Monitoring and modelling an industrial trickling filter using on-line off-gas analysis and respirometry

H. Vanhooren,* D. Demey,** I. Vannijvel*** and P.A. Vanrolleghem*

*BIOMATH Department, Ghent University, Coupure 653, 9000 Gent, Belgium
(E-mail: *Henk.Vanhooren@rug.ac.be*)

**EPAS NV, Technologiepark 3, 9052 Gent, Belgium

***Janssen Pharmaceutica NV, Janssen-Pharmaceuticalaan, 2440 Geel, Belgium

Abstract The process characteristics of an industrial scale trickling filter plant were quantified by means of a five day intensive measurement campaign with the use of on-line respirometry and on-line off-gas analysis. Respirometry was used to measure the readily biodegradable COD_{st} and the off-gas sensor was used to monitor the O_2 and CO_2 content of the off-gases. To model the biodegradation in the filters, the model developed by Rauch et al. (1999) was used. It is based on the decoupling of two basic processes in biofilm systems, substrate diffusion and biodegradation. This model was extended with equations for the production and the *pH*-dependent liquid-phase equilibrium for inorganic carbon (*IC*). The measured effluent and off-gas concentrations could be followed very closely by the calibrated model. O_2 and CO_2 measurements revealed that the system was not always oxygen limited. The model calibration thus required the use of a very low value of the diffusion constant for readily biodegradable substrate.

Keywords Biofilm; mathematical modelling; off-gas analysis; respirometry; trickling filter

Introduction

The process under study is an industrial wastewater treatment plant. A characteristic of the WWTP is that the influent concentration of *COD* is extremely high and varies dramatically over time. This paper describes part of a project, the aim of which is to optimise the plant by applying minor process changes and process control. On-line sensors were integrated and the plant was modelled and simulated to test out proposed process changes and control strategies.

A schema of the biofilm wastewater treatment plant under study is depicted in Figure 1. It consists of two trickling filters (TF01 and TF02) working in parallel. Each filter has a height of 6 m and a diameter of 18.5 m. The total reactor volume is 3160 m^3. This volume is filled with a PVC carrier material of the cross-flow type with a specific surface area of 100 m^2/m^3 and a porosity of about 95%. There are several recycle loops, which ensure that each filter receives a constant recycle flow of 300 m^3/h. Two "short" loops recycle the effluent of each filter to its pumping tank. A "long" recycle loop takes the water through an intermediate clarifier. Part of this flow serves as the influent to the activated sludge system, the rest is distributed again over both trickling filters. Both pumping tanks have a volume of 128 m^3. To provide the biomass in the filters with oxygen, two ventilators suck air through the bed volume with a flow rate of approximately 7800 m^3/h for TF01 and 9500 m^3/h for TF02. Both ventilators also have a "low position", providing a flow of 4300 m^3/h for TF01 and 6600 m^3/h for TF02. These flow rates have been measured using a pitot tube. The average total influent flow rate was 110 m^3/h. The organic load of the plant equals 15000 kg *COD*/d.

The measurements conducted were used to monitor/model the biodegradation of components in the filters and their behaviour under changing process conditions. To investigate the response of the system to a changing air flow rate through the filters, the air flow was halved halfway through the measurement campaign.
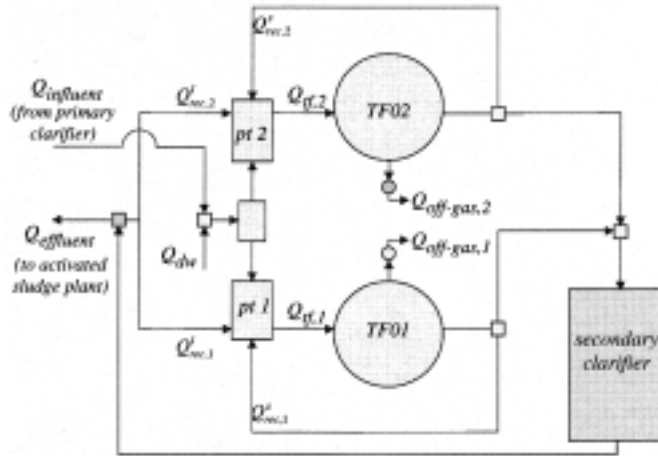
Figure 1 Hydraulic lay-out of the trickling filter system under study (pt=pumping tank, dw=dilution water)

Measurement techniques

Measurements of *COD*, *SS*, *N* and *P* were made using standard methods. The readily biodegradable COD_{st} measurement was conducted on-line with the RODTOX biosensor (Kelma bvba, Niel, Belgium) available on-site (Vanrolleghem, 1994). Measurements of COD_{st} were conducted in the influent as well as in the effluent of the filters by sensor multiplexing.

