MODELING ASPECTS OF ACTIVATED SLUDGE PROCESSES

PART II: Mathematical Process Modeling and Biokinetics of Activated Sludge Processes

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Abstract

Mathematical process modeling and biokinetics of activated sludge process were reviewed considering different types of models. It has been evaluated the task group models of ASM1, and 2, and 3 versioned by Henze et al considering the conditions of each model and the different processes of which every model consists. It is revealed that ASM1 contains some defects avoided in ASM3. Relied on homogeneity, Models can be classified into homogenous models characterized by taking the activated sludge process as one phase. In this type of models, the internal mass transfer inside the flocs was neglected.. Hence, the kinetic parameter produces can be considered inaccurate. The other type of models is the heterogeneous model. This type considers the mass transfer operations in addition to the biochemical reaction processes; hence, the resulted kinetic parameters can be considered more accurate than that of homogenous type.

1. Introduction

This part shows the importance of using mathematical models for the biological wastewater treatment systems. It presents also classification of the models depending on the number of used parameters in one time and depending on the homogeneity of the activated sludge system in another time. Activated sludge models number 1,2, and 3 by IAWPRC are explained and also the differences between them are shown in this part.

Mathematical models are powerful tools by which the designers of biological wastewater treatment systems can investigate the performance of a number of potential systems under a variety of conditions. They are particularly useful for those who are working with systems in which carbon oxidation, nitrification, and

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denitrification are accomplished with a single [1]sludge because the competing and parallel reactions in such systems are so complicated that it is difficult to estimate intuitively their response to changes in system configuration or load. Unfortunately, in spite of the benefits to be gained from the use of models, many engineers have not yet incorporated them into their routine practice.

Modeling and experimentation are interdependent, with each providing input to and taking information from the other. Consequently, as we have learned more about biofloc processes, we have been able to develop better models, which have helped us to see new applications and to develop better methods for design.

2.Classification of Models

Leslie Grady C.P (1983) divided mathematical models into two categories: empirical and mechanistic. Empirical models simply relate operating input and output variables to each other and make little pretense of representing individual phenomena. Such "black box" descriptions are quite useful for design from pilot plant data and have found wide use in environmental engineering. Many of the models for biological film processes fall into this category.

Mechanistic models, on the other hand, express the influence and interrelationships of individual mechanistic phenomena in a manner that allows the investigator to discover how the system might respond under unexpected conditions. One might argue that the primary purpose of a mechanistic model is further understanding. This additional understanding will be of direct benefit to practitioner, however, because it is the nature of practice to apply knowledge to areas in which no prior experience exists. Mechanistic models have broader utility than empirical ones. Consequently this review will be limited to models of this type.

Mechanistic (physical) models of biochemical processes, generally are developed by application of reactor engineering principles, i.e., they combine expressions representing intrinsic kinetic and transport events with mass balance equations describing the characteristics of particular physical system under the considerations. Consequently, simulation with such models gives insight into the basic events (*Leslie Grady C.P 1983).* Models can be classified as follow:

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2.1 Models based on a number of parameters

Models can be classified into simple and complex depending on the number of parameters that describe the microbial growth processes. Simple kinetic models such as Monod kinetics is still used and the complex models such as such as ASM1, ASM2 and ASM3 have different degrees of complexity as will be shown.

(A) Simple models

The simplest kinetic model has been, and is still being used, for the analysis of many microbial growth processes. These models are based on the assumption that the biomass concentration can also be adequately described by a single parameter. This simple model is not interested in the internal structure of the cell nor the diversity between the cell forms. However, it includes the most fundamental observations concerning microbial growth processes: that the rate of cell mass production is proportional to biomass concentration and that there is a decrease in cell mass also proportional to biomass concentration. The quality of the model predictions increases when the substrate concentration the reactor is high enough to permit equilibrium of the internal cell composition, the so-called growth conditions.

In batch fermentation for example the substrate concentration is usually sufficiently high to assume equal growth rate of all cell components, the so-called balanced growth conditions. Simple dynamic models can be used as a basis for control of industrial fermentation processes. (Villadsen and Nielsen, 1990).

The simple kinetic models cannot realize the same success when applied to continuous stirred tank bioreactor (CSTBR) (Nielsen et al., 1991). Because of often – low levels of substrate in the chemostat, a transient behavior like a sudden change in the volumetric flow rate or the recycle ratio can effect dramatically the cell environment, and the simple model may fail to predict the system behavior (Nielsen, 1991). The Monod kinetics expression for biological synthesis is a clear example for simple models. The Monod relation expression was used to describe the growth rate of both heterotrophic and autotrophic organisms in the IAWQ model

(B) Complex models

Complex models have different degrees of complexity. Their microbial kinetics are based on the knowledge accumulated in the fields of microbiology and biochemistry. Complex models such as such as ASM1, ASM2 and ASM3 have different degrees of complexity. Their microbial kinetics are based on the knowledge accumulated in the fields of microbiology and biochemistry.

They are sometimes called complex models. A good dynamic model should predict experimentally the dynamic behavior of the system and have a reasonable number of parameters to provide it with some levels of flexibility (Sheffer et al., 1984)

These models divide the biomass and wastewater into many constituents giving rise to many different processes, each with its own rate and yield equations. Andrew et al., 1977 have proposed a structured model that includes direct soluble substrate metabolism with concurrent storage of substrate.

(A) Activated sludge model No.1 (ASM1)

In 1983 IAWPRC formed a task group to facilitate the application of practical models to the design and operation of biological wastewater treatment system. They presented the model development for single sludge system performing carbon oxidation, nitrification. The first goal was to review existing models and the second goal was to reach a consensus concerning the simplest mathematical model having the capability of realistically predicting the performance of single-sludge systems carrying out carbon oxidation, nitrification and denitrification. The final result was presented in 1987 as the IAWQ Activated Sludge Model No. 1 (ASM1). The different processes incorporated in the IAWQ model are briefly described below.

• *Aerobic growth of heterotrophs*: A fraction of the readily biodegradable substrate is used for growth of heterotrophic biomass and the balance is oxidized for energy giving rise to an associated oxygen demand. The growth is modeled using Monod kinetics. Ammonia is used as the nitrogen source for synthesis and incorporated into the cell mass. Both the concentrations of S_S and S_O may be rate limiting for the growth process. This process is generally the main contributor to the production of new biomass and removal of COD. It is also associated with an alkalinity change.

• *Anoxic growth of heterotrophs*: In the absence of oxygen, the heterotrophic organisms are capable of using nitrate as the terminal electron acceptor with S_S as substrate. The process will lead to a production of heterotrophic biomass and nitrogen gas (denitrification). The nitrogen gas is a result of the reduction of nitrate with an associated alkalinity change. The same Monod kinetics as used for the aerobic growth is applied except that the kinetic rate expression is multiplied by a factor η_g (< 1). This reduced rate could either be caused by a lower maximum growth rate under anoxic conditions or because only a fraction of the heterotrophic biomass is able to function with nitrate as electron acceptor. Ammonia serves as the nitrogen source for cell synthesis, which in turn changes the alkalinity.

• *Aerobic growth of autotrophs*: Ammonia is oxidized to nitrate via a single-step process (nitrification) resulting in production of autotrophic biomass and giving rise to an associated oxygen demand. Ammonia is also used as the nitrogen source for synthesis and incorporated into the cell mass. The process has a marked effect on the alkalinity (both from the conversion of ammonia into biomass and by the oxidation of ammonia to nitrate) and the total oxygen demand. The effect on the amount of formed biomass is small, as the yield of the autotrophic nitrifiers is low. Once again the growth rate is modeled using Monod kinetics.

