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Combined Titrimetric Respirometer as a Real-Time Sensor to Monitor the Aerobic Biodegradation Process of Different Substrates

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Abstract: Off-line analysis of liquid phase samples have traditionally been used for the determination of organics and nitrogen load for process control or optimization in full-scale wastewater treatment plants. However, these sampling and analysis methods are labor-intensive and time-consuming. Besides, the results are not generally available on real-time to the operators who struggle on daily basis to meet the constant discharge license conditions of the effluent while the influent conditions change diurnally with varying loads. Combined respirometric titrimetric sensor is an on-line method that has been developed recently, indicating the oxygen demand exerted by organic and nitrogen loadings. This sensor monitors both the oxygen uptake as well as the proton production/consumption resulting from the biological reactions in activated sludge system. The basic-data can then be interpreted to find out the short-term BOD which can be used effectively for process control and optimization. Data interpretation and model development are still in progress as researchers keep on unraveling the mystery of how the substrates are biodegraded by activated sludge. Hence, in this study, it is aimed to develop an in-depth understanding about the aerobic biodegradation process using real-time biosensors through addition of different substrates such as acetate, surfactant (SDS) and ammonium to batch cultures of activated sludge by maintaining the pH of 7.8. Basic data interpretation was carried out to calculate Oxygen Uptake Rate (OUR) as well as proton production/consumption rate from the raw data. Besides, the improved bio-kinetic model calibration was presented in this study explaining the oxidation of different substrates in activated sludge system.

Key words: Oxygen Uptake Rate (OUR), proton, activated sludge, substrate, biodegradation

INTRODUCTION

The real wastewater is a mixture of organic and nitrogen load having readily biodegradable, slowly biodegradable or even non-biodegradable constituents in nature. In-depth understanding of substrates removal mechanisms in full-scale wastewater treatment plants (WWTPs) is essential for process optimization and control where stringent effluent discharge conditions are nowadays imposed by Environmental protection agencies because of the environmental concern prevailing as to the presence of organic wastewater contaminants in water resources albeit at very low concentrations (Kolpin *et al*., 2002). The off-line analysis of wastewater is a labor-intensive and time consuming process, for example, traditional BOD test requires at least 5 days, by which time it is not possible to take any remedial measures to correct the inefficiencies of the processes. However, on-line monitoring system provides the real-time information corresponds to the substrates biodegradation process that can contribute in improving the design and operation of WWTPs. From this aspect, respirometry and titrimetry can be very valuable tools to investigate the biodegradation rate of organics and nitrogen compounds employing high frequency data collection that preserves all the bio-kinetic information during the oxidation period. The respirometry deals with the oxygen consumption by the microorganism in activated sludge; on the other hand the relevant pH change in the system resulting from the biological reaction is monitored through titrimetry. While short term BOD can easily be extracted through this sensor, the parameters that relate to the growth of microorganisms such as yield and maximum growth rate when they consume the organics needs interpretation through modeling. In recent years the activate sludge modeling has been evolving that can better explain the substrates removal mechanisms occurring in the activated sludge. Calibration of such models is still a bottleneck facing the researchers, which is generally performed through using the respirometric (Spanjers and

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Vanrolleghem, 1995; Spanjers *et al*., 1998; Vanrolleghem *et al*., 1999; Carucci *et al*., 2001; Beccari *et al*., 2002; Vanrolleghem *et al*., 2004; Sin *et al*., 2005; Hoque *et al*., 2008a) as well as the titrimetric measurement (Gernaey *et al*., 2002a, b; Pratt *et al*., 2004; Sin and Vanrolleghem, 2007).

Therefore, in this study the aerobic biodegradation process for three different substrates such as acetate, sodium dodecyl sulfate-SDS (anionic surfactant) and ammonium are investigated using real-time titrimetric respirometer. Besides, the application of the real-time measurement in activated sludge model calibration is presented with the estimated model parameters explaining the respective substrate biodegradation process under aerobic conditions.

MATERIALS AND METHODS

Laboratory set-up: Activated sludge based titrimetric respirometer was installed in the laboratory that enable to provide the real time data corresponds to aerobic biodegradation of substrates (Fig. 1). Batch study was conducted by using a single reactor having a capacity of 3.5 L. Compressed air was supplied continuously for proper aeration and an overhead stirrer was used in the reactor in order to mix the contents uniformly. A titrimetric unit, consisting of Ionode pH electrode connected with the pH transmitter (TSP Mini Chem), two 3- way solenoid valves, an acid tank and a base tank, was installed in order to monitor and control the pH of the system during the experimental run. The 0-1 volt signals from the transmitter were logged by a PC equipped with the Labview software package (National Instruments) and a combined A/D I/O card (National Instruments, PCI-6013). The reactor was also equipped with a dissolve oxygen electrode (YSI).