The O_2 measurement was based on the paramagnetic characteristic of oxygen gas. The measuring cell contains a diamagnetic part suspended in a permanent magnetic field in such a way that it can rotate out of the magnetic field. An opto-electrical compensation circuit is provided to keep the dumbbell in a defined resting position. The paramagnetic characteristic of the O_2 in the sample gas will change the magnetic field. This effects an adaptation of the opto-electrical compensation which is used to calculate the O_2 concentration.

CO_2 was measured with the NDIR (non-dispersive infrared) method. The sample gas is pumped through one compartment (the measuring side) of a measuring cuvette. The other compartment (the reference side) is filled with a reference gas. The radiation is directed to one side of the cuvette at a time with a modulation wheel. A certain amount of the component of interest (CO_2 in this case) is also enclosed in a detector that consists of two optical absorption layers in series, pneumatically separated by a window. The amplitude of the pressure pulses of the window, due to unequal heating in both compartments, is used as a measure of the CO_2 concentration in the sample gas.

A single measurement of the CO_2 concentration in the off-gases of the filter is not sufficient to describe the inorganic carbon (*IC*) equilibrium. Indeed, some microbially produced CO_2 can leave the system in the water and not in the gas phase. For that reason, extra measurements of the *IC* concentration and the *pH* were needed. This was done using the titration technique developed by Van Vooren *et al.* (1999). Titration curves are monitored by adding a 0.1 M *HCl* solution to lower the *pH* from the actual *pH* of the sample, down to *pH* 2.5. Software developed in C++ calculates the buffer capacity profiles from the titration curves and estimates the *IC* concentration from them. Once the total *IC* is determined, the partitioning among the forms HCO_3^- and $CO_{2,(aq)}$ can be determined using a partitioning model that is a function of the actual *pH* of the sample (note that CO_3^{2-} is only present in very small concentrations at the *pH* values usually encountered in wastewater treatment systems). This

can be done using the following equations:

$$[CO_{2,aq}] = \frac{10^{-2pH}}{10^{-2pH} + 10^{-(pH+pK_{a1})} + 10^{-(pK_{a1}+pK_{a2})}} C_{IC} \quad [HCO_3^-]$$

$$= \left(1 - \frac{10^{-2pH} + 10^{-(pK_{a1}+pK_{a2})}}{10^{-2pH} + 10^{-(pH+pK_{a1})} + 10^{-(pK_{a1}+pK_{a2})}}\right) C_{IC} \tag{1}$$

Model building

Dynamic biofilm model

A simple dynamic model was used for simulation of the removal of substrates by bacterial species growing in a biofilm reactor (Rauch *et al.*, 1999). The fact that makes most biofilm models relatively complex is that not only the microbial conversion of substrates needs to be considered but also the diffusive transport of soluble substrates inside the biofilm (Figure 2). The basic idea behind this model implementation is to decouple the calculations of these two processes occurring in the biofilm. The model is an extension to the well known half-order reaction concept that combines a zero-order kinetic dependency on substrate concentration with diffusion limitation. The separate assessment of substrate diffusion means that the penetration depth of substrates can be related to a fraction of biomass that is active in conversion. The conversion is then calculated considering only the active fraction of the biomass. The major advantage of the model is the simple structure, which leads to a lower computational requirement than other state-of-the-art biofilm models. The model is solved by means of a two step procedure where (1) for each conversionprocess that is influenced by diffusion, the active fraction of the biomass within the biofilm is computed by
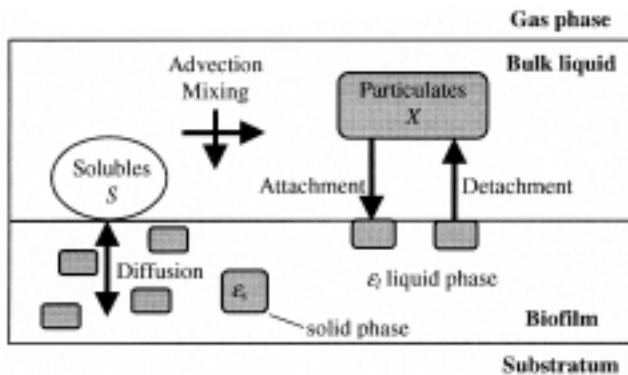

