debris	f_P	0.08	0.08	g debris COD/g biomass COD	-
Mass of nitrogen per mass of COD in active biomass	i_{XB}	0.08	0.08	gN/gCOD in active biomass	
Mass of nitrogen per mass of COD in biomass debris/ particulate products	i_{XD}/i_{XP}	0.06	0.06	gN/gCOD in biomass debris	

3.6 Results and discussion

The model is set up with **three series of biofilm reactor compartments which will be connected to the three fully mixed reactor**. It is necessary to define the input loadings for the first of the three biofilm reactor compartments in a series. Advective linkages will define the input for the other biofilm reactor compartments automatically while diffusive linkages will define the input for three mixed reactor compartments. The model will be run for 600 days in order to examine the process's behavior.

3.6.1 Liquid phase concentration variations in the biofilm reactor compartments

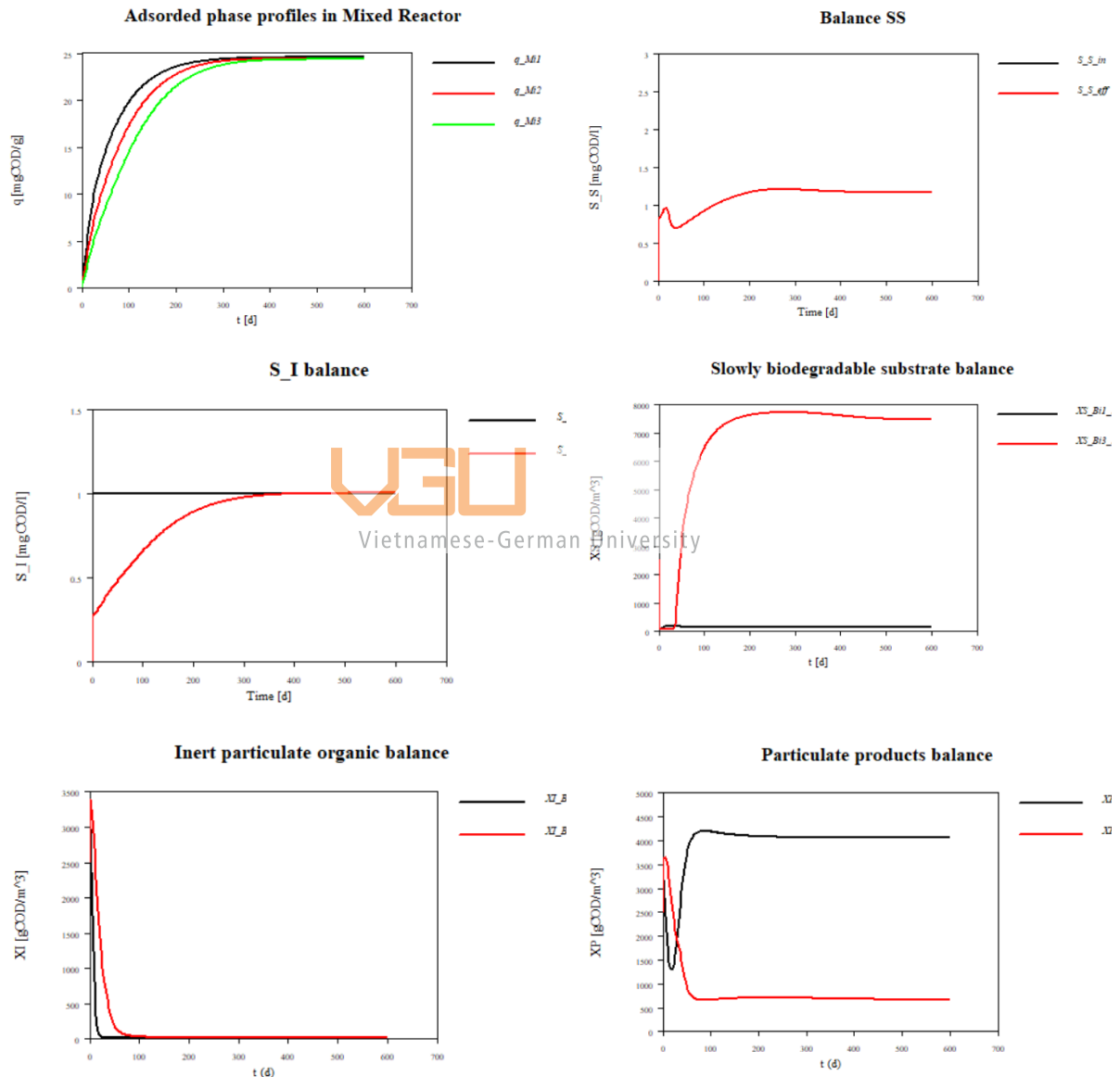
As the biofilm thickness (LF) is a programmable variable that describes the geometry of the biofilm matrix in the biofilm reactor compartment, it makes no difference which space (0.1 or 1) is used for the first plot depicting biofilm thickness. There's a lot of visual overlap between the 0.1 and 1 graphs. Therefore, just one line must be plotted for each reactor.



Three biofilm reactor compartments show varying biofilm thickness, with exponential growth in the first biofilm reactor and a significant decrease in the second and third biofilm reactors. Further, this expansion has been greatest in the first 200 days and has continued unchanged for the rest of the time period under review. There appears to be a link between this and the formation of biomass. According to the graph, there was a period of significantly reduced growth of both heterotrophic and autotrophic biomass in biofilm reactor compartment 3. After 50 days of operation in biofilm reactor compartment 3, the heterotrophic biomass has almost completely depleted, while the autotrophic biomass produced by the

growth of ammonia oxidizing bacteria and nitrite-oxidizing bacteria has decreased and remained stable.