• *Decay of heterotrophs*: The process is modeled according to the death regeneration hypothesis. The organisms die at a certain rate and a portion of the material is considered to be non-biodegradable and adds to the X_P fraction. The remainder adds to the pool of slowly biodegradable substrate. The organic nitrogen associated with the X_S becomes available as particulate organic nitrogen. No loss of COD is involved and no electron acceptor is utilized. The process is assumed to continue with the same rate under aerobic, anoxic and anaerobic conditions.

• *Decay of autotrophs*: The process is modeled in the same way as used to describe decay of heterotrophs.

• *Ammonification of soluble organic nitrogen*: Biodegradable soluble organic nitrogen is converted to free and saline ammonia in a first-order process mediated by the active heterotrophs. Hydrogen ions consumed in the conversion process results in an alkalinity change.

• *Hydrolysis of entrapped organics*: Slowly biodegradable substrate enmeshed in the sludge mass is broken down extracellularly, producing readily biodegradable substrate available to the organisms for growth. The process is modeled on the basis of surface

reaction kinetics and occurs only under aerobic and anoxic conditions. The rate of hydrolysis is reduced under anoxic conditions compared with aerobic conditions by a factor η_h (<1). The rate is also first-order with respect to the heterotrophic biomass present but saturates as the amount of entrapped substrate becomes large in proportion to the biomass.

• *Hydrolysis of entrapped organic nitrogen*: Biodegradable particulate organic nitrogen is broken down to soluble organic nitrogen at a rate defined by the hydrolysis reaction for entrapped organics described above.

With regard to denitrification, the group separated the processes of hydrolysis and growth. Finally, the fate of the organic nitrogen and source of organic nitrogen for synthesis were treated somewhat differently. The task group also introduced the concept of switching functions to gradually turn process rate equations on and off as the environmental conditions were changed (mainly between aerobic and anoxic conditions). The switching functions are 'Monod-like' expressions that are mathematically continuous and thereby reduce the problems of numerical instability during simulations. Furthermore, the work of the task group promoted the structural presentation of biokinetic models via a matrix format, which was easy to read and understand, and consolidated much of the existing knowledge on the activated sludge (AS) process.

(B) Activated sludge model No. 2 (ASM2 and ASM2d)

The Activated Sludge Model No. 2 (ASM2**)** is an extension of the Activated Sludge Model No. I (ASM I}; ASM2 is more complex and includes many more components which are required in order to characterize the wastewater as well as the activated sludge. Additional biological processes are included, primarily in order to deal with biological phosphorus removal. The most significant change from ASM l to ASM2 is the fact that the biomass now has tell internal structure, and therefore its concentration cannot simply be described with the distributed parameter XBM.. This is a prerequisite in order to include biological phosphorous removal in the model.

The Activated Sludge Model No. 2d (ASM2d), developed by Henze et al., 1999, is a minor extension of ASM2. It includes two additional processes to account for the fact that phosphorus-accumulating organisms (PAOs) can use cell internal organic storage products for denitrification. Whereas ASM2 assumes PAOs to grow only under aerobic conditions, ASM2d includes denitrifying PAOs. In addition to the

biological processes, ASM2 includes two 'chemical processes, which may be used to mode1 chemical precipitation of phosphorus.

Whereas ASMl was based entirely on COD for all particulate organic material, as well as the total concentration of the activated sludge, ASM2 includes poly-phosphates, a fraction of the activated sludge which is of prime importance for the performance of the activated sludge system, but which does not exert any COD. For this reason, the possibility of including total suspended solids (TSS) in the model is introduced. TSS also allow for inclusion of mineral particulate solids in the inf1uent to treatment plants, as well as generation of such solids in the context of precipitation of phosphorus.

ASM2 is introduced here in a form, which is more complex than a basic version, which could still predict many of the phenomena within a biological nutrient removal plant. The complex model as presented may easily be simplified by eliminating those components, which do not have a dominant effect upon the kinetics of the processes, or the aspects of performance of the plant, which are of interest.

ASM2 does not distinguish between the composition (cell internal structure) of individual cells but considers only the average composition of the biomass. Since each cell has a different history, its composition will typically deviate from the population average (e.g. it may not contain storage products whereas the average cell still has storage products available). This is of importance because kinetic expressions used in ASM2 are non-linear, and therefore average behavior may not necessarily be predicted from average properties. In view of the additional problems that population models would introduce e, the Task Group look the pragmatic decision to accept these problems and to propose ASM2'basedon average properties of the population.

Hydrolysis processes:

In ASM2 many high molecular weight, colloidal or particulate organic substrates cannot be utilized directly by microorganisms. These substrates must be made available by cell external enzymatic reactions, which are called hydrolysis processes. It is unclear whether the products of hydrolysis ever exist in true solution or whether they are taken up directly by the organisms, which catalyze hydrolysis. Typically hydrolysis processes are considered to be surface reactions, which occur in close contact between the organisms which provide the hydrolytic enzymes and the slowly biodegradable substrates themselves.

Parallel with hydrolysis, the activity of protozoa contributes to phenomena, which are assigned to hydrolysis. Whereas it is difficult to distinguish between true hydrolysis and protozoan activity it is becoming more and more evident that. The effect of electron acceptors upon the hydrolysis process may actually be due to the inactivity of protozoa under anoxic and anaerobic conditions. Experimental evidence that 'hydrolysis' reactions depend on the available electron acceptors leads to the differentiation of three hydrolysis processes in ASM2. It is, however, a difficult task to estimate hydrolysis rate constants under different electron acceptor conditions.

1. Aerobic hydrolysis of slowly biodegradable substrate characterizes hydrolysis under aerobic conditions (S_{O2} >0). '

2. Anoxic hydrolysis of slowly biodegradable substrate characterizes hydrolysis under anoxic conditions (S_{O2}≈0). S_{NO3}> 0). This process is typically slower than aerobic hydrolysis.

3. Anaerobic hydrolysis of slowly biodegradable substrate characterizes hydrolysis under anaerobic conditions (S_{O2}≈0, S_{NO3} ≈ 0). This process is not well characterized and is probably slower than aerobic hydrolysis. Its rate remains to be studied.

The hydrolysis processes are similar to those of ASM I: hyperbolic switching functions for S_{O2} and S_{NO3} consider the environmental conditions; a surface limited reaction (X_S /X_H) / (K_X +X_S/X_H) is assumed for the hydrolysis process itself. 1t is proposed that only heterotrophic organisms may catalyze hydrolysis. Typically hydrolysis is slower under denitrifying or anaerobic (fermentation) than under aerobic conditions. The rate for anoxic and anaerobic hydrolysis is therefore reduced by the factors η_{NO3} and η_{fe} respectively; -

4. and 5. Aerobic growth of heterotrbphic organisms on fermentable substrates S_F and on fermentation products S_A. These processes are modeled as two parallel processes, which consume the two degradable organic substrates S_F and S_A. For both processes identical growth rates μ_m and yield coefficients Y_H are assumed. The rate equations are designed such that the maximum specific growth rate of the heterotrophic organisms does not increase above μ_m even if both substrates, S_F and S_A, are present in high concentrations. These processes require oxygen, S_{O2}, nutrients, S_{NH4} and S_{PO4}, and possibly alkalinity, S_{ALK}, and they produce suspended solids, X_{TSS}.

6. and 1. Anoxic growth of heterotrophic organisms on fermentable substrates, S_F, and on fermentation products, S_A; denitrification. These two processes are similar to the aerobic growth processes, but they Activated Sludge Model No. 2d. ASM2d require

nitrate, S_{NO3}, as the electron acceptor rather than oxygen, The stoichiometry for nitrate is computed based on the assumption that a1l nitrate, S_{NO3}, is reduced to dinitrogen, S_{N2} Denitrification releases alkalinity, the stoichiometry of which is predicted from charge conservation. Denitrification is assumed to be inhibited by oxygen S_{O2} and the maximum growth rate μ_m is reduced relative to its value under aerobic conditions, by the factor η_{NO3}. This accounts for the fact that not all heterotrophic organisms X_H may be capable of denitrification or that denitrification may only proceed at a reduced rate.