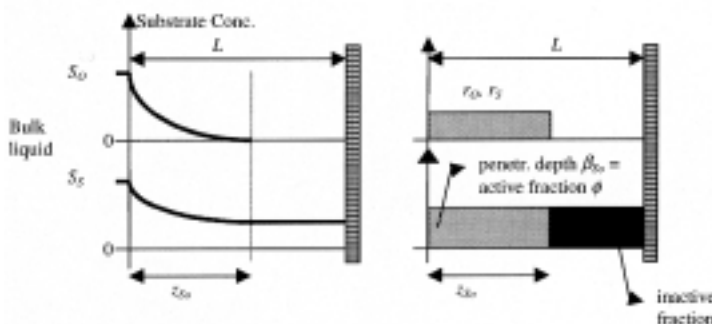**Figure 2** Transport processes in an ideal biofilm system

Figure 3 Illustration of a diffusion limited reaction in a system with 2 substrates (S_O being oxygen and S_S being organic matter) and 1 species. S_O is the limiting substrate

Table 1 Process matrix for biokinetic processes in the biofilm and corresponding effect on the concentration of soluble components in the bulk liquid

Process	Bulk Liquid					Biofilm			Process rate $ML^{-3}T^{-1}$
	$S_O\,ML^{-3}$	$S_S\,ML^{-3}$	$S_R\,ML^{-3}$	$S_{ND}\,ML^{-3}$	$S_{NH}\,ML^{-3}$	$X_{BH}\,ML^{-3}$	$X_{BS}\,ML^{-3}$	$X_{BI}\,ML^{-3}$	
aerobic het. growth	$1-1/Y_H$	$-1/Y_H$			$-i_x$	1			$\mu_H \cdot X_{FBH} \cdot \phi H$
decay heterotrophs						-1	$1-fp$	fp	$b_H \cdot X_{BH}$
hydrolysis of X_{BS}		1			i_x		-1		$k_h \cdot X_{BS}$
hydrolysis of S_R		1	-1						$k_r \cdot S_R$
hydrolysis of S_{ND}				-1	1				$k_a \cdot S_{ND}$

means of a simple analytical solution and (2) all conversions within the biofilm are calculated as if the biofilm was an ideally mixed reactor but with only the active fraction of the species contributing (Figure 3).

The assumptions this model relies upon are the following: (1) the biofilm is assumed to be of homogeneous structure and density, (2) the microbial species in the biofilm are uniformly distributed, (3) the traditionally modelled stagnant liquid layer is neglected, (4) reaction rates are of zero-order, (5) soluble components that emerge from conversion processes inside the film are assumed to be subject to immediate "out-diffusion" at the surface of the biofilm and (6) an instantaneous steady-state substrate profile is assumed.

The use of zero-order reaction rates (assumption 4) is very widespread in biofilm modelling, as it is a good description of biofilm kinetics when substrate concentrations are sufficiently high. Since the trickling filters are used as a pre-treatment step for the subsequent activated sludge system, effluent concentrations are sufficiently high to allow the use of zero-order reaction rates (Figure 9).

Assumption 5 is only of importance when a soluble component is produced inside the biofilm due to conversion processes (e.g. nitrate from nitrification). The assumption of immediate out-diffusion indeed neglects the possible accumulation of the component inside the biofilm. However, since nitrification and denitrification were not occurring, these processes were removed from the model and nitrate accumulation was not to be considered.
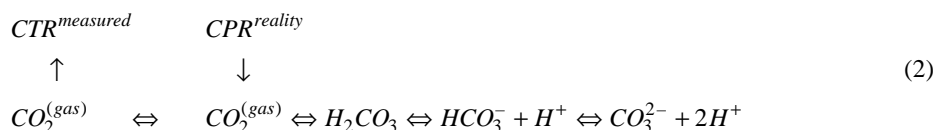
Assumption 6 is, in principle, violating the mass balances in a dynamic simulation. However, as outlined in Wik (1999), the characteristic time of the hydraulic and diffusion phenomena is about one order of magnitude smaller than the time scale of reactions in the film. It is thus reasonable to solve the equations for substrate diffusion in a steady state when simulating the relatively slow dynamics in the biofilm system.