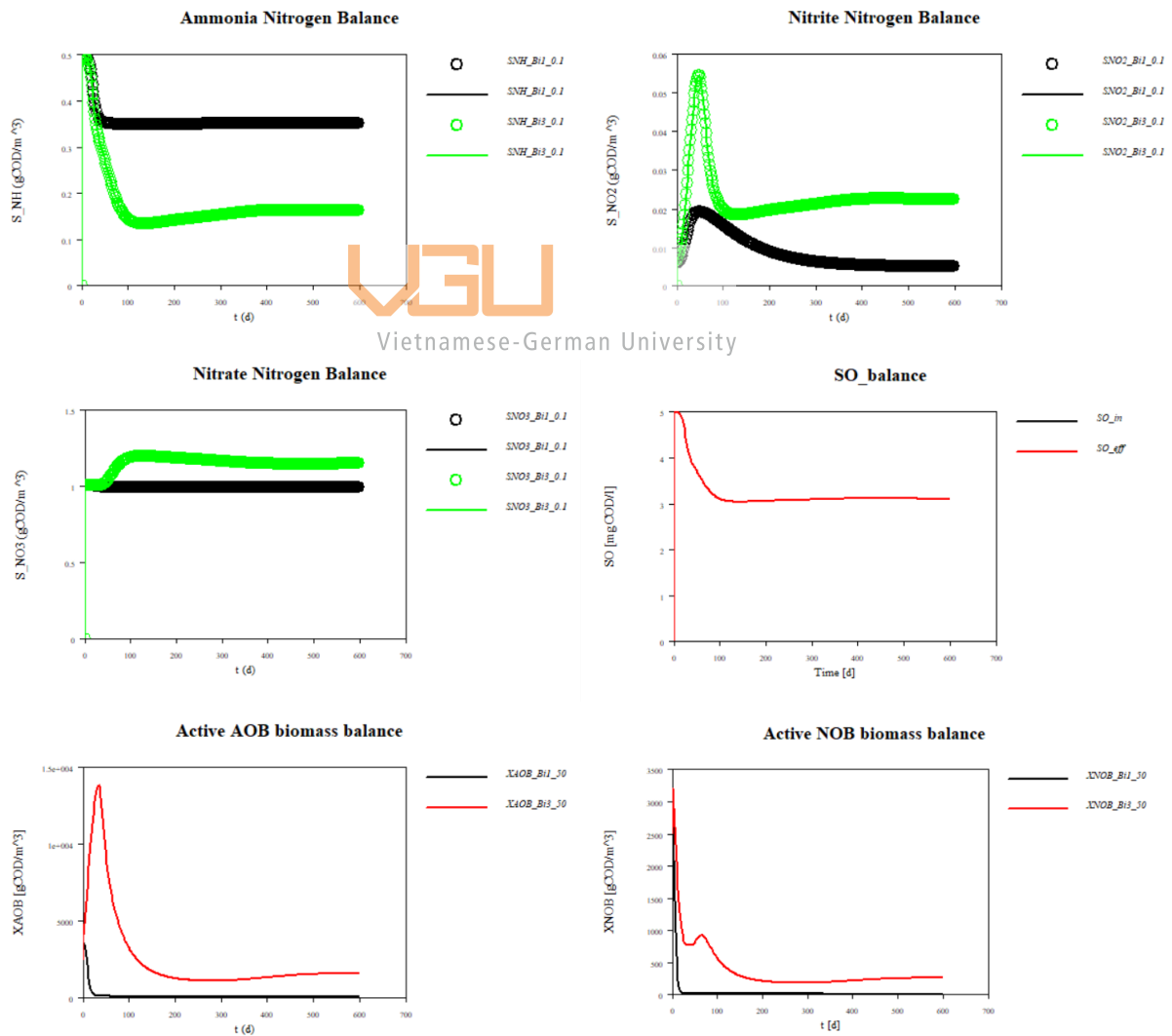
When examining the process of heterotrophic ammonification, it is evident that no heterotrophic biomass synthesis takes place. However, the rate at which ammonification occurs is sensitive to X_{BH} concentration; at higher X_{BH} levels, the ammonification reaction proceeds more quickly. It appears that heterotrophic ammonification does not take place in biofilm reactor 3, where X_{BH} levels are extremely low. The formation of S_{ND} in upstream biofilm reactors, where it is not fully transformed to S_{NH} , may account for the observed increase in S_{ND} . Furthermore, S_{ND} originates from biomass decay over the intermediate particulate organic nitrogen X_{ND} , and the increase in S_{ND} appears to correspond to the decrease in X_{AOB} and X_{NOB} . Variations in biofilm thickness in biofilm reactor 3 may also contribute to the shape of the S_{NH} concentration curve there, as a result of differences in S_{NH} consumption.



The amount of adsorbed species (q) has been shown to increase dramatically over time, with the largest increase occurring in the first 200 days. This is proof that the adsorption process is currently dominant. Saturation having been reached and no further adsorption processes having taken place, the q has remained constant since day 200. Additionally, heterotroph biomass X_{BH} is observed in the first 50 days, and is completely depleted after this time. In this case, the substantial decrease in heterotrophic biomass X_{BH} is likely due to the combination of the detachment process of heterotrophic biomass and the fact that heterotrophic bacteria no longer produce heterotrophic biomass under aerobic conditions. In

addition, the simultaneous adsorption and biodegradation processes seem to be replaced by the S_S adsorption process beginning around day 50, and this trend continues until day 200. At a later time, BAC will have reached a saturation point, and the concentration of the S_S effluent will have stabilized at around 30% of the influent concentration, indicating a treatment efficiency of 60%. In addition, there is a remarkable degree of consistency between the q values of the three mixed reactors. Furthermore, the decay process transforms biomass into slowly biodegradable substrate X_S and particulate products X_P . Due to the extremely low levels of heterotrophic biomass, its contribution to the total accumulated X_P is negligible.

Furthermore, the data demonstrate that the biofilm thickness increases rapidly in the first 50 days due to the significant growth of heterotrophs. It has been noted, however, that the biofilm thickness does not appear to have increased after this point, suggesting that biodegradation processes have ceased. At first, biodegradation and adsorption processes occur simultaneously to remove the organic substrate from the influent, but eventually the latter takes over. Regarding the slowly biodegradable substrate, a rise in X_S over the first 200 days is consistent with the fact that the producing heterotrophic biomass X_{BH} is primarily degraded into X_S . These results are in agreement with the hypothesis that a decrease in X_{BH} causes an increase in X_S in biofilm reactor 3. When only X_S is present as substrate, the growth of biomass is limited by the rate of hydrolysis of the substrate, which is typically much slower than the rate of utilization of the readily biodegradable substrate.



Both the bulk Zone (shown by the markers) and the Pore Water Zone must be taken into account when calculating S_{NO2} and S_{NO3} concentrations (displayed by lines). While the effluent's nitrite nitrogen concentration has continued to rise, nitrate nitrogen appears to have risen only slightly. Ammonia oxidizing bacteria use ammonia nitrogen as a substrate, converting it into nitrite nitrogen, which is then consumed by nitrite oxidizing bacteria or heterotrophic

bacteria (under anoxic conditions) to produce nitrate nitrogen. Due to the lack of anoxic conditions caused by the S_O concentrations in the graph shown, S_{NO_2} can only be consumed through the use of X_{NOB} . All biofilm reactors show S_{NO_2} formation, with more formation the closer we get to the effluent; this is also true for S_{NO_3} (more extreme, since biofilm reactor 1 shows no concentration change). An increase in S_{NO_3} concentration in the effluent suggested that S_{NO_3} was being formed by X_{AOB} and X_{NOB} , but that heterotrophic anaerobic consumption was not occurring. Thus, the nitrification process can be seen but the denitrification process cannot.



Vietnamese-German University

4 Chapter 4 - Sensitivity analysis of kinetic model parameters and discussion.

It is common practice for modelers to conduct sensitivity analyses (SA) to determine the relative impact of various inputs, such as parameters and their interactions, on the predicted results of a model. This can help the modeler in a variety of ways, including facilitating the simplification of models, prioritizing parameters for calibration, locating model flaws, and allocating uncertainty among model factors. If a parameter is found to have a negligible effect, it can be left at its default value, given an arbitrary value within the parameter range, or even removed from the model entirely as a means of model reduction, which simplifies the model and makes it easier to interpret without sacrificing accuracy. Therefore, the parameters with the largest impact, or those to which the model output is most sensitive, are the ones that should receive the most attention from experiments during calibration. For this reason, it is important to conduct additional research into the parameters that have the most impact and, hence, the greatest potential for error in order to better understand and, ultimately, reduce this uncertainty (Pryce et al., 2022).

If the standard deviations of the parameters are known, AQUASIM may do a sensitivity analysis, independently adjusting each parameter to see how it affects the model outputs. The **absolute-relative sensitivity** function (Sens AR) was utilized for this investigation. Absolute change in an arbitrary variable (effluent concentrations) for a 100% change in a model parameter is what the Sens AR measures. Because this represented the confidence interval seen in the batch kinetic testing (Wahman et al., 2006a), and because Reichert (1998) recommends using 10% of the value when a standard deviation is not determined by AQUASIM, a standard deviation for the parameters of 10% of its value was chosen.