8. Fermentation. Under anaerobic conditions ($S_{O2}\approx0$, $S_{NO3}\approx0$;) it is assumed that heterotrophic organisms are capable of fermentation, whereby readily biodegradable substrates SF are transformed into fermentation products S_A. Although this process may possibly cause growth of heterotrophic organisms, it is introduced here as a simple transformation process. A growth process would require more complex kinetics, more kinetic and stoichiometric parameters which are difficult to obtain, and possibly different yield coefficients for S_f and S_A in processes 4 to 7. A fermentation release negatively charged fermentation products SA, and therefore has a requirement for alkalinity, SALK. This is predicted from charge conservation. Fermentation is a process which, up to now, has not been well characterized. Little is known about the kinetics of this process, which may lead to a large range of kinetic parameters for modeling experimental results. Reliable application of ASM2 requires that research is directed towards characterizing what is described here with the process of fermentation.

9. Lysis of heterotrophic organisms. This process represents the sum of all decay and logs processes of the heterotrophic organisms: endogenous respiration, lysis, predation etc. 1t is modeled in analogy to ASM I; its rate is independent of environmental conditions.

Process of phosphorous-accumulating organisms

Some organisms, X_{PAO}, are known for their potential to accumulate phosphorus in the form of poly-phosphate X_{pp}. Currently these organisms are not well characterized; historically it was assumed that they would all be part of the Acinetobacter genus. However, today it is clear that Acinetobacter may contribute to, but by far do not dominate, biological phosphorus removal Initially it was assumed

that phosphorus-accumulating organisms. PAO, could not denitrify; now evidence has become available that some of them can denitrify. Phosphate release is sometimes slower in the presence of nitrate; this observation is not predicted with ASM2 but is included in ASM2d. Glycogen is found to be an important carbon storage material of PAO but is not considered in ASM2 in order to reduce model complexity. This restriction leads to limitations of the applicability ofASM2d, which will be discussed later. The greater the attempts to characterize P AG, the more complex this group of organisms becomes. The Task Group is well aware that the time has come when biological phosphorus removal is being designed and used in actual plants. The introduction of a very detailed mechanistic model for the processes responsible for biological phosphorus removal is, however, premature. The Task Group therefore has chosen to suggest a simple model, which allows prediction of biological phosphorus removal, hut does not yet include all observed phenomena. The model proposed may be the base for further development. With the introduction of ASM2d the most important criticism -that PAO contribute significantly to denitrification which is not described in ASM2 –is taken care of.

The following model for the behavior of phosphorus-accumulating organisms, XPAO, is valid for ASM2d only, .it assumes that these organisms can grow under aerobic (S_{O2}> 0) as well as anoxic. (S_{O2} ~ 0,. S_{NO3}; > 0) conditions. They can only grow on tell internal stored organic materials,. X_{PHA}. This assumption is a severe restriction of ASM2d and may lead to further extensions..

10. Storage of X_{PHA}. It is assumed that PAD may release phosphate. S_{PO4} from poly-phosphate, Xpp, and utilize the energy which becomes available from the hydrolysis of Xpp, in order to store cell external fermentation products S_A in the form of cell internal organic storage material X_{PHA}. The process is primarily observed under anaerobic conditions. However, since the process has also been reported to occur under aerobic and anoxic conditions, the kinetic expression does not include inhibition terms for S_{O2} and S_{NO3}. Experimental observation of this process is easy if the release of phosphorus is observed rather than the organics which are stored. Experience indicates, however, that the rate of storage of organics is relativeJy constant, whereas the release of phosphorus varies, indicating a variable stoichimetric relationship. The base for the stoichiometry of this process was therefore chosen to be the organics which are taken up, S_A and X_{PHA}.. Reliable estimation of the rate

constant, q_{PHA}, and the stoichiometric parameter, Y_{PO4}, requires independent measurement of both SA removal and Sp release. It has been shown that Y_{PO4} depends on pH.

11 and 12. Aerobic and anoxic storage of poly- phosphate. Storage of ortho-phosphate, S_{PO4}, in the form of cell internal poly-phosphates, Xpp, requires the PAO to obtain energy, which may be gained from the aerobic or anoxic respiration of X_{PHA}. The regeneration of poly-phosphates is a requirement für the growth of PAO, because the organic substrates, SA, are stored only upon the release of poly-phosphate. Storage of Xpp is observed to stop if the phosphorus content of the PAO becomes too high. This observation 1eads to an inhibition term of Xpp storage, which becomes active as the ratio Xpp/X_{PAO}, approaches the maximum allowable value of K_{MAX}. Under anoxic conditions the maximum rate of storage of poly-phosphate qPP is reduced relative to its value under aerobic conditions, by the factor TlNO3. This accounts for the fact that not all PAO (X_{PAO}) may be capable of denitrification or that denitrification may only proceed at a reduced rate. Process 12 is contained in ASM2d but not in ASM2.

13. and 14. Aerobic and anoxic growth of phosphorus-accumulating organisms.. These organisms are assumed to grow only at 1he expense of ce11 internal organic storage products X_{PHA}. As phosphorus is continuously released by the Iysis of Xpp, it is possible 10 assume that the organisms consume ortho-phosphate, S_{PO4}, as a nutrient for the production of biomass. It is known that PAO may grow at the expense of soluble substrates (e.g.S_A), but it is unlikely that such substrates ever become available under aerobic or anoxic conditions in a biological nutrient removal plant. The Task Group therefore suggests this possibility be ignored at this time. Under anoxic conditions the maximum growth rate of PAO μ_{PAO} is reduced relative to its value under aerobic conditions, by the factor η_{NO3}. This accounts for the fact that not all PAO (X_{PAO}) may be capable of denitrification or that denitrification may only proceed at a reduced rate. Process 13 is contained in ASM2d but not in ASM2.

15, 16. and .17.. Lysis of phosphorus-accumulating organisms and their storage products. Death, endogenous respiration and maintenance all result in a lass or decay of all fractions of PAO.. Since the storage products Xpp and X_{PHA} are accounted for separately from the biomass X_{PAO}, all three components must be subject to separate decay processes. ASM2 includes three lysis processes, which are alt first-order

relative to the component, which is lost. If all three-rate constants are equal, the composition of the organisms does not change due to decay. There is experimental evidence that Xpp decays raster than X_{PAO} and X_{PHA}. This additional loss of polyphosphates may be modeled by the choice of an increased rate, bpp, for the lysis of this component. The products of lysis are chosen in analogy to the lysis of heterotrophic organisms; storage products are assumed to decay to ortho-phosphate S_{PQ4} and fermentation products S_A

Nitrification Processes

Nitrification is assumed to be a one-step process, from ammonium S_{NH4} directly to nitrate S_{NO3}. The intermediate component, nitrite, is not included as a model component. In the context of nitrification, modeling nitrite production and consumption would be relatively' easy. However, nitrite is also produced and consumed in

The context of denitrification where the Task Group felt that the required addition to the model complexity does not warrant its inclusion at the present time. Modeling nitrite in nitrification but not in denitrification would, however, not be consistent and could lead to erroneous model predictions.

18. Growth of nitrifying organisms.. Nitrifying organisms are obligate aerobic, they consume ammonium as a substrate and a nutrient, and produce nitrate. Nitrification reduces alkalinity,. The process is modeled as proposed in ASM 1 with the exception of a phosphorus uptake into the biomass.

19. Lysis of nitrifying organisms. The process of lysis of nitrifiers is modeled 1n analogy to ASM l and to the process of lysis of heterotrophic organisms. Since the decay products of lysis (Xs and ultimately S_f) are available substrates for heterotrophie organisms only, endogenous respiration of nitrifiers becomes manifest as an increased growth and oxygen consumption of heterotrophs. This is in analogy to ASM l.