The biokinetic process description is straightforward once the active fractions of the biomass have been computed. The concepts formulated in the activated sludge model No 1 (Henze *et al.*, 1987) are followed as closely as possible (Table 1). However, a new influent component was introduced, named S_R. This was needed to make the dynamics of soluble *COD* fit. Hydrolysis of SR is described by a simple first order equation and is linked to S_S.
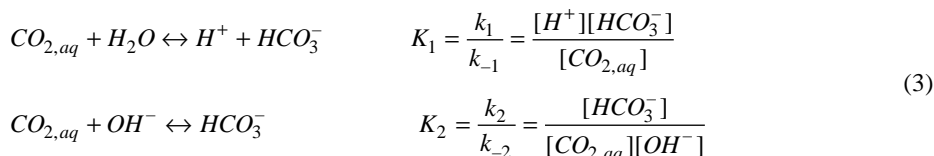
Model extension for inorganic carbon production and transport
The model described above was extended with a model for the description of the carbon dioxide production rate (*CPR*) in the biofilm reactor, partly based on the model developed by Spérandio and Paul (1997). The *CPR* is, however, not directly measurable. Production of *IC* from bacterial conversion takes place in the form of $CO_{2,aq}$. The dynamic equilibria in which CO_2 plays a role result in a distribution of CO_2 over the liquid and the gas phase so

that a CTR (CO_2 transfer rate), rather than a *CPR*, is measured (Govind *et al.*, 1997), that is:

$$CTR^{measured} \qquad CPR^{reality}$$
$$\uparrow \qquad\qquad \downarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2)$$
$$CO_2^{(gas)} \quad \Leftrightarrow \quad CO_2^{(gas)} \Leftrightarrow H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \Leftrightarrow CO_3^{2-} + 2H^+$$

Since the hydration of CO_2 is established very slowly, a combination of the equilibria is allowed (Noorman *et al.*, 1992). The following equilibrium reactions with their corresponding dissociation constants K_1 and K_2 can take place:

$$CO_{2,aq} + H_2O \leftrightarrow H^+ + HCO_3^- \qquad K_1 = \frac{k_1}{k_{-1}} = \frac{[H^+][HCO_3^-]}{[CO_{2,aq}]}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3)$$
$$CO_{2,aq} + OH^- \leftrightarrow HCO_3^- \qquad K_2 = \frac{k_2}{k_{-2}} = \frac{[HCO_3^-]}{[CO_{2,aq}][OH^-]}$$

In this model, the *IC*-equilibrium is modelled kinetically. The *pH*-dependent production rate of bicarbonate can be written as:

$$r_{HCO_3^-} = k_1[CO_{2,aq}] - k_1[HCO_3^-][H^{\neq}] + k_2[CO_{2,aq}][OH^-] + k_{-2}[HCO_3^-] \qquad (4)$$

The mass transfer between gas and liquid phase for carbon dioxide is expressed as:

$$\Phi_{CO_2}^{G \rightarrow L} = CTR - K_L a^{CO_2} \cdot ([CO_{2,aq}]^* - [CO_{2,aq}]) \cdot V \quad \text{with} \quad [CO_{2,aq}]^* = \frac{p_{CO_2}}{H} \qquad (5)$$

where H is the Henry's constant for CO_2 (atm-1M) (Sander, 1996).