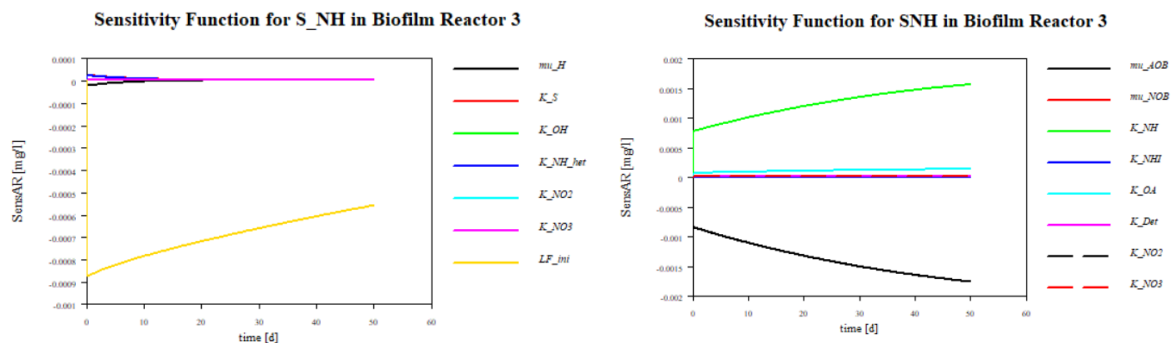
$$\delta_{y,p}^{a,r} = p \frac{\partial y}{\partial p}$$

In order to conduct sensitivity analysis, AQUASIM features four distinct sensitivity functions. The absolute-relative sensitivity function (Sens AR) was utilized for this investigation. Absolute change in an arbitrary variable (here, effluent steady-state q , S_s , S_i , S_{NH} , S_{NO_2} , S_{NO_3} , S_O concentrations) due to a 100% change in a model parameter is represented by the Sens AR (i.e., μ_H , K_S , K_{NO_2} , K_{NO_3} , μ_{AOB} , μ_{NOB} , K_{NH} , K_{OH} , K_{OA} , K_{NH} , K_{NHhet} , k_{Det} , k , n , k_{des} , K , LM , LF_{ini}).

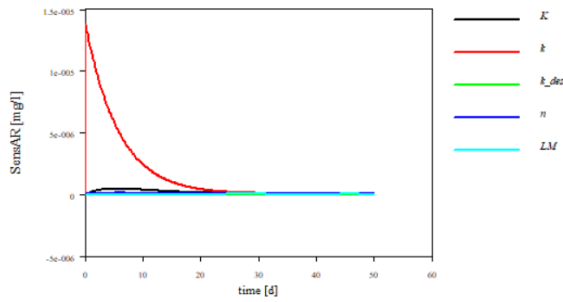
4.1 For the biological reactors compartments

4.1.1 Location: Bulk Volume

For the S_{NH} , the dependency of the S_{NH} on K_{NH} and μ_{AOB} results in changes with a similar shape, but a different sign and amplitude. Consequently, fluctuations in μ_{AOB} can roughly counteract variations in K_{NH} . The measured values of S_{NH} make it impossible to determine either of these parameters. Moreover, LF_{ini} has a minor impact on S_{NH} . The decrease in soluble ammonia nitrogen with increasing biofilm thickness LF_{ini} is indicated by the negative sign (S_{NH}). Rather than being consumed by heterotrophic bacteria, soluble ammonia nitrogen (S_{NH}) is used as a source of energy by autotrophic bacteria.



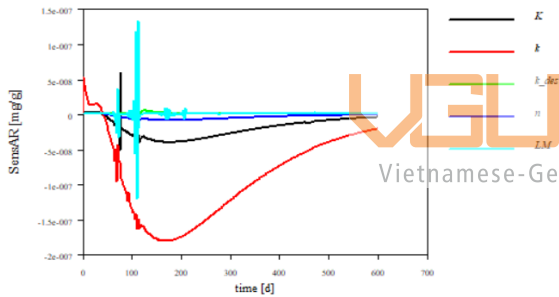
Sensitivity Function for SNH in Biofilm Reactor 3



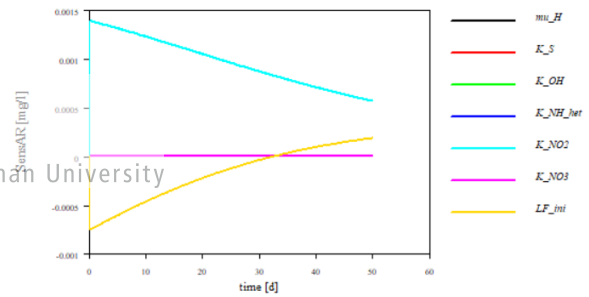
Variables S_{NH} (gCOD/m ³)	Para- meters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	μ_{AOB}	-0.001387	0.00177
2.	K_{NH}	0.001231	0.00155
3.	LF_{ini}	-0.00069	0.0008
4.	K_{OA}	0.000102	0.0001
5.	μ_H	-3.57E-06	2.4E-05

S_{NO_2}/S_{NO_3} follows a similar pattern for its variations, depending on μ_{AOB} and K_{NH} , but with a different sign and magnitude. In addition, this is also true for μ_{NOB} and K_{NO_2} . This suggests that the effects of modifying the μ_{AOB}/μ_{NOB} parameter can be roughly countered by modifying the K_{NH} and K_{NO_2} parameters. This means that the S_{NO_2}/S_{NO_3} measurement data is not uniquely dependent on either of these two amounts. Because the parameters μ_{NOB} and K_{NO_2} cannot be identified, the concentrations of S_{NO_2} and S_{NO_3} are not significantly greater than the half-saturation concentration of K_{NO_2} . Under aerobic conditions, NOB growth can be linearized to μ_{NOB}/K_{NO_2} within this concentration range. S_{NO_2} , a term indicating the non-identifiability of μ_{NOB} and K_{NO_2} . This also applies to the parameters μ_{AOB} and K_{NH} . Nonetheless, it has been observed that LF_{ini} has only a minor effect on S_{NO_3} variation.

