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Development and calibration of bio-kinetic model for surfactant biodegradation with combined respirometric and titrimetric measurements

V. Aravinthan *, M.A. Hoque

Australian Centre for Sustainable Catchments, University of Southern Queensland (USQ), Qld 4350, Australia

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ABSTRACT

Substrate removal mechanism in aerobic activated sludge processes was lately modeled using the simultaneous storage and growth (SSAG) phenomenon. The SSAG model was further refined with titrimetric components and successfully calibrated using both respirometric and titrimetric measurements for common substrate acetate. However, the improved SSAG model calibration was not verified with other organic substrates. Furthermore, very few studies are available in the literature on surfactant bio-kinetics, which generally use off-line experimental measurements with limited model-based interpretation. Therefore, the aim of this paper is to demonstrate its applicability for surfactant biodegradation using on-line measurements. Batch experiments were conducted using sodium dodecyl sulfate (SDS) as a test surfactant. Model calibration was done successfully for three different SDS concentrations using respirometric, titrimetric and combined respirometric–titrimetric measurement approaches. The parameter estimation results from all three stated combinations were statistically evaluated and found to be very close validating the model.

1. Introduction

Surfactants are widely used in the manufacture of detergents and personal care products (Hotantai and Nardello-Rataj, 2001). Consequently, the presence of such organic contaminants in raw wastewater has remarkably increased. Substantial research has been conducted to investigate the biodegradation of surfactants under aerobic and/or anaerobic conditions over the last decade (Huber et al., 2000; Qin et al., 2005; Sharvelle et al., 2007). It is indeed a complicated process since surfactants have heavy molecular weights and complex chemical structures. In addition, surfactants exhibit characteristics that make them prone to escape with the effluent as well as to adsorb onto the sludge during primary tank settling (Jahan, 2005). Though significant research has been performed that focused on the extent and pathways of surfactant degradation, the resulting recalcitrant products, their biological activities and applications (Ahmed et al., 2010; Hrenovic and Ivankovic, 2007; Lara-Martin et al., 2006; Qin et al., 2005; Thanomsub et al., 2006), there is little evidence reported regarding the determination of biodegradation kinetics (Chen et al., 2005; Mohan et al., 2006) using activated sludge models.

In-depth understanding of substrate removal mechanisms via improved models is essential for process optimization and control in full-scale wastewater treatment plants (WWTPs). These plants encounter stringent effluent discharge conditions imposed by Environmental Protection Agencies because of the prevailing environmental concerns regarding the presence of organic wastewater contaminants in water resources, albeit at very low concentrations (Kolpin et al., 2002). Activated sludge models have been evolving from a simple growth-based concept (Gernaey et al., 2002b; Guisasola et al., 2005; Vanrolleghem et al., 2004) to more complicated models using the simultaneous storage and growth (SSAG) phenomenon (Beccari et al., 2002; Pratt et al., 2004; Sin et al., 2005) to interpret the organic carbon removal mechanisms in a mixed culture. Researchers commonly employ on-line monitoring tools such as respirometry and titrimetry for experimental investigation on aerobic biodegradation, precise model calibration and parameter estimation purposes (Gernaey et al., 2002b; Hoque et al., 2010; Petersen et al., 2001; Sin and Vanrolleghem, 2007). These tools investigate the biodegradation rate of organics employing high frequency data collection that preserves all the bio-kinetic information during the oxidation period. The SSAG model proposed by Sin et al. (2005) was calibrated using the experimental oxygen uptake rate (OUR) of carbon-based compound such as acetate biodegradation. This model was further extended by Hoque et al. (2010), introducing the titrimetric components in each step of the growth and storage phases in the SSAG process, along with the consideration of the dynamic carbon dioxide transfer rate (CTR) in the liquid phase. However, calibration of the recently developed SSAG has been done using an easily biodegradable compound such as acetate. Therefore, the model needs to be verified using different

* Corresponding author. Tel.: +61 7 4631 2299; fax: +61 7 4631 2526.
E-mail address: aravintv@usq.edu.au (V. Aravinthan).