Model implementation

The dynamic model along with the extension described above was implemented in the simulator WEST++ (Hemmis NV, Kortrijk, Belgium). The hydrodynamics of the filter system were taken into account (De Clercq *et al.*, 1999; Vanhooren *et al.*, 2000). The model implementation is represented in Figure 4.
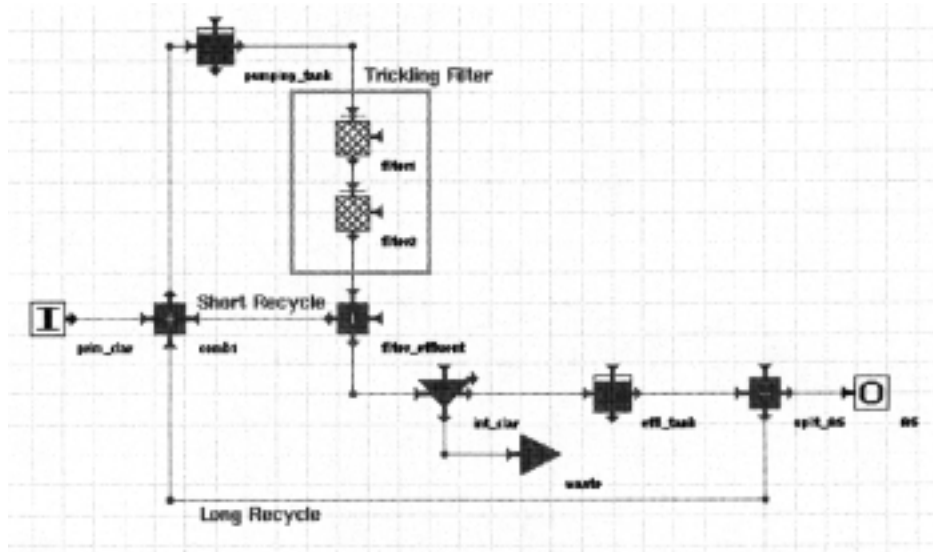
Figure 4 Layout of the trickling filter system in the simulator WEST
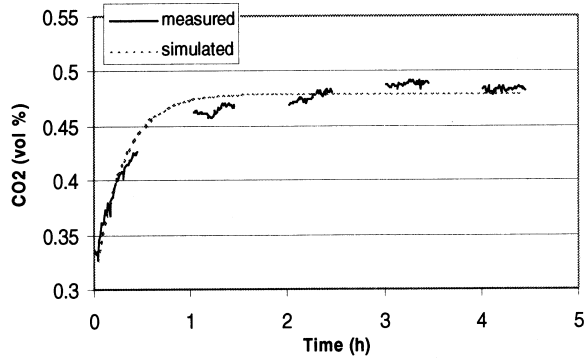
Figure 5 Comparison between simulated and measured CO_2-concentration in the off-gas of TF02 after lowering the air flow rate at time 0
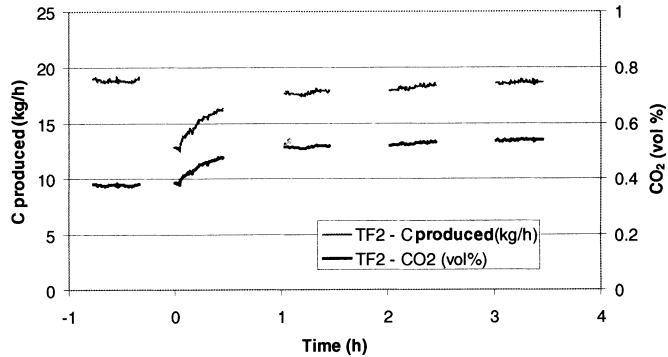
Figure 6 Influence of the air flow change on the *IC* production and CO_2 concentration of TF02

Hydrodynamics of the trickling filters

The hydraulic behaviour of the trickling filter was modelled using the results of a tracer test. The tracer, 5 kg of *LiCl*, was injected as a pulse in the pumping tank (De Clercq *et al.*, 1999). It was found that the free flowing liquid in the trickling filter could be described as a two tanks-in-series system of 15 m^3 each.

Gas mixing in the trickling filters

To investigate the gas mixing in the trickling filter system, the ventilators were switched from "high" to "low" position. CO_2 and O_2 concentrations were monitored. The system response provided information about the mixing properties of the gas phase inside the reactor. The gas phase could be modelled as a single perfectly mixed tank of 2000 m^3 (Figure 5). The model predictions were made using the measured values of the air flow rate, together with a fixed production rate of CO_2 and a fixed consumption rate of O_2.