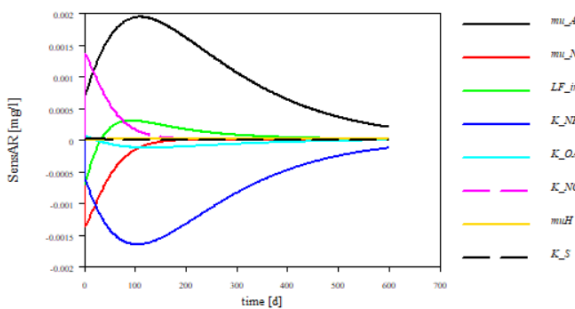
Sensitivity Function for SNO2 in Biofilm Reactor 3



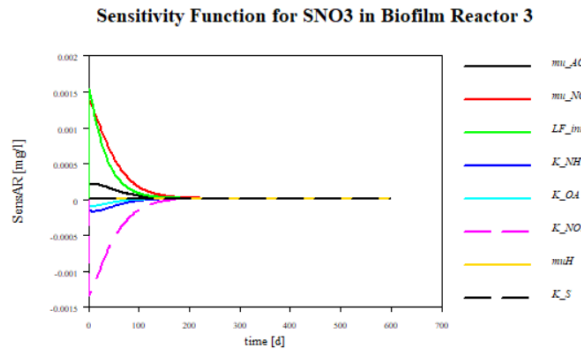
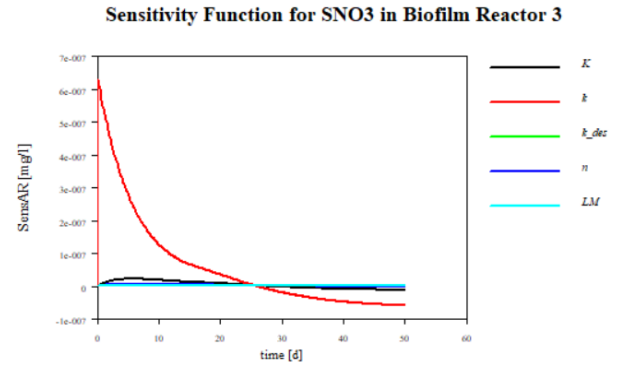
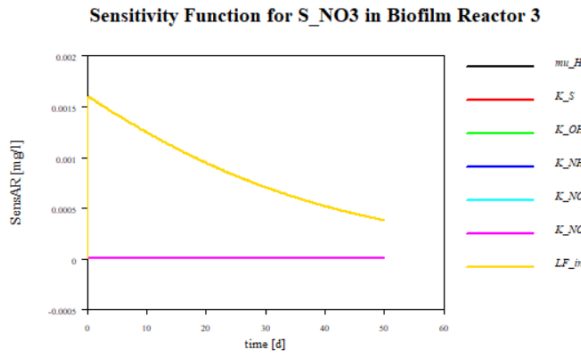
Sensitivity Function for S_NO2 in Biofilm Reactor 3



Sensitivity Function for SNO2 in Biofilm Reactor 3

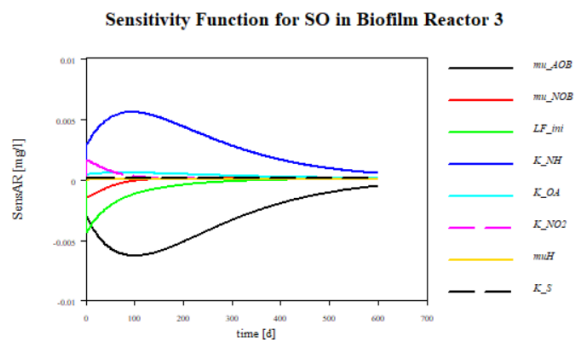
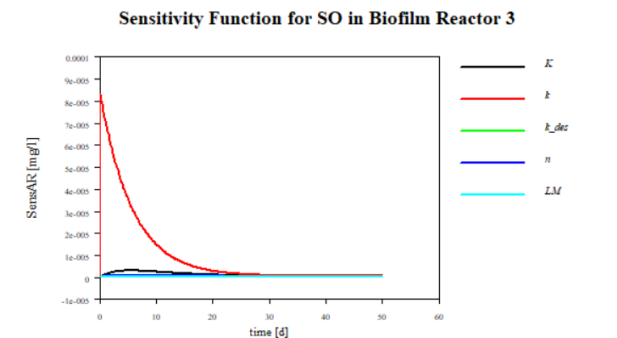
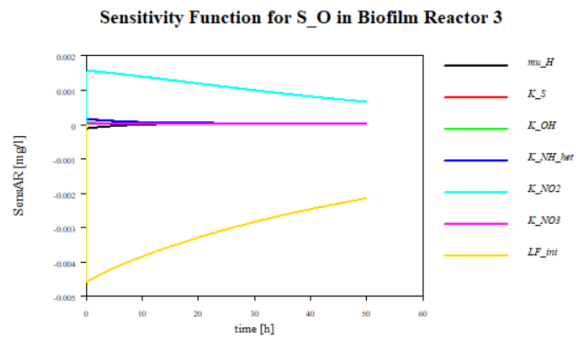


Variables S_{NO_2} (gCOD/m ³)	Para- meters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	μ_{AOB}	0.00119	0.00161
2.	K_{NH}	-0.00106	0.00142
3.	μ_{NOB}	-0.00098	0.00140
4.	K_{NO_2}	0.00096	0.00138
5.	LF_{ini}	-0.00018	0.00076



Variables S _{NO3} (gCOD/m ³)	Para- meters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	μ_{NOB}	0.000978	0.001403
2.	K_{NO2}	-0.00096	0.001384
3.	LF_{ini}	0.000865	0.001591
4.	μ_{AOB}	0.000175	0.000202
5.	K_{NH}	-0.00016	0.000181

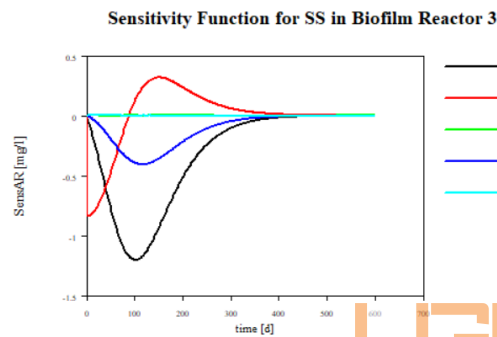
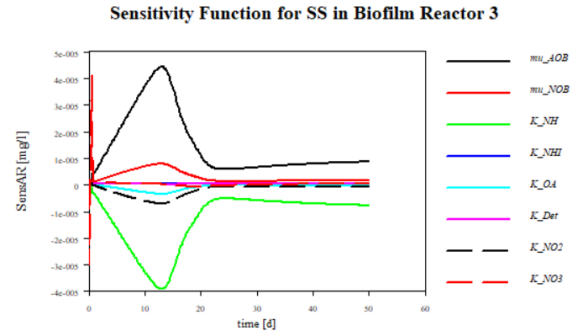
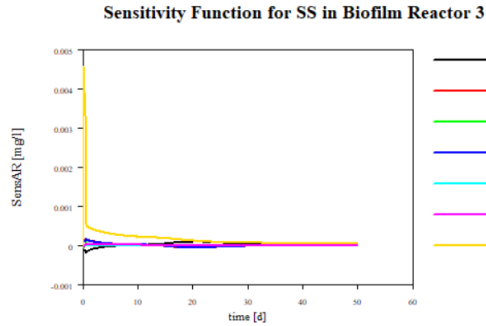
Regarding the S_o , it is evident that the same identical changes have occurred in relation to these few variations in μ_{AOB} and K_{NH} , μ_{NOB} and K_{NO2} . Moreover, it is observed that LF_{ini} reaches its maximum value at time zero and then decreases exponentially; this indicates that **an increase in LF_{ini} results in a decrease in S_o** . Most adsorption parameters, including K , k , k_{des} , n , and LM , have little impact on S_o .