Labview software package (National Instruments) was used to monitor dissolved oxygen as well as temperature serial output from dissolved oxygen meter (TPS 90-D). The acid and base were continuously pumped around by a peristaltic pump to keep a constant liquid pressure in the dosage system and to maintain constant dose rate.

During the batch experiments, both pH and DO profiles were monitored every 5 seconds and pH was controlled at a set point of 7.8±0.03 by automatic addition of base (0.05 N) or acid (0.05 N) solutions with two 3-way solenoid valves. The dosage system in this study was calibrated according to the procedure followed by Gernaey *et al.* (2002a). The experiments were performed at a temperature of 20±0.5°C. Three different substrates such as acetate, sodium. The respirograms presented here were obtained after proper acclimatization of the sludge with the test substrate.

Data analysis: The Oxygen Uptake Rate (OUR) is the combination of endogenous (OUR_{exo}, oxygen consumption in the absence of external carbon source) and exogenous (OUR_{exo}, substrate degradation induced) oxygen uptake rates (Spanjers, 1993) that can be derived from the dissolved oxygen profile resulting from the metabolic functions of bacteria during the biodegradation process. Following expression is used to calculate the OUR_{exo} in the system (Gernaey *et al*., 2001; Hoque *et al*., 2008b) for the details.

$$\frac{dS_o}{dt} = K_L a(S_{eq} - S_o) - OUR_{exo}$$

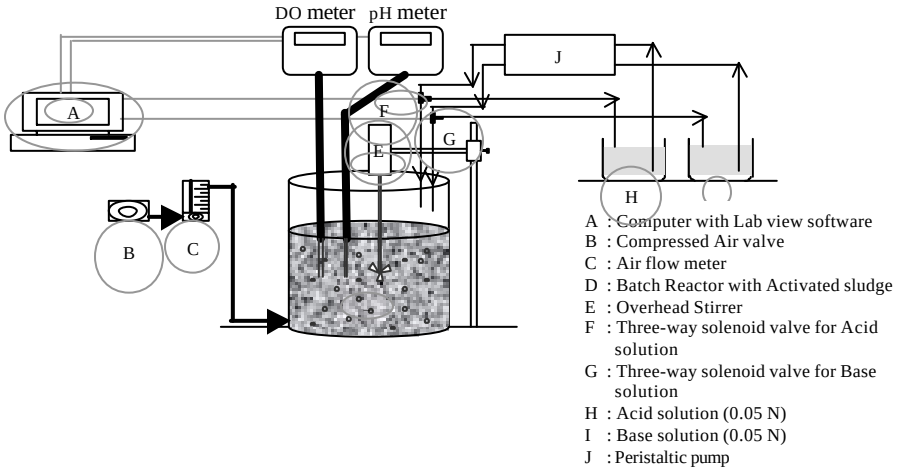

Fig. 1: A schematic overview of titrimetric respirometer

where, the moving window regression was applied for the determination of change in Dissolved Oxygen (DO) concentration, dS_o/dt calculation. The term S_{eq} represents the equilibrium concentration of DO in the bioreactor. Separate reaeration process was carried out to calculate the K_La value. The difference between the equilibrium concentration (Seq) and the saturated dissolved oxygen level (S0o) multiplied by K_La reflects the OUR_{exo}. Titration data was processed by using the relation as mentioned below (Hoque *et al*., 2008b) for the details.

$$H_{meq/L} = \frac{H_{pulse} \times Q_{flux} \times N}{V_{reactor}}$$

where, H_{pulse} represents the pulse number during the reaction, Q_{flux} is the acid/base flux (mL/pulse), N refers to the normality of acid or base (meq/mL) and $V_{reactor}$ is the volume of the bio-reactor (L). Spreadsheet program was used to process the dissolved oxygen and titration raw data.