Chemical Precipitation of Phosphates

In bio1ogical nutrient removal systems, metals, which are natural1y present in the wastewater (e.g. Ca^{+2}), together with the high concentration of released soluble

ortho-phosphate, S_{PO4}, may result in chemical precipitation of phosphorus (e.g. in the form of apatite or calcium phosphate).

Further, simultaneous precipitation of phosphorus via the addition of iron or aluminum salts is a very common process for phosphorus removal worldwide. Simultaneous precipitation may be used in combination with biological phosphorus removal if the carbon to phosphorus ratio is unfavorably small.

In order to model the low effluent concentrations of ortho-phosphate, S_{PO4}, which are observed in practice and which are partly due to chemical precipitation, the Task, Group suggests a very simple precipitation model, which may be calibrated for a variety of situations. For this purpose, two processes (precipitation and redissolutlon) and two more components (X_{MeOH} and X_{MeP}) are added to ASM2. If chemical precipitation is not of any interest, these additions may be deleted from the model.

20. and 21. Precipitation and redissolution of phosphate SP04. The precipitation model is based on the assumption that precipitation and redissolution are reverse processes,

(C) Activated sludge model No. 3 (ASM3)

Recently, the IAWQ task group introduced ASM3 (Gujer et al., 1999) as a possible replacement for ASM1.The main difference between ASM1 and ASM3 is the recognition of the importance of storage polymers in the heterotrophic conversions in activated sludge processes. At the same time an endogenous respiration process replaces the decay process from ASM1. The endogenous respiration concept originated from the observation that internal storage materials are used for maintenance purposes when the external substrate is depleted. (Wilkinson, 1959; Van Loosdrecht and Henze 1999).

A major difference for the wastewater characterization between ASM1 and ASM3 is that soluble (Ss) and particulate (Xs) biodegradable components in ASM3 are supposed to be differentiated with filtration over 0.45- μm membrane filters whereas a significant fraction of the slowly biodegradable organic substrates (Xs) in ASM1 would be contained in the filtrate of the influent wastewater (Gujer et al., 1999). The latter is most likely caused by the conversion of soluble biodegradable COD to storage polymers in the respiration tests. The kinetics of conversion of storage polymers resembles more the degradation rates of Xs than Ss in the model.

The aerobic storage process in ASM3 describes the storage of readily biodegradable substrate (Ss) in the form of cell internal storage products ($X_{storage}$) . This process requires energy in the form of ATP, which is obtained from aerobic respiration. In ASM3 it is assumed that the readily biodegradable organic substrates are first taken up by the heterotrophic organisms and converted to stored material which is subsequently assimilated to biomass.

Henze et al., (1999) showed that that there are some defects had become apparent with the application of ASM1:

- ASM1 does not include kinetic expressions, which can deal with nitrogen and alkalinity limitations of heterotrophic organisms. This results in the fact that computer code cannot be based on the original form of ASM1, which allows under some circumstances for negative concentrations of e.g. ammonium. These led to the creation of different versions of ASM1, which can hardly be differentiate any more.
- ASM1 includes biodegradable soluble and particulate organic nitrogen as model components. These cannot easily be measured and have in the meantime been eliminated in many versions of ASM1.
- The kinetics of ammonification in ASM1 cannot be really be quantified. Again in many versions of ASM1 this process has been eliminated by assuming a constant composition of all organic components (constant N to COD ratio)
- ASM1 differentiates inert particulate organic material depending on its origin, influent or biomass decay. It is impossible to differentiate these two fractions in realty.
- The process of hydrolysis has a dominating effect upon the prediction of oxygen consumption and dentrification by heterotrophic organisms. At the same time the quantification of the kinetic parameters for this process is difficult.
- Lysis combined with hydrolysis and growth is used to describe the lumped effects of endogenous respiration of e.g. storage compounds, death predation, lysis, etc. of the biomass. This leads to difficulties in the evaluation of kinetic parameters.
- Storage of ploy-hydroxy-alkanoates and sometimes glycogen is observed under aerobic and anoxic conditions in activated sludge plants, provided that elevated concentrations of readily biodegradable organic substrates are available. This process is not included in ASM1.

- ASM1 does not include the possibility to differentiate decay rate of nitrifiers under aerobic and anoxic conditions. At high solids retention times (STR) and high fractions of anoxic reactor volumes this leads to problems with the prediction of maximum nitrification rates.
- ASM1 does not allow for the prediction of directly observable mixed liquor suspended solids.

Considering all these defects, the Task Group has decided to propose the Activated Sludge Model No. 3 (ASM3) which should correct for all these defects and which could become a standard again. ASM3 relates to the same dominating phenomena, as does ASM1: Oxygen consumption, sludge production, nitrification, and denitrification in activated sludge systems treating primarily domestic wastewater. Biological phosphorus removal is contained in the Activated Sludge Model No. 2 (Henze et al., 1995) and will not be considered in ASM 3. Table 1 introduces the stoichiometric matrix $v_{j,I}$ of ASM 3 together with the composition matrix $t_{jk,I}$ as proposed by Gujer and larsen (1995)

2.2 Homogeneity Models

This section shows the nature and limits of two main categories of models based on homogeneity: homogeneous and heterogeneous models.

(A) Homogeneous models

These models may be described by a set of fist order nonlinear differential equations. At steady state it results a set of non-linear algebraic equations which can be solved by traditional analytical or numerical methods according to the dimensionality of the system.

A great deal of studies, have been performed on this type of models, made a large success to design and operate the process, and predict the kinetic parameters. These models considered the activated sludge system as one phase. They neglected the internal mass transfer inside the flocs. Hence, this makes the kinetic parameters inaccurate enough. In other words, these models assumed the rate of the reaction at the center of the floc is the same as the outer surface. This means that the whole floc is effective and no diffusional resistance and the biochemical reaction is not limited by diffusion. It can be said that these models neglected the important role of mass

transfer, subsequently they neglected the importance of mechanical agitation, which helps to increase mass transfer rates,. It is logical, when the rates of mass transfer of substrate, oxygen, and ammonia are increased, the concentrations of these substances existing in the aerobic film of the activated sludge floc (as will be shown later) will also increase.

It is very important to consider the mass transfer operations beside the biochemical reactions to characterize these processes accurately and improve the efficiency of the activated sludge processes. Task group models can be considered as good examples for homogeneous models.

(B) Heterogeneous models

These models consider the mass transfer operations besides the biochemical reaction processes. They consider the internal diffusion of the floc beside the external mass transfer between gas, liquid, and solid phases through different processes occurring in the system. Hence, the resulted kinetic parameters are more intrinsic than resulted from homogenous models. In fact, the researches which concentrate on mass transfer within flocs of the activated sludge processes are few except some researchers like Benefield and Molz, 1983, 1984; Mikesell, 1984; Andrews, 1991; Bakti and Dick, 1992 and Tyagi, 1996). *Benefield and Molz*, (1983,1984) proposed a distributed parameter model including the material balance equations with Monod-type kinetics for the substrates inside the flocs and assumed an average floc size instead of considering the floc size distribution in the system in order to account for the effect of flocs on the dynamics of the system. *Beccari et al.,* (1992) developed a simple floc model with emphasis on the nitrification process in suspended culture taking into account the resistance related to oxygen diffusion inside the biofloc.

Tyagi et al., (1996) developed a simple floc model taking into account two growth processes: carbonaceous oxidation and nitrification that were thus interacting through their competition for dissolved oxygen inside the floc. This study can be considered as good examples for heterogeneous models. They developed a simple floc model taking into account two growth processes: carbonaceous oxidation and nitrification that were thus interacting through their competition for dissolved oxygen inside the floc. They did not consider two important notes: the first is that the anoxic decomposition of nitrate by denitrifcation was not incorporated into the floc model.