Variables S _o (gCOD/m ³)	Para- meters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	μ_{AOB}	-0.00458	0.00574
2.	K_{NH}	0.004069	0.005042
3.	LF_{ini}	-0.00317	0.004611
4.	μ_{NOB}	-0.00109	0.001558
5.	K_{NO2}	0.001064	0.001536

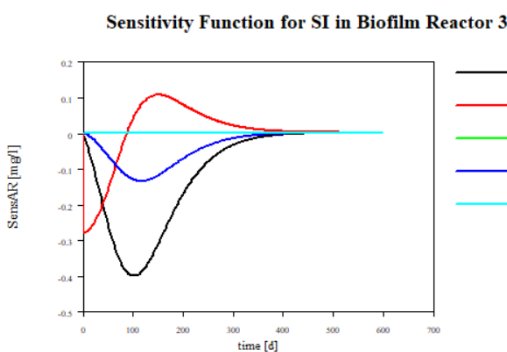
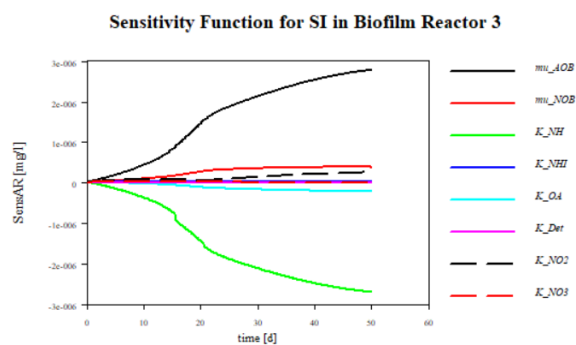
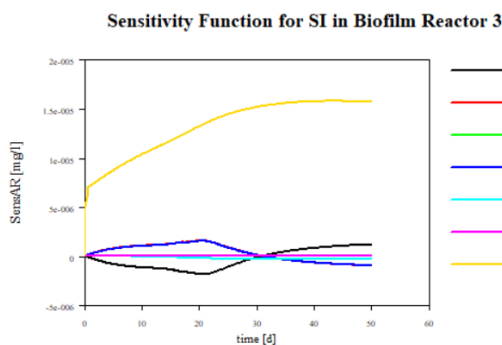
In terms of S_s , while the values of model parameters involving the biological process have no effect on S_s , the adsorption kinetics parameters k , K , n and LF_{ini} have distinct effects

on S_s . While the sensitivity of S_s to \mathbf{k} goes up from zero, peaks at its maximum, and then drops back down to zero (this is the behavior of the absolute value of the sensitivity function; the negative sign indicates that S_s **decrease with increasing** values of \mathbf{k}), the sensitivity of S_s to \mathbf{k} and LF_{ini} peaks at time zero and decreases exponentially; the negative sign indicates that S_s **decreases** with **increasing** values of \mathbf{k} , \mathbf{K} , \mathbf{n} . This allows us to distinguish these three parameters from S_s concentration data. This makes sense when considering the role of the adsorption process in the simulation's COD removal.



Variables S_s (gCOD/m ³)	Parameters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	k	-0.71	0.8458
2.	K	-0.3656	0.767
3.	n	-0.08087	0.1931
4.	LF_{ini}	0.000162	0.004564
5.	μ_H	1.27E-05	0.000216

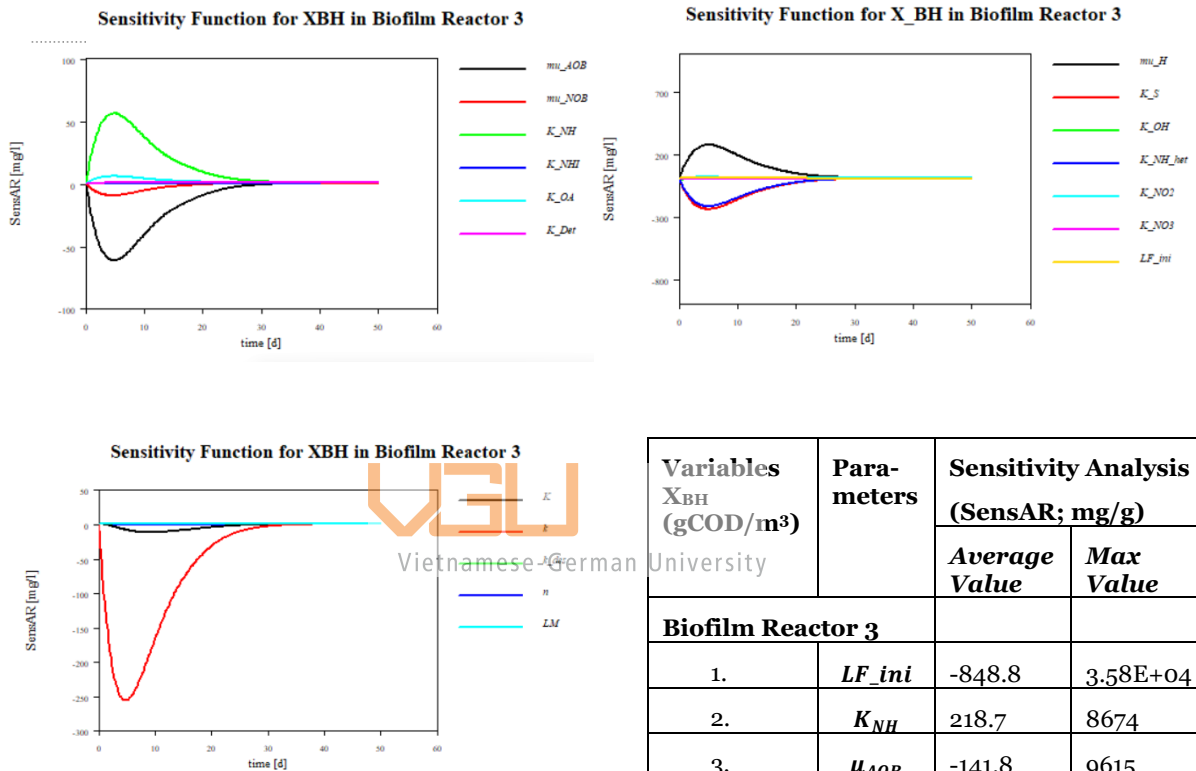
As can be observed, \mathbf{k} , \mathbf{K} , \mathbf{n} , and LF_{ini} all have the same impact on SI.



Variables S_I (gCOD/m ³)	Parameters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	k	-0.2366	0.281
2.	K	-0.1219	0.2557
3.	n	-0.02696	0.06438
4.	LF_{ini}	1.32E-05	1.57E-05
5.	μ_{AOB}	1.57E-06	2.76E-06