The short term BOD (BOD_{st}) represents the amount of substrates oxidized by the sludge that can be determined using the relationship $BOD_{st} = K_La \times PA$ where PA stands for the peak area referring the area under the DO profile. Along with respirometry, the titrimetric data can also be used to determine the nitrogen load in the wastewater using the following expression (Gernaey *et al*., 2001).

$$S_N = \frac{(B2 - B1) \times Q_{flux} \times N \times 7}{V_{reactor}}$$

where, S_N is the initial concentration of nitrogenous compound (mg N/L), B1 represents the number of base pulses needed to adjust the pH of the sludge to the pH set point, B2 is the cumulative base pulses corresponds to the nitrification process plus B1 pulses and 7 is the conversion factor (to change the unit from meq to mg N). The estimation of activated sludge model parameters was done following non-linear techniques employing the algorithms in the optimisation toolbox included in MATLAB (R2007a).

RESULTS AND DISCUSSION

Batch study: The dissolved oxygen profile resulting from the substrates oxidation process is termed as respirogram that is directly influenced by the substrates characteristics as well as the biomass population. In current study, three different substrates such as acetate (simple carbon source), SDS (complex carbon source) and ammonium (nitrogen source) were used to investigate the biodegradation process under aerobic condition applying on-line respirometric-titrimetric measurements technique.

Figure 2 illustrates the DO profiles along with the titrimetry corresponds to the biodegradation process of

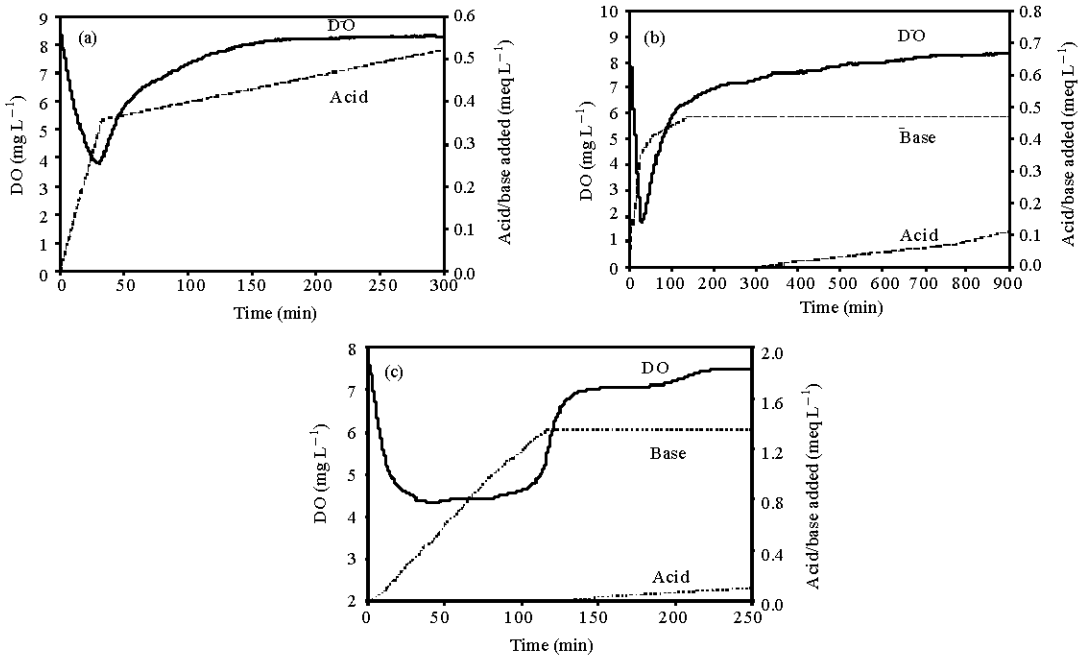

Fig. 2: Dissolved oxygen and titrimetric data collected from the titrimetric respirometer during (a) acetate = 50 mg COD/L (b) SDS = 100 mg COD/L and (c) ammonium = 10.8 mg N/L biodegradation

the test substrates. In every case, the DO value was found to decrease drastically after dosing the substrates until the substrates were fully exhausted in the liquid medium and then gradually started to increase to reach the steady state equilibrium DO level. However, the biodegradation period for the complex carbon source (SDS) is found longer than that for simple carbon source (acetate) indicating SDS as a slowly biodegradable compound in nature (Fig. 2a, b). Besides, a clear tail in DO profile is observed during ammonium oxidation (Fig. 2c) representing the second step nitrification (oxygen consumption takes place during the conversion of nitrite to nitrate) in the system. Like the respirometry, distinctive titrimetric data was observed for the respective substrates biodegradation study. While the acetate dosing caused acid addition in the system (proton consumption takes place), base was added for both the substrates SDS and ammonium indicating proton production during their biodegradation period (Fig. 2). Moreover, only acid pulse was marked for all three cases when the oxidation processes reached to their endogenous level (at pH 7.8).