These assumptions could be made because the wastewater composition did not change significantly during the short period around the step change in air flow rate and because previous studies have shown that the biodegradation was not affected by the air flow rate change (Vanhooren *et al.*, 2000). Indeed, the change of air flow and air retention time apparently had no effect on the oxygen and carbon dioxide mass transfer to and from the water and the biofilm. Figure 6 shows that the total amount of carbon leaving the system via the gas phase returned to the same value as that before the change. As no accumulation of inorganic carbon in the liquid was observed, the microbially produced CO_2 could be assumed constant.

Wastewater fractionation

The fraction of readily biodegradable substrate S_S was estimated from the available on-line respirometric data. The soluble, inert non-biodegradable substrate was determined by a mass balance using data of the final effluent (after activated sludge treatment). The soluble hydrolysable substrate S_R was determined by a mass balance of soluble *COD*. More details on this estimation can be found in Petersen (2000). The amount of particulates in the influent was insignificant but in the effluent it was estimated as the difference between total and soluble *COD*. It was further subdivided into the fractions X_S and X_I. Nitrogen was measured as total nitrogen and ammonia. Since the particulate organic nitrogen was considered insignificant, the fractions S_{ND} and S_{NH} could easily be determined from the measurements.

Model calibration

In the calibration of the model, the model parameters were adapted to fulfil:

1. The sludge balance: It is important that the sludge balance of the model matches. Good data about the sludge production of the plant were not available. Only suspended solids measurements of the intermediate clarifier influent and effluent were available. It was chosen to change attachment and detachment model coefficients to approximate the suspended solids measurements. To have an extra check on the sludge balance, the removal of nitrogen from the system was monitored. Since nitrification and denitrification were not occurring, these processes were removed from the model. The remaining nitrogen removal is then only via assimilation and, thus, due to sludge removal from the intermediate clarifier.

2. The effluent concentrations: An aim of the model is that it describes the concentrations of the biodegradable substrates and the nitrogen components. The parameters to which the model is most sensitive in this respect are the specific growth rate μ_{max}, the decay rate b_H and the yield coefficient Y_H. For this case study, lab experiments have shown that the well-accepted yield (Henze *et al.*, 1987) of 0.67 is too high and that a value of 0.5 is more appropriate (Petersen, 2000). Typically, also for biofilm models the diffusion coefficients of substrates in the biofilm (D_I) have to be calibrated. In the measured data, it is clear that a load-peak in the influent is followed by a peak in the O_2 uptake and the CO_2 production in the filters (Figure 7 and Figure 9). Initially, it was assumed that the system would be oxygen limited. In this case, these peaks could not occur. The system observations could thus not be modelled by an oxygen limited system and a very low diffusion constant for the readily biodegradable substrate S_S had to be implemented.

Table 2 Biodegradation model parameters

CO_2/HCO_3^- equilibrium and mass transfer parameters			Biofilm characteristics		
k_1	0.018 [a]	s^{-1}	μ_H [growth rate heterotrophs]	2.5	d^{-1}
K_1	$4.065 \cdot 10^{-7}$ [a]	$mol.L^{-1}$	Y_H [heterotrophic yield]	0.5	$g\ COD/\ g\ COD$
k_2	4600 [a]	$L.(mol/s)^{-1}$	b_H [heterotrophic decay]	0.25	d^{-1}
K_2	$4.065 \cdot 10^{+7}$ [a]	$L.mol^{-1}$	k_r [hydrolysis of S_R]	50	d^{-1}
$K_L a\ (O_2)$	5000	d^{-1}	k_h [hydrolysis of X_S]	2	d^{-1}
$K_L a\ (CO_2)$	4500	d^{-1}	k_a [ammonification of S_{ND}]	0.005	$m^3.(g\ COD/d)^{-1}$
$D_i\ (O_2)$	$2 \cdot 10^{-5}$ [b]	cm^2/s	k_{at} [attachment coefficient]	20	d^{-1}
$D_i\ (S_S)$	$6 \cdot 10^{-7}$	cm^2/s	k_{dt} [detachment coefficient]	0.05	d^{-1}