4.1.2 Location: Biofilm Matrix

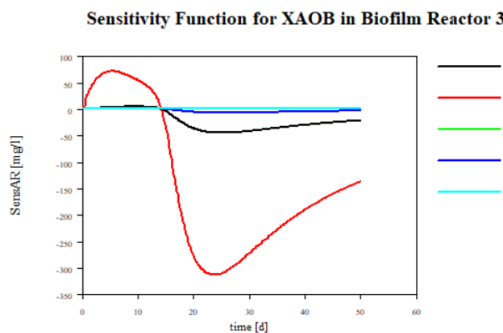
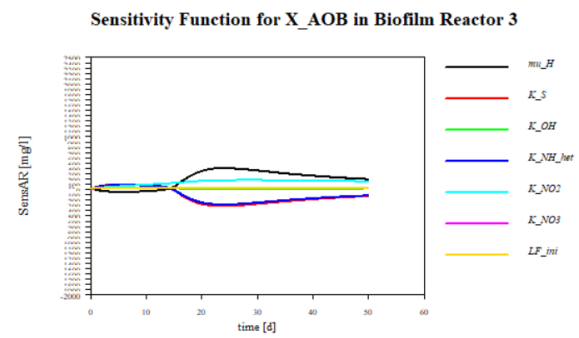
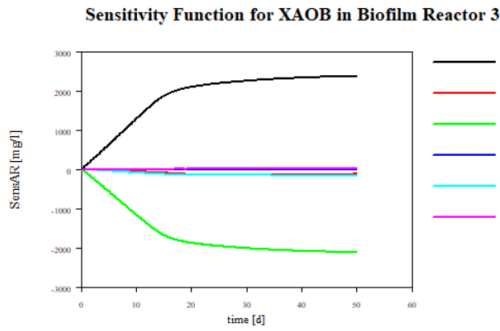
Most of the studied biological kinetic parameters were significantly related to the heterotrophic biomass X_{HB} . LF_{ini} , K_{NH} , μ_{AOB} , μ_H , and K_S were among the variables considered. LF_{ini} has the greatest negative impact on heterotrophic biomass. With respect to μ_H and K_S , the sensitivity function of X_{BH} takes on a roughly identical form. The μ_H maximum on the sensitivity function is close to 200 mg/l, while the K_S minimum is close to 300 mg/l. Using the linear approximation, a smaller change in μ_H is required to achieve the same effect as a larger change in K_S . If the μ_H was raised from 4.0 (1/d) to 8.0 (1/d), mgN/l, the K_S concentration would shift from 10 mgN/l to 13 mgN/l or by a factor of $2 \cdot 200/300$. Furthermore, LF_{ini} inhibits X_{BH} expansion. Because no ammonification takes place in compartment 3 of the biofilm reactor, no heterotrophic biomass is generated, and the biofilm growth is not triggered by heterotrophic biomass.



Variables X_{BH} (gCOD/m ³)	Para- meters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	LF_{ini}	-848.8	3.58E+04
2.	K_{NH}	218.7	8674
3.	μ_{AOB}	-141.8	9615
4.	μ_H	80.68	4554
5.	K_S	-60.88	4134

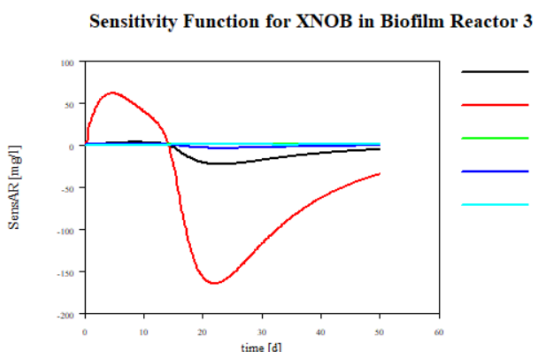
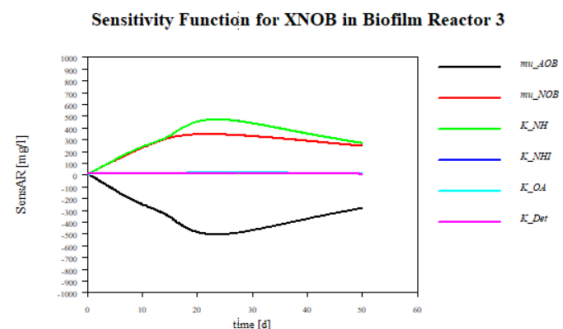
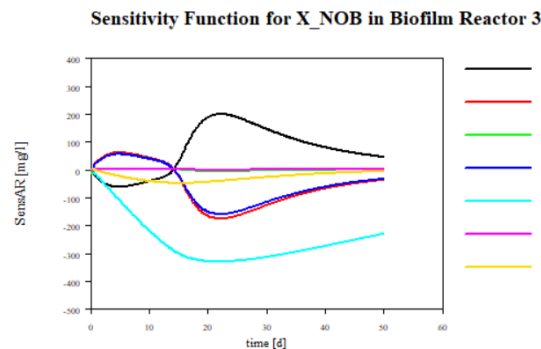
As can be seen in the below figures, the sensitivity function of X_{AOB} with regard to μ_{AOB} and K_{NH} are nearly identical in shape. Maximum value of the sensitivity function to μ_{AOB} is around 2500 mg/l, and minimum value to K_{NH} is around 2300 mg/l. Because the result is more sensitive to μ_{AOB} , a smaller change in μ_{AOB} is required to achieve the same effect as a larger change in K_{NH} under the linear approximation. Since the shifts in X_{AOB} have a different sign, any adjustments to the parameters must also be of the same sign. A change in K_{NH} from 1 mg/l to 2 mg/l would result in a μ_{AOB} shift from 0.5 (1/d) to 0.92 (1/d), or a factor of $2 \cdot 2300/2500$.

A further correlation between X_{AOB} and biofilm thickness is observed. Consequently, the autotrophic biomass is the activating factor for X_{AOB} (Amonia oxidizing bacteria in this situation).



Variables X_{AOB} (gCOD/m ³)	Para- meters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	LF_{ini}	747.6	2.51E+04
2.	μ_{AOB}	1882	6795
3.	K_{NH}	-1739	6055
4.	μ_H	173.2	2865
5.	K_S	-163.6	2597

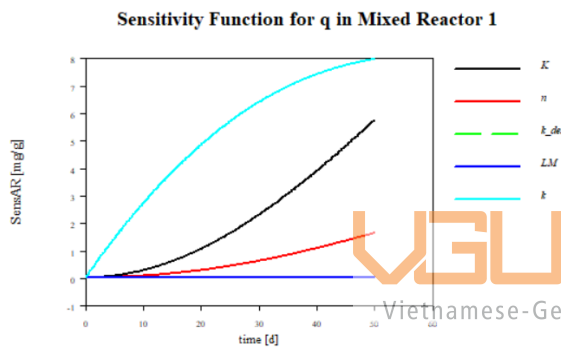
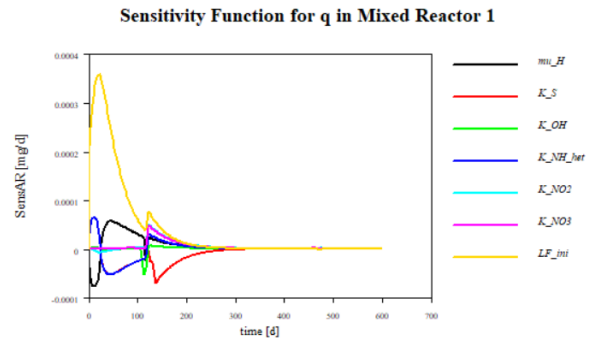
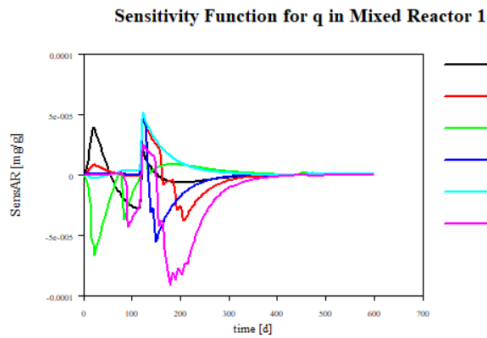
As can be seen, the sensitivity function of X_{NOB} with regard to μ_{AOB} and K_{NH} are nearly identical in shape. Maximum value of the sensitivity function to μ_{AOB} is around 347 mg/l, and minimum value to K_{NH} is around 310 mg/l. Because the result is more sensitive to μ_{AOB} , a smaller change in μ_{AOB} is required to achieve the same effect as a larger change in K_{NH} under the linear approximation. Since the shifts in X_{NOB} have a different sign, any adjustments to the parameters must also be of the same sign. A change in K_{NH} from 1 mg/l to 2 mg/l would result in a μ_{AOB} shift from 0.5 (1/d) to 0.89 (1/d), or a factor of $2 \cdot 310/347$.