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Nomenclature

ASM3	activated sludge model no. 3
b_H	endogenous decay coefficient of biomass (day^{-1})
b_{STO}	endogenous decay of storage products (day^{-1})
$CH_aO_bN_c$	elemental composition of biomass (C-mol)
CH_pO_q	elemental composition of storage products (C-mol)
CH_yO_z	elemental composition of substrate (C-mol)
$C_{T,init}$	total inorganic carbon in the aqueous medium (mmol CO_2/L)
CTR	CO_2 transfer rate (mmol CO_2/L day)
DO	dissolved oxygen
f_{STO}	fraction of substrate used for storage (mg COD X_{STO}/mg COD S_S)
f_{XI}	inert fraction of biomass (mg COD/mg COD)
Hp	proton concentration in liquid phase (meq/L)
i_{NXI}	nitrogen content of the inert fraction of biomass (g N/g COD X_I)
i_{NBM}	nitrogen content of biomass (g N/g COD X_H)
K_1	forward reaction rate for aqueous CO_2 equilibrium (day^{-1})
K_S	substrate affinity constant (mg COD/L)
K_La	oxygen mass transfer coefficient (day^{-1})
$K_La_{CO_2}$	CO_2 mass transfer coefficient (day^{-1})
k_h	hydrolysis rate (day^{-1})
k_{NHacc}	nitrogen accumulation rate of biomass (day^{-1})
k_{STO}	maximum storage rate of biomass (day^{-1})
K_X	hydrolysis saturation constant (mg COD/mg COD)
K_1	regulation constant of biomass controlling degradation rate of X_{STO} (mg COD X_{STO}/mg COD X_H)
K_2	a lumped parameter related to the affinity of biomass to storage fraction of biomass (mg COD X_{STO}/mg COD X_H)
MSE	mean squared error
OUR	oxygen uptake rate (mg O_2/L day)
OUR_{end}	endogenous oxygen uptake rate (mg O_2/L day)
PHB	polyhydroxybutyrate
pK_1	negative logarithm of the first acidity constant in the CO_2equilibrium
pK_{NH_4}	negative logarithm of the equilibrium constant for NH_4^+ dissociation
q_{MAX}	maximum substrate uptake rate (day^{-1})
S_{CO_2}	CO_2 concentration in liquid phase (mmol/L)
$S^*_{CO_2}$	CO_2 saturation concentration at 1 atm (mmol/L)
SDS	sodium dodecyl sulfate
S_{HCO_3}	bicarbonate concentration in liquid phase (mmol/L)
S_{NH}	ammonium concentration (mg N/L)
S_O	dissolved oxygen concentration in liquid phase (mg/L)
S_S	readily biodegradable substrate concentration (mg COD/L)
SSAG	simultaneous storage and growth
X_H	biomass concentration (mg COD/L)
$X_H(0)$	initial biomass concentration (mg COD/L)
X_I	inert particulate COD (mg COD/L)
X_{NHacc}	nitrogen accumulation (mg N/L)
X_S	slowly degradable particulate COD (mg COD/L)
X_{STO}	storage products concentration (mg COD/L)
$Y_{H,S}$	yield coefficient for growth on substrate (mg COD X_H/mg COD S_S)
$Y_{H,STO}$	yield coefficient for growth on storage products (mg COD X_H/mg COD X_{STO})
Y_{STO}	yield coefficient for storage on substrate (mg COD X_{STO}/mg COD S_S)
τ	first order time constant (day)
$\mu_{MAX,S}$	maximum growth rate of biomass on substrate (day^{-1})
$\mu_{MAX,STO}$	maximum growth rate of biomass on storage products (day^{-1})
γ_S	degree of reduction of substrate (mol electron/C-mol)
γ_{STO}	degree of reduction of storage products (mol electron/C-mol)
γ_X	degree of reduction of biomass (mol electron/C-mol)

substrates to interpret these biodegradation mechanisms to be confident in its use for wider application. Moreover, the existing models describing the surfactant biodegradation were based on first-order or a simple Monod function without considering its biodegradation pathway. These models were calibrated using off-line substrate depletion measurements that result in an inaccurate parameter estimation process due to the non-availability of high-frequent measurements.

Hence, the objective of this paper is to demonstrate the applicability of the improved SSAG model (Hoque et al., 2010) for surfactant biodegradation using on-line measurements considering the biodegradation pathway of surfactants. Sodium dodecyl sulfate (SDS), a common anionic surfactant used in household products, was used as a calibration substrate for the batch experiments. Moreover, three different calibration approaches: using the respirometric measurements alone, the titrimetric measurements alone and combined respirometric-titrimetric measurements were performed to estimate the parameters more precisely and to validate the proposed model.

2. Model development

A bio-kinetic model was proposed to describe both the respirometric and the titrimetric behavior resulting from the aerobic biodegradation of the surfactant, SDS, in an activated sludge system. Fig. 1 illustrates the proposed model diagram with processes involved during SDS biodegradation. The SSAG model developed by Hoque et al. (2010) for acetate biodegradation was further extended here by newly introducing hydrolysis component.

The proposed SSAG model for SDS biodegradation includes the stoichiometric parameters involved in titrimetry in each step of the growth and storage phases along with consideration of the non-linear carbon dioxide transfer rate in the liquid phase. The major steps, other than hydrolysis, during the aerobic biodegradation of SDS are the formation of storage products, aerobic growth on the substrate, aerobic growth on the storage, endogenous respiration, respiration on storage products, aqueous CO_2 equilibrium and stripping of CO_2 (see Table 1 for the process matrix).

The conversion of sodium dodecly sulfate to alcohol (1-dedecanol) occurs through a hydrolysis process that releases H^+ in the liquid medium (Eq. 1). The proton production during hydrolysis can be estimated by using the matrix shown in Table 1, where the parameter "C" represents the molecular weight of the substrate, SDS (576 g COD/mol)

$$C_{12}H_{25}O_4SNa + H_2O \rightarrow C_{12}H_{26}O + NaSO_4 + H^+ \quad (1)$$

The alcohol undergoes a multi-step oxidation process producing lauric acid in a liquid medium (Yao, 2006). During the modeling, the course of oxidation was consolidated into one step to keep the proposed model simple. While the SDS biodegradation pathway shows proton production during the lauric acid formation, a fraction of the proton is consumed for lauroyl-CoA synthesis. The net H^+ production that occurs in the liquid medium is shown in Table 1 considering lauric acid as a readily biodegradable compound (S_S) to be used for biomass growth. The stoichiometry related to the