Using the respirometry, the BOD_{st} was estimated as 16.14 and 54.26 mg COD/L for the initial acetate and SDS concentrations of 50 mg and 100 mg COD/L, respectively. On the other hand, the BOD_{st} for the dosing of ammonium (10.8 mg N/L) was calculated as 47.47 mg COD/L from the respirometry, this confirms that 1 g N required 4.4 g O_2. Gernaey *et al.* (2001) also observed similar result (4.44 g O_2 g/N)) which is slightly higher than the typical value (4.33 g O_2 g/N) (Henze *et al.*, 1987). Besides, the initial concentration of ammonium added can be easily calculated using the tirimetric data, which in this case comes around as 9.4 mg N/L.

The difference between the concentrations of initial dose and the estimated one represents the amount of organics or nitrogen taken for the biomass growth in the form of yield.

Activated sludge model calibration: Modeling of aerobic biodegradation of substrates has been continuously evolving that enables improved interpretation of the process kinetics of substrate removal mechanisms in activated sludge processes. While the nitrification process by autotrophic bacteria was successfully modeled (Spanjers and Vanrolleghem, 1995; Gernaey *et al.*, 1998; Petersen *et al.*, 2001) based on simple growth approach, the modeling for organic compounds removal by heterotrophic bacteria underwent substantial improvement from simple growth based models (Gernaey *et al.*, 2001; Gernaey *et al.*, 2002a,b; Vanrolleghem *et al.*, 2004) to eventual simultaneous storage and growth (SSAG) model (Van Aalst-van Leeuwin *et al.*, 1997; Krishna and van Loosdrecht, 1999; Beccari *et al.*, 2002; Carucci *et al.*, 2001; Guisasola *et al.*, 2005).

A second-order type kinetic expression was introduced by Sin *et al.* (2005) as a further improvement of SSAG model during growth on storage and successfully calibrated using respirometric measurements which was also justified by the study conducted by Hoque *et al.* (2008a). The biokinetic model used in this study is presented in matrix format Table 1, a simple growth model for autotrophic biomass along with simultaneous growth and storage model for heterotrophic bacteria using ammonium and organic carbon as substrates, respectively. The model consists of kinetic and

Table 1: Model matrix for the respiration process governed by autotrophs and heterotrophs

Process	X_B	X_{NHacc}	X_{STO}	S_S	X_S	S_{NO_3}	S_{NO_2}	S_{NH}	S_O	Kinetics
Hydrolysis	--	--	--	1	-1	--	--	--	--	$k_h.M_{X_S/X_B}.X_B$
Autotrophic organisms										
S_{NH} Oxidation (Nitrification 1)	1	--	--	--	--	--	$\frac{1}{Y_{A1}}$	$-\frac{1}{Y_{A1}}-i_{NBM}$	$-\frac{3.43-Y_{A1}}{Y_{A1}}$	$(1-e^{-t/\tau}).\mu_{MAX,A1}.\frac{S_{NH}}{K_{SA1}+S_{NH}}.X_B$
S_{NO_2} Oxidation (Nitrification 2)	1	--	--	--	--	$\frac{1}{Y_{A2}}$	$-\frac{1}{Y_{A2}}$	-i_{NBM}	$-\frac{1.14-Y_{A2}}{Y_{A2}}$	$(1-e^{-t/\tau}).\mu_{MAX,A2}.\frac{S_{NO2}}{K_{SA2}+S_{NO2}}.X_B$
Heterotrophic organisms										
Formation of X_{STO}	--	--	1	$-\frac{1}{Y_{STO}}$	--	--	--	--	$-\frac{1-Y_{STO}}{Y_{STO}}$	$(1-e^{-t/\tau}).k_{STO}.M_S.X_B$
S_{NH} accumulation	--	i_{NBM}	--	--	--	--	--	-i_{NBM}	--	$(1-e^{-t/\tau}).k_{NHacc}.M_S.X_B$
Aerobic growth on S_S	1	--	--	$-\frac{1}{Y_{H,S}}$	--	--	--	-i_{NBM}	$-\frac{1-Y_{H,S}}{Y_{H,S}}$	$(1-e^{-t/\tau}).\mu_{MAX,S}.M_S.X_B$
Aerobic growth on X_{STO}	1	-i_{NBM}	$-\frac{1}{Y_{H,STO}}$	--	--	--	--	--	$-\frac{1-Y_{H,STO}}{Y_{H,STO}}$	$\mu_{MAX,STO}.\left(\frac{(X_{STO}/X_B)^2}{K_2+K_1.(X_{STO}/X_B)}\right).\left(\frac{K_S}{S_S+K_S}\right).X_B$
Endogenous respiration	-1	--	--	--	--	--	--	i_{NBM}-$i_{NXI}f_{XI}$	-(1-f_{XI})	$b.X_B$
X_{STO} respiration	--	--	-1	--	--	--	--	--	-1	$b_{STO}.X_{STO}$