Table 1 Stoichiometric matrix n_j and composition $t_{k,i}$ of ASM 3. The values of x_j, y_j. z_j. and t_j can be obtained in the sequence from mass and charge conservation and composition.

J v	Components I> Process Expressed as >	1 s_O O_2	2 s_I COD	3 s_S COD	4 s_{NH} N	5 s_{N2} N	6 s_{NO} N	7 s_{HCO} Mole	8 X_I COD	9 X_S COD	10 X_H COD	11 X_{STO} COD	12 X_A COD	13 X_{TS} TSS
1	Hydrolysis		f_{SI}	X_I	y_I			z_I		-1				$-i_{XS}$
Heterotrophic organisms, denitrification														
2	Aerobic storage of COD	X_2		-1	y_2			Z_2				$Y_{STO,O2}$		t_2
3	Anoxic storage of COD			-1	y_3	$-x_3$	x_3	Z_3				$Y_{STO,NO}$		t_3
4	Aerobic growth	X_4			y_4			Z_4			1	$-1/Y_{H,O2}$		t_4
5	Anoxic growth (denitrification)				y_5	$-x_5$	x_5	Z_5			-1	$-1/Y_{H,NO}$		t_5
6	Aerobic endog. respiration	X_6			y_6			Z_6	f_I		-1			t_6
7	Anoxic endog. respiration				y_7	$-x_7$	x_7	Z_7	f_I		-1			t_7
8	Aerobic respiration of X_{STO}	X_8										-1		t_8
9	Anoxic respiration of X_{STO}					$-x_9$	x_9	Z_9				-1		t_9
Autotrophic organism, nitrification														
10	Nitrification	x_{10}			y_{10}			Z_{10}					1	t_{10}
11	Aerobic endog. respiration	x_{11}			y_{11}			Z_{11}	f_I				-1	t_{11}
12	Anoxic endog. respiration				y_{12}			Z_{12}	f_I				-1	t_{12}
Composition matrix $t_{k,j}$														
k	Conservatives													
1	COD g COD	-1	1	1		-1.71	-4.57		1	1	1	1	1	
2	Nitrogen g N		i_{NSI}	i_{NSS}	1	1	1		i_{NXI}	i_{NXS}	i_{NBM}		i_{NBM}	
3	Ionic charge Mole +				1/14		-1/14	-1						
	Observable													
4	TSS g TSS								i_{TSXI}	i_{TSXS}	i_{TSBM}	0.6	i_{TSBM}	

Table 2 Kinetic rate expressions pj for ASM3 all $p_j > 0$

j	Process	Process rate equation p_j all $p_j > 0$
1	Hydrolysis	$K_H \frac{X_S / X_H}{K_X + X_S / X_H} X_H$
Heterotrophic organisms, denitrification		
2	Aerobic storage of COD	$k_{STO} \quad \frac{S_O}{K_O + S_O} \frac{S_O}{K_S + S_{S\ g}} \quad X_H$
3	Anoxic storage of COD	$k_{STO} \ .\eta_{NO} \quad \frac{K_O}{K_O + S_O} \frac{S_{NO}}{K_{NO} + S_{NO}} \frac{S_S}{K_S + S_S} X_H$
4	Aerobic growth	$\mu_H . \frac{S_O}{K_O + S_O} \frac{S_{NH}}{K_{NH} + S_{NH}} \frac{S_{HCO}}{K_{HCO} + S_{HCO}} \frac{X_{STO} / X_H}{K_{STO} + X_{STO} / X_H} X_H$
5	Anoxic growth (denitrification)	$\mu_H . \eta_{NO} . \frac{K_O}{K_O + S_O} . \frac{S_{NO}}{K_{NO} + S_{NO}} \frac{S_{NH}}{K_{NH} + S_{NH}} \frac{S_{HCO}}{K_{HCO} + S_{HCO}} \frac{X_{STO} / X_H}{K_{STO} + X_{STO} / X_H} X_H$
6	Aerobic endog. respiration	$b_{H,O2} . \frac{S_O}{K_O + S_O} . X_H$
7	Anoxic endog. respiration	$b_{H,NO} . \frac{K_O}{K_O + S_O} . \frac{S_{NO}}{K_{NO} + S_{NO}} . X_H$
8	Aerobic respiration of X_{STO}	$b_{STO,O2} . \frac{S_O}{K_O + S_O} . X_{STO} \qquad b_{STO,O2} \geq b_{H,O2}$
9	Anoxic respiration of X_{STO}	$b_{STO,NO} . \frac{K_O}{K_O + S_O} . \frac{S_{NO}}{K_{NO} + S_{NO}} . X_{STO} \qquad b_{STO,NO} \geq b_{H,NO}$
Autotrophic organism, nitrification		
10	Nitrification	$\mu_A . \frac{S_O}{K_{A,O} + S_O} \frac{S_{NH}}{K_{A,NH} + S_{NH}} \frac{S_{HCO}}{K_{A,HCO} + S_{HCO}} X_A$
11	Aerobic endog. respiration	$b_{A,O2} . \frac{S_O}{K_O + S_O} . X_A$
12	Anoxic endog. respiration	$b_{A,NO} . \frac{K_O}{K_O + S_O} . \frac{S_{NO}}{K_{NO} + S_{NO}} . X_A$

Table 2.5 Typical values of kinetic parameters for ASM3.

Symbole	Characterization	Units
k_H	Hydrolysis rate constant	g X_S g^{-1} X_H d^{-1}
K_x	Hydrolysis saturation constant	g X_S g^{-1} X_H
Heterotrophic organisms, denitrification, X_H		
k_{STO}	Storage rate constant	g S_S g^{-1} X_H d^{-1}
η_{NO}	Anoxic reduction factor	-
K_O	Saturation constant for S_o	g O_2 m^{-3}
K_{NO}	Saturation constant for S_{NO}	g NO_3- N m^3
K_S	Saturation constant for substrate S_s	g COD m^3
K_{STO}	Saturation constant for X_{STO}	g X_{STO} g^{-1} X_H
μ_H	Heterotrophic max. growth rate	d^{-1}
K_{NH}	Saturation constant for ammonium S_{NH}	g N m^{-3}
K_{HCO}	Biocarbonate Saturation constant of X_H	mole HCO_3 - m^{-3}
$b_{H, O2}$	Aerobic endogeneous respiration rate of X_H	d^{-1}
$b_{H, NO}$	Anoxic endogeneous respiration rate of X_H	d^{-1}
$b_{STO, O2}$	Aerobic respiration rate of X_{STO}	d^{-1}
$b_{STO, NO}$	Anoxic respiration rate of X_{STO}	d^{-1}
Autotrophic organisms, denitrification, X_A		
μ_A	Autotrophic max. growth rate	d^{-1}
$K_{A,NH}$	Ammonium subsrtate saturation for X_A	g N m^{-3}
$K_{A,O}$	Oxygen saturation for nitrifiers	g O_2 m^{-3}
$K_{A,HCO}$	Biocarbonate saturation for nitrifiers	mole HCO_3 - m^{-3}
$b_{A, O2}$	Aerobic endogeneous respiration rate of X_A	d^{-1}
$b_{A, NO}$	Anoxic endogeneous respiration rate of X_A	d^{-1}

Consequently, they assumed the aerobic portion represents 100 % weight of the total floc. The important role of the anoxic growth of heterotrophs is neglected. The second is that they neglected the external mass transfer resistance due to boundary layer.