Variables X_{NOB} (gCOD/m ³)	Para- meters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Biofilm Reactor 3			
1.	LF_{ini}	260.2	1.62E+04
2.	μ_{AOB}	-347.1	973.6
3.	K_{NH}	310.7	878.8
4.	μ_H	255.2	336.9
5.	K_S	-252.7	370.7

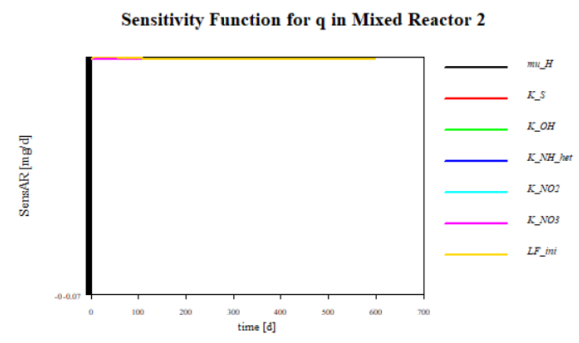
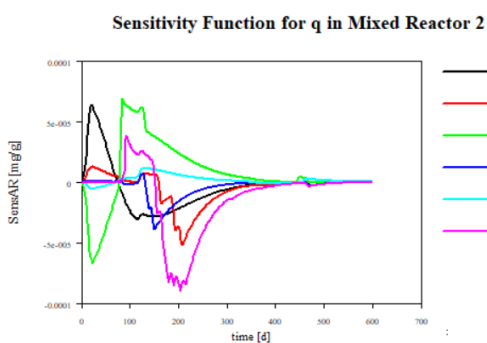
4.1.3 For the mixed reactors compartments

Adsorption kinetic parameters (K, n, k) have a strong influence on q , particularly K while other biological treatment process characteristics ($LF_{ini}, \mu_H, K_{NHhet.}$) have little impact on q . The positive sign indicates that q increases with increasing values of adsorption kinetic parameters K, n or k . Similar tendencies are visible in the remaining two mixed reactors. It is evident that the exponential term n in the Freundlich isotherm, which determines the scale of adsorption exponentially and the adsorption rate, is one of the most sensitive variables, as a small change in n causes a drastic shift in the simulated curve, in terms of the concentration of the adsorbed phase (q).

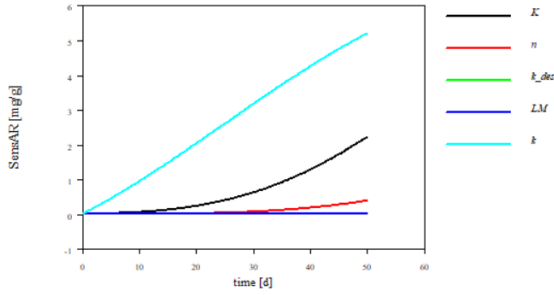


Variables q (mg/g)	Parameters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Mixed Reactor 1			
1.	k	5.11	7.951
2.	K	2.05	5.749
3.	n	0.5604	1.636
4.	LF_{ini}	0.000297	0.000358
5.	μ_H	-5.8E-06	7.82E-05

For the mixed reactor 2



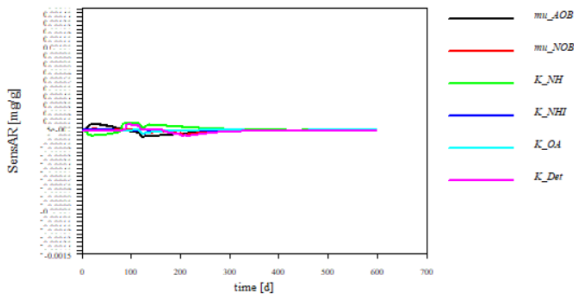
Sensitivity Function for q in Mixed Reactor 2



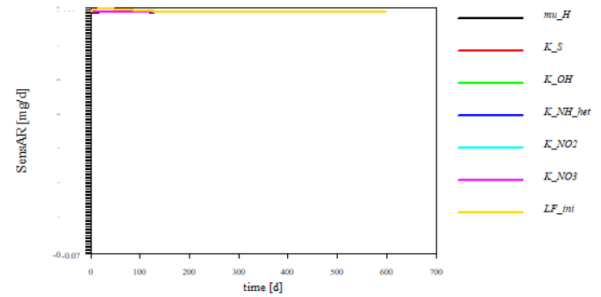
Variables q (mg/g)	Parameters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Mixed Reactor 2			
1.	<i>k</i>	-0.6007	0.8809
2.	<i>K</i>	-0.3652	0.6967
3.	<i>n</i>	-0.09217	0.1955
4.	<i>LF_ini</i>	0.000117	0.0036
5.	μ_H	1.44E-05	0.000225

For the mixed reactor 3

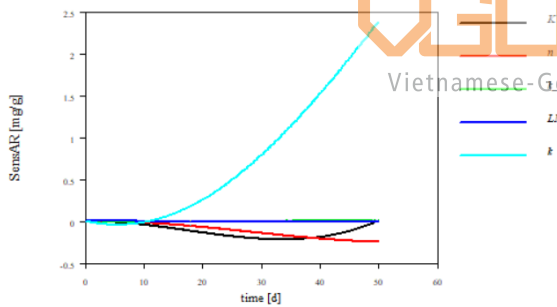
Sensitivity Function for q in Mixed Reactor 3



Sensitivity Function for q in Mixed Reactor 3



Sensitivity Function for q in Mixed Reactor 3



Variables q (mg/g)	Parameters	Sensitivity Analysis (SensAR; mg/g)	
		Average Value	Max Value
Mixed Reactor 3			
1.	<i>k</i>	-0.2002	0.2931
2.	<i>K</i>	-0.1217	0.2322
3.	<i>n</i>	-0.03072	0.06518
4.	<i>LF_ini</i>	5.63E-06	6.98E-06
5.	μ_H	-5.2E-08	1.60E-06

5 Chapter 5 – Discussions and Conclusion

In this simulation process, the substrates are assumed to pass through the biofilm reactor compartments before being adsorbed by the activated carbon in the mixed reactor compartments; consequently, the biofilm covering the GAC can be seen as a resistance to the mass transfer of adsorption.

A model is said to be sensitive to parameters when even a small change in that parameter has a large impact on the simulation result. Each model parameter contributes some to the model prediction, but the sensitivity of each parameter varies. It's possible that the adsorption rate coefficient (k), the exponential term n in the Freundlich isotherm and the biofilm thickness (LF) are the most sensitive parameter in this simulation model. The half-saturation autotroph/heterotroph concentration (K_{NH} , K_S), and the autotrophic growth rate (μ_{AOB} , μ_{NOB}) all have a relative impact and can be balanced against one another. There is little effect from the other kinetic parameters on the liquid phase state variable.