M represents the Monod function, e.g. $M_S = S_S/(K_S+S_S)$

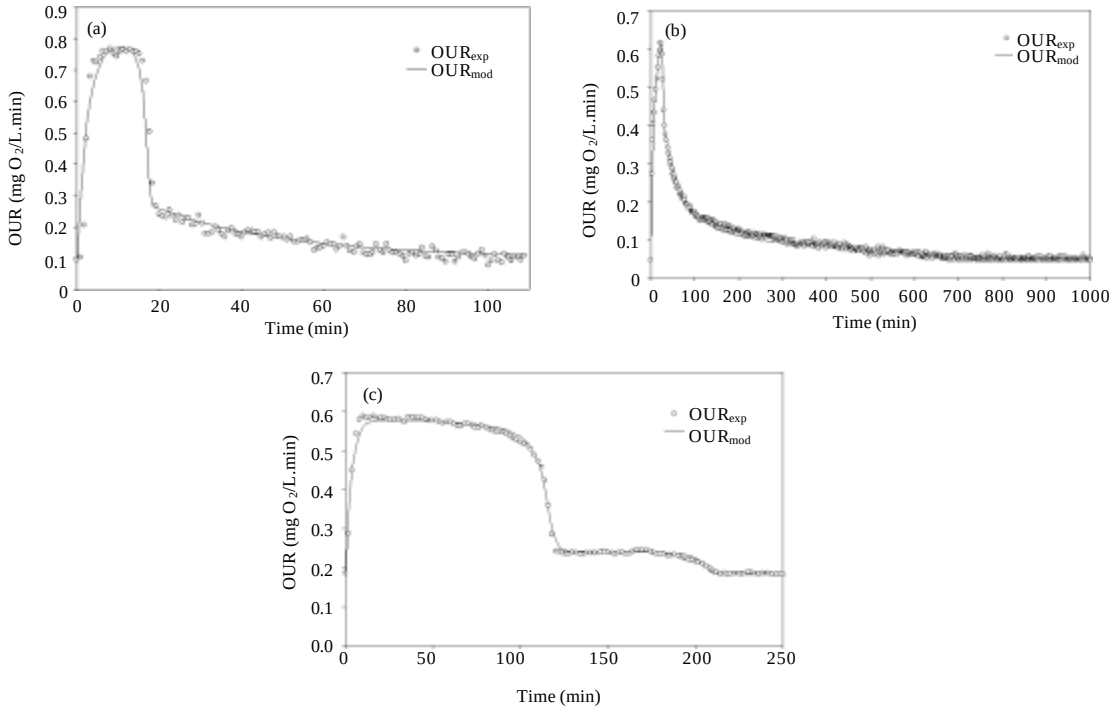

Fig. 3: Model calibration using the OUR corresponds to (a) acetate = 50 mg COD L^{-1} (b) SDS = 100 mg COD L^{-1} and (c) ammonium = 10.8 mg N L^{-1} biodegradation

stoichiometric parameters representing the process dynamics as well as biomass growth. The model calibration was found to be satisfactory using the experimentally observed OUR measurement resulting from the acetate, SDS and ammonium biodegradation processes (Fig. 3). Titrimetric measurement was also used for the model calibration which is not presented in this paper. Table 2 shows the estimated model parameters from acetate, SDS and ammonium biodegradation study.