G. Ibrahim et al., (2002), based on the IAWPRC kinetic model developed, an appropriate mathematical model for activated sludge flocs to study the biofloc characteristics from the kinetics-mass transfer interaction point of view. The model was taking into account three growth processes: carbon oxidation, nitrification and denitrification in terms of four components: substrate, nitrate, ammonia, and oxygen. The effect of their bulk concentrations, diffusivity and external mass transfer of substrates on the biofloc characteristics in terms of the aerobic portion weight to the

total floc was studied. It can be said that the aerobic portion was found to be more sensitive to the change of the bulk concentrations of oxygen, substrate, and ammonia in addition to the power input and substrate diffusivity. It was less sensitive to the change of nitrate bulk concentration. This model describes quantitatively the biofloc activity, as it may be totally active, which is totally aerobic or aerobic-anoxic, or it may be partially active.

Table 4 Typical stoichiometric and composition parameters for ASM3.

Symbol	Characterization	Units
f_{SI}	Production of S_I in hydrolysis	g S_I g^{-1} X_S
$Y_{STO,O2}$	Aerobic yield of stored product per S_S	g X_{STO} g^{-1} S_S
$Y_{STO,NO}$	Anoxic yield of stored product per S_S	g X_{STO} g^{-1} S_S
$Y_{H,O2}$	Aerobic yield of heterotrophic biomass	g X_H g^{-1} X_{STO}
$Y_{H,NO}$	Anoxic yield of heterotrophic biomass	g X_H g^{-1} X_{STO}
Y_A	Yield of autotrophic biomass per NO_3- N	g X_A g^{-1} S_{NO}
i_{NSI}	N content of S_I	g N g^{-1} S_I
i_{NSS}	N content of S_S	g N g^{-1} S_S
i_{NXI}	N content of X_I	g N g^{-1} X_I
i_{NXIS}	N content of X_S	g N g^{-1} X_S
i_{NBM}	N content of biomass, X_H , X_A	g N g^{-1} $X_{H\ ORA}$
i_{TSXI}	TSS to COD ratio for X_I	g TS g^{-1} X_I
i_{TSXS}	TSS to COD ratio for X_S	g TS g^{-1} X_S
i_{TSBM}	TSS to COD ratio for biomass, X_H ,X_A	g TS g^{-1} $X_{H\ or\ A}$
i_{TSSTO}	TSS to COD ratio for X_{STO} based on PHB	g TS g^{-1} X_{STO}

3. Aeration and Mass Transfer

Mass transfer is an important consideration in many wastewater treatment systems. In order to carry out chemical or biological reactions. It is necessary to transfer substances into or out of the wastewater as well as to move them adequately within the water to control concentration differences. The material transferred can be as diverse as gases, liquids, ions, charged colloids, or suspended solids. However, the rate at which these substances are transferred is the important consideration and is the primary concern of the field of mass transfer. The principles of mass transfer do not vary with each process.

Guellil et al., (2001) fractionated the organic matter of wastewater into settleable (i.e., particulate) and non- settleable (i.e., colloidal +soluble) fractions.

Particulate, colloidal and soluble proportions were found to be relatively constant (45, 31 and 24% of the total COD, respectively). Transfer of soluble fraction always occurred from the wastewater to the activated sludge flocs, whereas bi-directional transfer occurred for the colloidal fraction. He showed that the transfer of soluble and colloidal matter reached a steady state after 40 min -mixing and 20 min -mixing, respectively.

The rate of oxygen transport is of great importance. We will consider the rate at which oxygen enters the water and the rate which oxygen and other dissolved species are transferred to the biological floc.

3.1 Limiting resistance for mass transfer

The study of Guellil et a., (2001) shows that a fraction of the organic matter is transferred between the aqueous phase and the activated sludge flocs within a few minutes. On an average, 45% of the non-settleable (i.e., colloidal + soluble) fraction of the wastewater from Maxe ĩville WWTP (Nancy, France) was removed during this short contact time at an initial rate of about 14 mg COD g-1 TSS min،-1 Fractionation of the non-settleable matter into a colloidal and a soluble fraction revealed that steady state was obtained after 20 and 40 min, respectively. One can assume that steady state obtained for soluble matter is delayed because of its diffusion into the floc matrix. This diffusion becomes a limiting step of soluble organic matter removal. Colloids do not penetrate into the matrix because of their size (Jimenez et al., 1988; Tanaka et al., 1984), and may then be trapped very early in the outermost part of the floc.

When an oxygen molecule passes from the gas into the liquid phase and hence, to the biological floc, it must go through many separate resistances. Before any specie will move through the water, there must be some driving potential, usually concentration differences, which will make a molecule, move from one region to another. The rate of flow of any substances is directly proportional to driving potential and inversely proportional to the sum of the resistances between the two points of mass transfer. The important resistances occur most often at the interface between two phases. Consider the transport of oxygen from the gas phase to a solid phase, e.g., biological floc, as shown in Figure 1. The oxygen molecule in the gas phase, must first overcome a resistance on the gas side within the bubble and then make jump to the liquid side where it again meets another resistance before it reaches the bulk

liquid. Once in the liquid the oxygen molecule must now move through the fluid and eventually reach the solid phase and encounter another liquid-solid resistance, which it must overcome to become adsorbed onto the solid surface. Once the oxygen becomes on the surface it must then diffuse into the pores or cells of the solids and reach the reaction site where it is consumed. Another reaction products,. e.g., CO_2 must go through the same resistances in the reverse order before they can reach the gas phase. Physically it can be said that these various resistances occur at points where the motion of the molecules is in the surrounding areas. The slower molecular motion may be caused by either decreased kinetic energy from lower temperature and forming chemical complexes or poor fluid mixing from increased shear stresses near a boundary.

In the aeration of water, the most important resistances are:

1.Liquid-film resistance between the gas-liquid interface and the bulk of the liquid.

2.Bulk-liquid resistance caused by poor mixing in the liquid.

3. Liquid-film resistance at the solid interface.

4. Bulk-solid resistance caused by slow diffusion rates in the solid.

5. Reaction resistance caused by slow chemical reaction rates at the site.

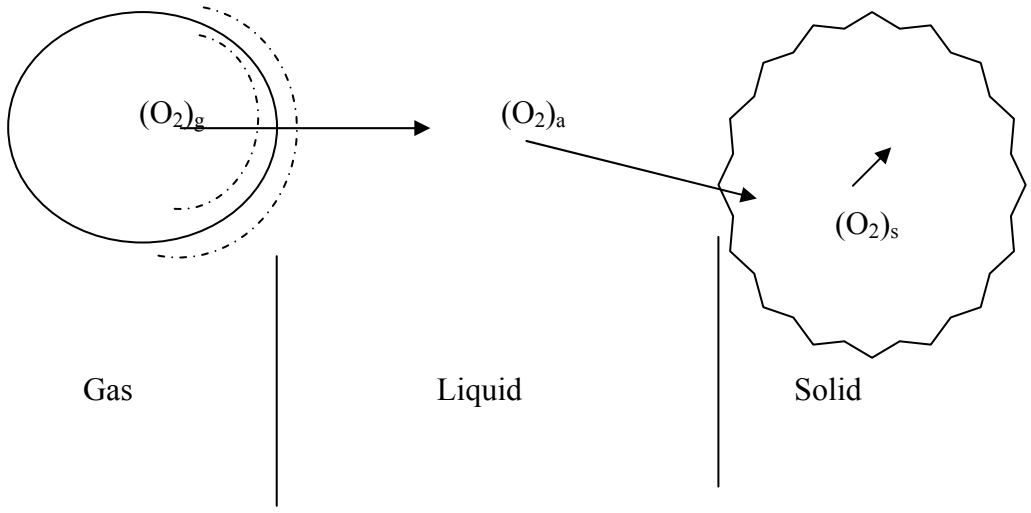

Figure (1): Resistance to oxygen transfer (-----)

3.2 Evaluation of mass transfer coefficients

It has been found that at high agitation intensities, turbulence is expected to affect mass transfer rate at the biofloc surface. However, the actual floc velocity is unknown and conventional Reynolds numbers cannot be deduced. In this case, the concept of local isotropic turbulence may be applied. (*Moo–Young and Blanch, 1981*).