For the nitrite nitrogen and nitrate nitrogen substrates, it is obviously seen that, μ_{AOB} and K_{NH} is usually counterchanged since an increase in this parameter can be compensated by the other ones. This is also observed in the μ_{NOB} and K_{NO_2} . This means that these 04 kinetics parameters are non-identifiability by the S_{NO_2} and S_{NO_3} .

The results of this study support the hypothesis that the concentration of dissolved oxygen (DO) significantly affects the rates of nitrifier growth and nitrification in biological treatment systems, as evidenced by the observed variation of K_{OA} in response to Ammonia Nitrogen. Dissolved oxygen has been modeled using the Monod relationship because it is thought to be a limiting substrate for growth.

As displayed in the graph, biofilm thickness LF have a substantial effect on most of the liquid phase state variables including Ammonia Nitrogen, Nitrite Nitrogen, Nitrate Nitrogen. It has been found that as biofilm thickness increases during operation, nutrient substrates decrease. Both autotrophic and heterotrophic organisms can take in nutrients. This is appropriate that nutrients are uptaken by autotrophic and heterotrophic bacteria. Additionally, the correlation between biofilm thickness and nutrients varies slightly. Even after the nitrite nitrogen consumed by Ammonia oxidizing bacteria has been depleted, the biofilm continues to form after a given amount of time (around day 50 in this study). This is because the nitrite nitrogen generated served as the substrate for the nitrite-oxidizing bacteria in the two-step nitrification process, and the phenomena is explained by the considerable aerobic development of heterotrophs when S_S is used as the substrate. In addition, heterotrophic ammonification does not occur in biofilm reactor 3 because S_{ND} in upstream biofilm reactors is not completely converted to S_{NH} by heterotrophic bacteria. This also demonstrates that ammonium nitrate S_{NH} does not contribute significantly to the production of heterotrophic biomass X_{BH} , but rather rapidly biodegradable substances S_S . An elevated S_{NO_3} concentration in the effluent also suggested that S_{NO_3} was being formed by X_{AOB} and X_{NOB} , but that no heterotrophic anaerobic consumption was taking place. Therefore, nitrification can be seen, but denitrification is not possible to detect.

The graph depicts a relative dependence on the adsorption kinetic parameters k for both the readily biodegradable substrate S_S and the slowly biodegradable substrates S_I . As the adsorption kinetic rate constant k increases, the S_S concentration in biofilm reactor 3 decreases. This illustrates that if the adsorption rate is high sufficiently, the biological process for S_S or S_I is inhibited, hence making adsorption the potential treatment method for S_S .

The growth of heterotrophs and autotrophs are both significantly affected by the initial biofilm thickness LF_{ini} for the biomass concentration. The LF_{ini} has a negative effect on X_{BH} but a beneficial effect on autotrophic biomass. Inhibition of X_{BH} growth by LF_{ini} provides a plausible explanation for this phenomenon. Biofilm growth is not stimulated by heterotrophic biomass because ammonification does not occur in compartment 3 of the biofilm reactor.

Regarding the adsorbed phase concentration, there is an observation that q has a substantial dependence on k , n , and K ; It is clear that the exponential term n in the Freundlich isotherm, which determines the scale of adsorption exponentially, and the adsorption rate is

one of the most sensitive variables, as a small change in n causes a drastic shift in the simulated curve.

Generally, in the first 50 days, adsorption and biodegradation have typically occurred simultaneously in the biofilm reactor compartments. The exponential growth of biofilm thickness occurs within the first 50 days, and there is a considerable increase in the concentration of the adsorbed phase q within the first 200 days. After 50 days of operation, biofilm reactor 3's biofilm thickness has somewhat decreased due to the detachment process, and the adsorption process has become dominant as q still grows. By day 200, the adsorption has reached saturation, and q will no longer rise.

According to the research of Erlanson et al., 1997, a biogrowth-supporting adsorption column comprises three phases of operation. Adsorption removes chemicals from the influent stream before microorganisms are acclimated to the column. The second phase, biodegradation, begins with a fast, steep drop in the biodegradable chemical's liquid-phase concentration. Some of the adsorbed chemicals desorb back into the liquid phase because the solid-phase loading of biodegradable chemicals on GAC is no longer in equilibrium with the liquid phase. Bioregeneration is the desorption and biodegradation of previously adsorbed compounds because biological activity reopens GAC adsorption sites for biodegradable and nonbiodegradable substances. Third phase of column operation involves adsorption and biodegradation. The biodegradable chemical's liquid-phase concentration is fairly constant, and bioregeneration is slower. This step continues until effluent concentration exceeds treatment goal. In this study, it is difficult to see the substantial variation between the two periods of this investigation. In other words, the impact of the biodegradation process on the efficacy of the treatment of rapidly biodegradable substrates has not been demonstrated in an experimental setting. This could be because the influent S_s , S_i , and S_{NH} values are relatively low (typical values for residential sewage characteristics are listed in Table 2-7 above) compared to the initial liquid phase state variable. Additionally, according to Badriyha, 2003, in order to further support microbial growth, acetate was included in the feed solution; this meant that both acetate and the target compound governed the biodegradation behavior.

For the next step, in terms of nitrate nitrogen (as target compound) it is necessary to do experiment to add more nitrate nitrogen in the influent to check the variation of it as well as the effect of biodegradation.

Conclusion

On the basis of ASML, a basic biokinetic model capable of modeling COD biodegradation, 2-step nitrification, and denitrification was created, along with the incorporation of a simple adsorption model for COD (e.g. Freundlich isotherm, reaction kinetic model approach). The BGAC filter is incorporated into the AQUASIM 2.1g program in order to evaluate the established biokinetic model and the influence of kinetic parameters on bGAC performance and effluent concentration. The simulation findings demonstrate that biodegradation and adsorption takes simultaneously in the first period of time. Later on, the adsorption takes precedence over biodegradation until equilibrium is achieved in adsorption. Obviously, the adsorbed phase increases significantly before becoming stable. In addition, due to the very low concentration of resulting active heterotroph biomass, the heterotrophic ammonification does not occur. Additionally, an elevated NO_3 concentration in the effluent also suggested that NO_3 was being formed by growth of autotrophic aerobic (amonia oxidizing bacteria and nitrite oxidizing bacteria), but that no heterotrophic anaerobic consumption was taking place. Therefore, nitrification can be seen, but denitrification is not possible to detect.

In this work, the sensitivity analysis of kinetic model parameter regarding the differentiation of adsorptive and biological COD removal and its impact on simulate biological removal of nitrogen were carried out. The sensitivity analyses identified three important parameters: the adsorption rate coefficient (k), the exponential term n in the Freundlich isotherm and the biofilm thickness (LF). The model output is relatively insensitive to the half-saturation autotroph/heterotroph concentration (K_{NH} , K_s), and the autotrophic growth rate (μ_{AOB} , μ_{NOB}).

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List of Abbreviations

BGAC	Biological granular activated carbon
BTC	Breakthrough curve
DOC	Dissolved organic matter
EPS	Extracellular polymeric molecules
MCRT	High mean cell residence time
MTBL	Mass-transfer boundary layer
MTZ	Mass transfer zone
PAC	Powdered activated carbon
SND	Simultaneous Nitrification and Denitrification
TKN	Total Kjeldahl Nitrogen
NOM	Natural Organic Matters
ASM	Activated Sludge Model
EBCT	Empty-bed contact time
ASM-Ad	Activated Sludge Model in combination with Adsorption Process



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