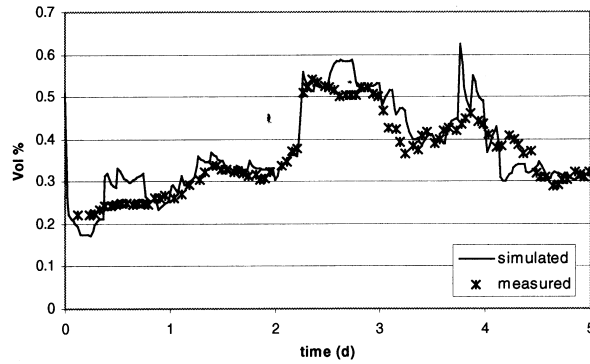[a] Spérandio and Paul, 1997 [b] Bird *et al.*, 1960

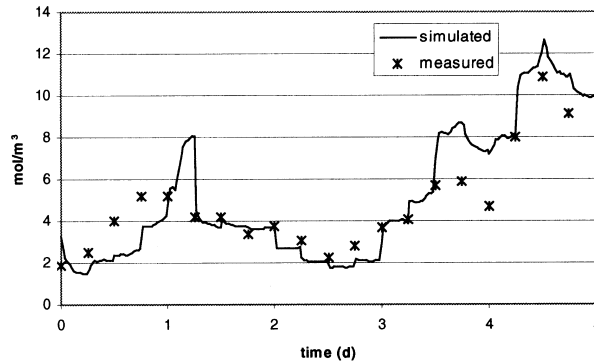**Figure 7** Measured and simulated off-gas CO_2 concentration

Figure 8 Measured and simulated effluent concentration of HCO_3^-

3. The off-gas concentrations: The model parameters should be adapted to make the predictions follow the measured off-gas concentrations. For the inorganic carbon components, it is also important to model the liquid phase inorganic carbon concentrations, $CO_{2,(aq)}$ and HCO_3^-. Particularly, the knowledge of *IC* in both the liquid and the gas phase can be used to obtain good estimates of the K_La for CO_2 and thus also for O_2. It can be shown that $(KLa)^{CO2} \approx 0.9(K_La)^{O2}$ (Spérandio and Paul, 1997).

The calibration results are given in Figure 7 to Figure 10. The parameters used are shown in Table 2. A *TOC/COD* ratio of 0.33 was selected using the results of a measuring campaign with a *TOC* sensor at the influent of the plant.

Despite the good fit, there was still some doubt about the validity of the model regarding the substrate limitation in the biofilm. For that reason, the hypothesis that biodegradation in the liquid phase outside the biofilm and in the pumping tank could remove sufficient substrate so that the biofilm would become oxygen limited, was studied. In this case, the observed variations in off-gas concentrations would be due only to varying degradation rates outside the biofilm. Therefore, measurements of the respiration rate were conducted in the short recycle loop of the trickling filters. An oxygen uptake of 0.22 mg O_2/l.min was measured. Biodegradation in the pumping tank and in the liquid phase of the trickling filters was implemented in the model, using the parameters of the calibrated activated sludge model (Petersen, 2000). The maximum specific growth rate of the biomass was adapted so as to obtain the measured respiration rate. Also, a small reaeration volume was integrated before the pumping tank to model the reaeration of the liquid that flows out of the filters in a very turbulent way. However, the simulations showed that only 2% of the total biodegradation was due to degradation outside the biofilm.
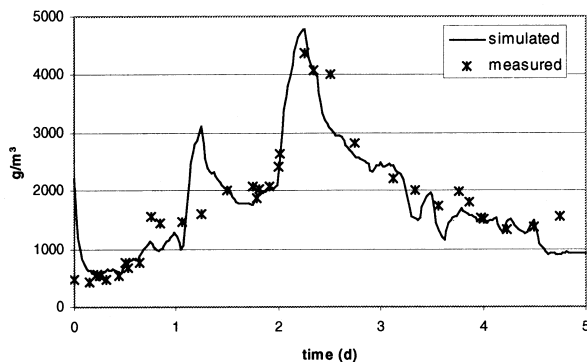
Figure 9 Measured and simulated concentration of effluent readily biodegradables (S_S)
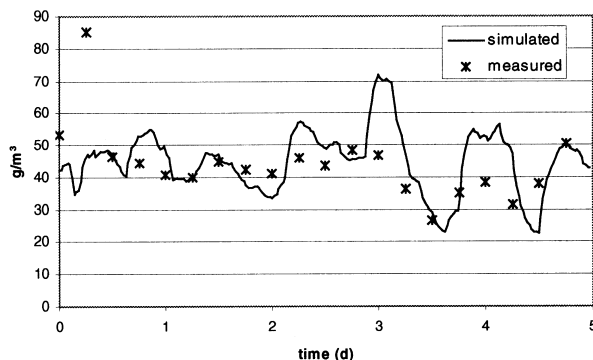
Figure 10 Measured and simulated concentration of effluent ammonia-N (S_{NH})