They proposed that an isotropic turbulence Re-no., Re_e , for the floc particle diameter *d*. This can be given as:

$$Ree = \frac{d^{4/3}\rho^{2/3}(P/V)^{1/3}}{\mu} \qquad (1)$$

They developed a correlation for rigid surface particle mass transfer in biochemical reactors in terms of the energy input to the system as follows:

$$Sh = 0.13Ree^{3/4}Sc^{1/3} \qquad (2)$$

Where:

$$\mathrm{Sh}\left(\text{Sherwood number}\right) = \frac{\text{total mass transfer}}{\text{diffusive mass transfer}} = \frac{K_1\, d}{D_1}$$

$$\mathrm{Sc}\left(\text{Schmidit number}\right) = \frac{\text{momentum diffusivit y}}{\text{diffusive mass transfer}} = \frac{\mu}{\rho D_1}$$

$$\mathrm{Re}\left(\text{Reynolds number}\right) = \frac{\text{inertia forces}}{\text{vescous forces}} = \frac{\rho dv}{\mu}$$

The mass transfer coefficient (K_l) is seen to be dependent on $(P/V)^{1/4}$ which can be expressed by the effect of power input on interfacial area. These both relations, by Moo-Young and Blanch, are used to calculate the mass transfer coefficients of the considered four components as a function of the power input.

3.3 Estimation of K_la

The overall volumetric mass transfer coefficient or oxygen transfer function, K_la, is the common design parameters for specifying the rate of aeration of wastewater. When air is blown into the wastewater of an activated sludge process, oxygen is transferred to the water.

The function, which describes the oxygen transfer to the wastewater by the aeration system, is called the K_la function. The most common way to describe the rate of change in dissolved oxygen, due to the air blown into water, is given by the following expression:

$$\frac{dC}{dt} = K_{la}\left(C^* - C(t)\right) \qquad (3)$$

Integrating using the boundary conditions of $C=C^0$ at t=0 gives,

$$ln\left[\frac{C^* - C^0}{C^* - C}\right] = K_{la}\ t \qquad (4)$$

Where C(t) is the DO and C^* is the saturated DO

In a real plant K_la depends on several factors, for example, type of diffusers, wastewater composition, temperature, design of aeration tank, tank depth,..etc., but the main time varying dependence is the airflow rate. K_la can be considered to consist of parts, K_l and *a*. The K_l part can be seen as a mass transfer coefficient and the a part as an area/volume ratio. Both K_l and *a* are however ,usually unknown so they are lumped into one parameter denoted K_la.. *(Carl- Fredric Linberg 1997).*

A large number of different empirical correlations for volumetric mass transfer coefficients, K_la, have been presented in the literature (*Moo–Young and Blanch, 1981*). Most of these correlations can be written in the form:

$$K_{la} = K\ u_s^{\alpha}\ (\frac{P}{V})^{\beta} \qquad (5)$$

Where: u_s is the superficial gas velocity (the gas flow rate divided with the cross sectional area of the tank. Unit; m/s), K is constant, and (P/V) is the power per unit volume (W/m^3).

Normally the correlation (5) holds independently whether mixing is performed mechanically in stirred tank reactor and or a bubble column. It is, however, possible to obtain much higher power input in stirred tank reactors than in bubble columns, and stirred tanks are therefore traditionally used in aerobic fermentation processes where there is a high oxygen demand, e.g. antibiotic fermentation. New fermentor designs based on cleverly designed static mixers or gas injection nozzles can, however, outperform the stirred tanks.

When the range of process variables for which the correlation (5) holds is studied in more detail, it is observed that the mass transfer coefficient K_la for non-coalescing medium is about a factor 2 greater than for a coalescing medium at the same operating conditions. It is found that the influence of the power input is larger in the non- coalescing medium whereas the influence of the superficial gas velocity is smaller compared with a coalescing medium (e.g. pure water). If one calculates the

kla value for a certain set of operating conditions it is, however, found that the variations using the different parameters values in Table (5) are relatively small.

Table 5 Parameter values for the empirical correlation (5). The parameter values are specified with all variables being in SI- unites, i.e. the power input is in units W/m^3 and the superficial gas flow rate is in units m/s.

Medium	K	α	β	Agitator	Reference
coalescing	0.025	0.5	0.4	6 bladed rushton turbines	Moo-Young and Blanch
	0.00495	0.4	0.953	6 bladed rushton turbines	Linek et al.(1987)
	0.01	0.4	0.475	Different agitators	Moo-Young and Blanch
	0.026	0.5	0.4	Not specified	Van't Riet(1977)
Non- coalescing	0.0018	0.3	0.7	6 bladed rushton turbines	Moo-Young and Blanch
	0.02	0.4	0.475	Different agitators	Moo-Young and Blanch
	0.002	0.2	0.7	Not specified	Van't Riet(1977)

It was found that the effect of (P/V) on volumetric mass transfer coefficient, $K_l a$, exhibits saturation like behavior. This effect assumed saturation like correlation (6). This correlation is considered as a possible alternative approach, deduced to calculate $K_l a$ as shown in correlation (5). It resembles the correlations deduced by James Baily (1986) and Mervat (1995). The correlation (6) is a function of power input per unit volume and maximum overall volumetric mass transfer coefficients, $K_l a$

$$K_{la} = \frac{K_{la\,\max.}\ (P/V)}{(P/V) + k} \qquad (6)$$

Where: $K_l a_{\max}$ is the maximum value of overall volumetric mass transfer coefficients, (P/V) is power input per unit volume in (W/m^3), and k is constant.

4. Diffusion in the sludge floc

This section explains flow through activated sludge flocs and explains how diffusion coefficients inside the flocs can be evaluated.

4.1 Flow through activated sludge flocs

Activated sludge flocs are irregular shaped, fragile almost transparent aggregates, which have a high water content and spread over a wide size range (Li

and Ganczarczyk, 1986). Coinciding with the high water content, high porosity of activated sludge flocs has been reported by many investigators (Muller et al., 1966; Smith and Coakley, 1984; Li and Ganczarczyk, 1987). However, diffusion models have been predominantly applied in the analysis of mass transfer within the activated sludge floc (e.g., Baillod and Boyle, 1970; Smith and Coakley, 1984), despite the fact that the flocs are highly porous and the outcomes from measurements of substrate uptake rates of the flocs are sometimes controversial. These diffusion models led to the conclusion that cells within a bacterial floc could never have a greater substrate uptake rate than dispersed cells (Aris, 1975; Matson and Characklis, 1976).

Based on the diffusion concept, many researchers hypothesized that an anoxic core existed in a bacterial floc of certain size as a result of oxygen transfer limitations (Matson and Characklis, 1976; Benefield and Molz, 1984).

Da-Hung Li and J. Ganczarczyk (1988) showed that for non-biological systems, some theoretical analyses described possible fluid flow through highly porous aggregates. The analyses showed that the hydrodynamic resistance experienced by an aggregate permeable to the liquid flow would be less than that by an impermeable aggregate. Correspondingly, the terminal settling velocity of a permeable aggregate would be higher than that of an impermeable aggregate of the same size and density.

Hunt and Logan (1988) indicated that the traditional diffusion models for substrate transport into microbial aggregates such as activated sludge flocs were difficult to justify. From the genetic point of view, bacteria should not expend energy to form flocs under-nutrient conditions, if floc formation had only resulted in a reduced nutrient availability to the cells. They theorized that bioflocculation was an advantageous microbial response to substrate limitations. According to their prediction, the microbial aggregates were so porous that they might be permeable to fluid flow within flocs.