In organic oxidation, the complex source such as SDS is hydrolyzed first to form simple carbon component that can be uptaken by the bacteria, where as the pure carbon compound, acetate is directly consumed for storage formation and biomass growth without undergoing any hydrolysis process. From the parameter estimation the hydrolysis related components like hydrolysis rate (k_h) and half-saturation coefficient for slowly biodegradable compound (K_X) were found to be 0.044 min^{-1} and 1.39 mg mg^{-1}, respectively. The half-saturation coefficient, K_S was estimated as 1.27 and 0.54 mg L^{-1} for acetate and SDS, respectively. The storage products formation rate (k_{STO}) and maximum growth rate of biomass on substrate ($\mu_{MAX, S}$) were observed higher for

Table 2: Model calibration results correspond to acetate, SDS and ammonium oxidation

Parameters	Acetate	SDS	Ammonium
k_h (1 min^{-1})	--	0.044	--
K_X (mg mg^{-1})	--	1.39	--
k_{STO} (1 min^{-1})	0.002174	0.0075	--
K_{STO} (1 min^{-1})	0.001235	0.003	--
K_S (mg L^{-1})	1.27	0.54	--
$Y_{H,S}$ (mg mg^{-1})	0.71	0.63	--
$Y_{H,STO}$ (mg mg^{-1})	0.78	0.73	--
Y_{STO} (mg mg^{-1})	0.88	0.84	--
$\mu_{MAX, A1}$ (1 min^{-1})	--	--	2.6×10^{-5}
$\mu_{MAX, A2}$(1 min^{-1})	--	--	6.4×10^{-6}
K_{SA1} (mg N L^{-1})	--	--	0.29
K_{SA2} (mg N L^{-1})	--	--	0.08
Y_{A1} (mg mg^{-1})	--	--	0.13
Y_{A2}(mg mg^{-1})	--	--	0.06

SDS as compared with that for acetate, where as the yield coefficients for growth on substrate ($Y_{H, S}$), for growth on storage products ($Y_{H, STO}$) and for storage on substrate (Y_{STO}) was found to be higher for acetate than SDS. The estimated model parameters related to nitrification is presented in Table 2 where the parameters $\mu_{MAX, A1}$, K_{SA1}, Y_{A1}, $\mu_{MAX, A2}$, K_{SA2} and Y_{A2} stand for maximum growth rate of biomass, half-saturation substrate concentration and autotrophic biomass yield for first step and second step nitrification, respectively. The knowledge of the

parameters obtained from the calibration process, can be used in routine testing to evaluate the initial concentration of the specific substrate. Further development of the modeling and calibration with real wastewater is needed, which will enable the operators to find out the wastewater load in the inflow of a treatment plant to optimize the performance of the aerators.

CONCLUSION

Real time (on-line) monitoring of aerobic biodegradation of substrates (acetate, SDS and ammonium) was investigated in this study using combined respirometric-titrimetric measurements technique. This sensor allows high-frequency data collection that preserves all the bio-kinetic information related to oxygen uptake and proton production/ consumption during the aerobic biological reaction. The on-line sensors enable evaluation of short term BOD during the biodegradation process, thus facilitating immediate remedial measures to be taken to improve the efficiencies of the processes in WWTPs where needed. The study also reveals that SDS and ammonium biodegradation result proton production where as proton consumption takes place for acetate oxidation. Moreover, the endogenous state results only acid pulse (for all three substrates oxidation) in the system where pH was maintained at 7.8. The on-line respirometric measurement was successfully applied in this study for the biokinetic model calibration, where the estimated model parameters yield valuable information that can help for optimizing the operation and process control of WWTPs.

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REFERENCES

Beccari, M., D. Dionisi, A. Giuliani, M. Majone and R. Ramadori, 2002. Effect of different carbon sources on aerobic storage by activated sludge. Water Sci. Technol., 45: 157-168.

Carucci, A., D. Dionisi, M. Majone, E. Rolle and P. Smurra, 2001. Aerobic storage by activated sludge on real wastewater. Water Res., 35: 3833-3844.

Gernaey, K., H. Bogaert, A. Massone, P. Vanrolleghem and W. Verstraete, 1997. On-line nitrification monitoring in activated sludge with a titrimetric sensor. Environ. Sci. Technol., 31: 2350-2355.

Gernaey, K., P. Vanrolleghem and W. Verstraete, 1998. On-line estimation of *Nitrosomonas* kinetic parameters in activated sludge samples using titration in-sensor-experiments. Water Res., 32: 71-80.