Conclusions

A model, based on the simple multispecies biofilm model developed by Rauch *et al.* (1999), was built and calibrated to describe the biodegradation in an industrial scale trickling filter. The calibration was based on the results of a five day intensive measurement campaign with the use of on-line respirometry and off-gas analysis. Respirometry was used to measure the readily biodegradable *COD* in the influent and the effluent of the plant. Off-gas analysis was used to monitor the O_2 and CO_2 content of the off-gases. The model was extended with a section describing the production and transport of CO_2 and inorganic carbon (*IC*). The measured effluent and off-gas concentrations could be followed very closely by the calibrated model. O_2 and CO_2 measurements revealed that the system was not always oxygen limited. The model calibration thus required the use of a very low value of the diffusion constant for readily biodegradable substrate. Liquid film biodegradation will be investigated further to shed more light on this matter.

Acknowledgements

References

Bird R.B., Steward, W.E. and Lightfoot, E.N. (1996). *Transport Phenomena*. New York, Wiley.

De Clercq, B., Coen, F., Vanderhaegen, B. and Vanrolleghem, P.A. (1999). Calibrating simple models for mixing and flow propagation in waste water treatment plants. *Wat. Sci. Tech.,* **39**(4), 61–69.

Govind, R., Gao, C., Lai, L. and Tabak, H.H. (1997). Continuous, automated and simultaneous measurement of oxygen uptake and carbon dioxide evolution in biological systems. *Wat. Env. Res.*, **69**, 73–80.

Henze, M., Grady, C.P.L., Gujer, W., Marais, G.v.R. and Matsuo, T. (1987). *Activated sludge model No. 1.*, IAWQ, London, ISSN: 1010-707X.

Noorman, H.J., Luijkx, G.C.A., Luyben, K.Ch.A.M. and Heijnen, J.J. (1992). Modeling and experimental validation of carbon dioxide evolution in alkalophilic cultures. *Biotechnol. Bioeng.*, **39**, 1069–1079.

Petersen, B. (2000). *Optimal experimental design in activated sludge*. PhD thesis, Faculty of Agricultural and Applied Biological Sciences, Ghent University, Belgium.

Rauch, W., Vanhooren, H. and Vanrolleghem, P. (1999). A simplified mixed-culture biofilm model. *Wat. Res.*, **33**, 2148–2162.

Sander (1996). Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry (version 2).
http://www.mpch-mainz.mpg.de/sander/res/henry.html

Spérandio, M. and Paul, E. (1997). Determination of carbon dioxide evolution rate using on-line gas analysis during dynamic biodegradation experiments. *Biotechnol. Bioeng.*, **53**, 243–252.

Vanhooren, H., Vanderhaegen, B. and Vanrolleghem, P.A. (2000). Modelling stripping of volatile organics in an industrial trickling filter system. *Accepted at the 1st World Congress of the IWA*, Paris, France, July 3–7, 2000.

Vanrolleghem, P.A. (1994). *On-line Modelling of Activated Sludge Processes: Development of an Adaptive Sensor*. PhD thesis, Faculty of Agricultural and Applied Biological Sciences, Ghent University, Belgium.

Van Vooren, L., Lessard, P., Ottoy, J.-P. and Vanrolleghem, P.A. (1999). pH buffer capacity based monitoring of algal wastewater treatment. *Environ. Technol.*, **20**, 547–561.

Wik, T. (1999). *On modeling the dynamics of fixed biofilm reactors*. PhD thesis, Control Engineering Laboratory, Department of Signals and Systems, Chalmers University of Technology.