The hypothetical behavior of diffusion in the sludge floc was qualitatively described as follows: Initially the sludge floc can be assumed fully penetrated with dissolved oxygen and lacking substrate. When substrate is added to the bulk liquid, substrate diffuses into the activated sludge floc. Their aerobic microorganisms convert the substrate consuming an amount of oxygen. This oxygen consumption induces a difference in oxygen concentration between the floc and the bulk, and oxygen diffuses from the bulk into the floc.

4.2 Estimation of diffusion coefficients

Although the aeration of the biological reactor may be excellent and sufficient agitation is present to prevent local concentration gradients in the liquid, the rate of substrate removal may be still be low because of either interfacial resistances around the biological floc, or poor diffusion of the oxygen and substrate into the interior of the floc. It can be said that transport within biological solids (films or flocs) is generally attributed to diffusion alone and assumed to adhere to Fick' s law:

$$N_s = -D_s \frac{ds}{dr} \qquad (7)$$

Where:

N_s is the mass flux, D_s is the intrafilm diffusivity and ds/dr is the spatial concentration gradient.

The presence of intrafilm adjective transport is plausible in many situations but is inadequately quantified and routinely ignored for purposes of simplification. Application of Fick' s law requires knowledge of D_s. Investigators have reported widely varying ratios of intrafilm to pure water diffusion coefficients (Grady, 1983).

Tanaka et al., (1984) found that the diffusion coefficient of glucose in the calcium alginate is close to that of water, while Hannoun and Stephanonpoulus (1986) measured smaller values than for water. Merchant (1987), Itamunoala (1987), Axelsson and Persson (1988) and Scott et al., (1989) also observed that effective diffusion coefficient of glucose and ethanol are smaller than that for water. Hence, in some cases diffusivities have been used as fitting parameters in substrate utilization models. Uncertainty in values of kinetic parameters compounds uncertainty in estimates of diffusion coefficient determined in this manner. Failure to consider external mass transfer resistance may also affect resulting estimates of diffusivity.

Table (6**)** summarizes published results of experiments (Kissel 1985) in which diffusivities through inactivated biomass were measured. Substantial variability is seen even this narrowed sample of experiments. Possible explanations for this variability include differences in biomass growth conditions and film preparation and differences in hydraulic characteristics of experimental systems. For example, Matson and Characklis (1976) and Onuma and Omura (1982) have reported variance in film diffusivities with carbon to nitrogen ratio in the media in which the biomass was

grown interestingly, Smith and Coackley (1984) found essentially no dependence of intrafilm oxygen diffusivity on biomass density. Siegrist and Gujer (1984) found reduced overall mass transfer resistance in their experimental apparatus with biofilms of more than a certain thickness. They attributed their results to penetration of the external laminar fluid layer by biological growth and subsequent induction of turbulent transport in the outer portion of the biofilm that effectively reduced the depth of biofilm through which solutes only diffused. The significance of this phenomenon in conventional treatment processes is unknown. Internal fluid flow probably occurs at least near the biofilm/liquid interface (which is often hard to define) in many fixed – film processes. However, fluid velocities relative to biomass in Siegrist and Gujer' s reactor were almost certainly significantly greater than that would be found in treatment systems. (Their experiments were conducted at a Reynolds number greater than 4000 based on impeller speed and diameter.)

Table (6) shows diffusion coefficients for various compounds through microbial aggregates that have been reported in the literature, mostly for floc particles. Matson and Characklis report variation in the diffusion coefficient for glucose and oxygen with growth rate and carbon-to- nitrogen ratio. In biofilms, the diffusion coefficient is most probably related to biofilm density.

It is noted that from Table (5) and Table (7) there is uncertainty in estimates of diffusion coefficients determined according to the method used for measuring.

There is a large range in estimation of diffusivities of substrate and other compounds and its evaluation with respect to diffusivity of water (D_w). There seems to be confusion about diffusivity estimation, which leads to confusion about mass transfer coefficient estimation. To deal with this situation it has been assumed that the diffusivities in a sludge floc are 80% of those in water.

Table 6 Ratios of experimentally determined diffusivities in inactivated biomass to diffusivities in water

D_f / D_w							Method of "Biofilm" preparation	Reference
Oxygen	Glucose	NH_4^+	NO_2^-	NO_3^-	Na^+	Br^-		
0.85	-	0.8-87	0.86	0.93-1.0	-	-	Filtered	Williamson and MvCarty (1976)
0.2-1.0	0.3-0.5	-	-		-	--	Centrifuged, pressed into mold	Matson and Characklis (1976)
1.2	0.15-1.2	0.7	-	-	-	-	Settled/ Filtered	Onumuma and Omura (1982)
-	0.6	-	-	-	0.6	0.5	Grown in place	Siegrist and Gujer (1984)
0.3	-	-	-	-	-	-	Settled/ Centrifuged	Smith and Coackley (1984)

Table (7). Experimental diffusion coefficient measurements from the literature

Reactant	Diffusivity 10^{-5} cm^2/s	F_{loc}/D_{H2O} x100%	Biomass Type	Growth System	Procedure
Oxygen	1.5	70	Bacterial Slime	Rotating Tube	Reaction products Analysis
Oxygen	0.21	8	Fungi Slime Zooglea ramigera	Fluidized reactor	Nonlinear Curve Fit
Glucose	0.048	8	Zooglea ramigera	Fluidized reactor	Nonlinear Curve Fit
Glucose	0.06-0.6	10-100	Nitrifier culture	Fluidized reactor	Two Chamber
Oxygen Ammonia Nitrate	2.2 1.3 1.4	90 80 90	Mixed culture	Fluidized reactor	Two Chamber
Oxygen*	0.4-2.0	20-100	Mixed Culture	Fluidized reactor	Two Chamber
Glucose*	0.06-0.21	10-30			

Conclusions

Mathematical process modeling and biokinetics of activated sludge process were reviewed considering different types of models. It has been evaluated the task group models of ASM1, and 2, and 3 versioned by Henze et al considering the conditions of each model and the different processes of which every model consists. It is revealed that ASM1 contains some defects apparent with lts application. These defects avoided in ASM3. One of the most important defects that ASM1 does not include kinetic expressions, which can deal with nitrogen and alkalinity limitations of heterotrophic organisms. This results in the fact that computer code cannot be based on the original form of ASM1, which allows under some circumstances for negative concentrations of e.g. ammonium. These led to the creation of different versions of ASM1, which can hardly be differentiate any more. Another important defect is that ASM1 includes biodegradable soluble and particulate organic nitrogen as model components. These cannot easily be measured and have in the meantime been eliminated in many versions of ASM1.

Relied on homogeneity, Models can be classified into homogenous models characterized by taking the activated sludge process as one phase. In this type of models, the internal mass transfer inside the flocs was neglected. Hence, the kinetic parameter produces can be considered inaccurate. The other type of models is the heterogeneous model. This type considers the mass transfer operations in addition to the biochemical reaction processes; hence, the resulted kinetic parameters can be considered more accurate than that of homogenous type.

The mass transfer coefficients (K_l) of substances such as substrates, oxygen, nitrates, and ammonia were evaluated by Moo-Young and Blanch relations as a function of power input. The overall volumetric mass transfer coefficient or oxygen transfer function, $K_l a_{,}$ is the common design parameters for specifying the rate of aeration of wastewater. A large number of different empirical correlations for volumetric mass transfer coefficients, $K_l a$, have been presented; however the most practical relations that introduced by (*Moo–Young and Blanch, 1981*). These relations present $K_l a_{,}$ as a function of power input and superficial gas velocity. There seems to be confusion about diffusivity estimation, which leads to confusion about mass transfer coefficient estimation due to uncertainty in estimates of diffusion coefficients determined according to the method used for measuring. To deal with this

situation it has been assumed that the diffusivities in a sludge floc are 80% of those in water.

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