Gernaey, K., B. Petersen, J.P. Ottoy and P.A. Vanrolleghem, 2001. Activated sludge monitoring with combined respirometric-titrimetric measurements. Water Res., 35: 1280-1294.

Gernaey, K., B. Petersen, I. Nopens, Y. Comeau and P.A. Vanrolleghem, 2002a. Modeling aerobic carbon source degradation processes using titrimetric data and combined respirometric-titrimetric data: Experimental data and model structure. Biotech. Bioeng., 79: 741-753.

Gernaey, K., B. Petersen, D. Dochain and P.A. Vanrolleghem, 2002b. Modeling aerobic carbon source degradation processes using titrimetric data and combined respirometric-titrimetric data: Structural and practical identifiability. Biotechnol. Bioeng., 79: 754-767.

Guisasola, A., G. Sin, J.A. Baeza, J. Carrera and P.A. Vanrolleghem, 2005. Limitations of ASM1 and ASM3: A comparison based on batch oxygen uptake rate profiles from different full-scale wastewater treatment plants. Water Sci. Technol., 52: 69-77.

Henze, M., C.J. Grady, W. Gujer, G. Marais and T. Matsuo, 1987. Activated sludge model No. 1. IAWQ Scientific and Technical Report No. 1. International Association of Water Quality, London, UK.

Hoque, M.A., V. Aravinthan and N.M. Pradhan, 2008a. Evaluation of simultaneous storage and growth model to explain aerobic biodegradation of acetate. Res. J. Biotechnol., 2008: 274-281.

Hoque, M.A., V. Aravinthan and M. Porter, 2008b. Respirometric and titrimetric techniques for monitoring aerobic biodegradation of surfactant. Res. J. Biotechnol., 2008: 399-405.

Kolpin, D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber and H.T. Buxton, 2002. Pharmaceuticals, hormones and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance. Environ. Sci. Technol., 36: 1202-1211.

Krishna, C. and M.C.M. van Loosdrecht, 1999. Substrate flux into storage and growth in relation to activated sludge modeling. Water Res., 33: 3149-3161.

Petersen, B., K. Gernaey and P. Vanrolleghem, 2001. Practical identifiability of model parameters by combined respirometric-titrimetric measurements. Water Sci. Technol., 43: 347-355.

Pratt, S., Z. Yuan and J. Keller, 2004. Modelling aerobic carbon oxidation and storage by integrating respirometric, titrimetric and off-gas CO_2 measurements. Biotechnol. Bioeng., 88: 135-147.

Sin, G., A. Guisasola, D.J.W. De Pauw, J.A. Baeza, J. Carrera and P.A. Vanrolleghem, 2005. A new approach for modelling simultaneous storage and growth processes for activated sludge systems under aerobic conditions. Biotechnol. Bioeng., 92: 600-613.

Sin, G. and P.A. Vanrolleghem, 2007. Extensions to modeling aerobic carbon degradation using combined respirometric-titrimetric measurements in view of activated sludge model calibration. Water Res., 41: 3345-3358.

Spanjers, H., 1993. Respirometry in activated sludge. Ph.D. Thesis, Landbouwuniversiteit Wageningen, The Netherlands.

Spanjers, H. and P.A. Vanrolleghem, 1995. Respirometry as a tool for rapid characterization of wastewater and activated sludge. Water Sci. Technol., 31: 105-114.

Spanjers, H., P.A. Vanrolleghem, G. Olsson and P.L. Dold, 1998. Respirometry in control of the activated sludge process: Principles. IAWQ Scientific and Technical Report No. 7. London, UK.

Van Aalst-van Leeuwen, M.A., M.A. Pot, M.C.M. van Loosdrecht and J.J. Heijnen, 1997. Kinetic modelling of poly (β-hydroxybutyrate) production and consumption by *Paracoccus pantotrophus* under dynamic substrate supply. Biotechnol. Bioeng., 55: 773-782.

Vanrolleghem, P.A., H. Spanjers, B. Petersen, P. Ginestetf and I. Takacs, 1999. Estimating (combinations of) activated sludge model No. 1 parameters and components by respirometry. Water Sci. Technol., 39: 195-214.

Vanrolleghem, P.A., G. Sin and K.V. Geraney, 2004. Transient response of aerobic and anoxic activated sludge activities to sudden substrate concentration changes. Biotechnol. Bioeng., 86: 277-290.