WATER RESEARCH 47 (2013) 5986–5994

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/watres

A new approach to assess the dependency of extant half-saturation coefficients on maximum process rates and estimate intrinsic coefficients

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ARTICLE INFO

Article history:
Received 1 April 2013
Received in revised form
26 June 2013
Accepted 3 July 2013
Available online 12 July 2013

Keywords:
Denitrification
Diffusion
Extant
Half-saturation
Intrinsic
Monod kinetics

ABSTRACT

The Monod equation is often used to describe biological treatment processes and is the foundation for many activated sludge models. The Monod equation includes a "half-saturation coefficient" to describe the effect of substrate limitations on the process rate and it is customary to consider this parameter to be a constant for a given system. The purpose of this study was to develop a methodology, and its use to show that the half-saturation coefficient for denitrification is not constant but is in fact a function of the maximum denitrification rate. A 4-step procedure is developed to investigate the dependency of half-saturation coefficients on the maximum rate and two different models are used to describe this dependency: (a) an empirical linear model and (b) a deterministic model based on Fick's law of diffusion. Both models are proved better for describing denitrification kinetics than assuming a fixed K_{NO_3} at low nitrate concentrations. The empirical model is more utilitarian whereas the model based on Fick's law has a fundamental basis that enables the intrinsic K_{NO_3} to be estimated. In this study data was analyzed from 56 denitrification rate tests and it was found that the extant K_{NO_3} varied between 0.07 mgN/L and 1.47 mgN/L (5th and 95th percentile respectively) with an average of 0.47 mgN/L. In contrast to this, the intrinsic K_{NO_3} estimated for the diffusion model was 0.01 mgN/L which indicates that the extant K_{NO_3} is greatly influenced by, and mostly describes, diffusion limitations.

1. Introduction

1.1. *Prevalence of the Monod equation to describe biological wastewater treatment processes*

The Monod equation (Monod, 1942) has gained almost universal acceptance for modeling the majority of biological treatment processes in wastewater treatment. The International Water Association (IWA) has issued a series of activated sludge models (ASM) starting with ASM1 (Henze at al., 1987) – that uses Monod equations to describe the growth of heterotrophic and nitrifying bacteria and utilizes a "death and regeneration" model for death processes. The last model in this series is ASM3 (Gujer et al., 1999) which uses similar

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0043-1354/$ – see front matter
http://dx.doi.org/10.1016/j.watres.2013.07.003

Monod expressions for bacterial growth but incorporates substrate storage and "endogenous respiration" model for death processes. Many authors have used ASM1 and similar models as the basis for other biological growth processes in wastewater treatment such as biological phosphorus removal (Barker and Dold, 1997), sulfur removal (Guisasola et al., 2009) and dual populations for ammonia oxidation (Wett et al., 2011). The wide acceptance of the Monod equation to describe biological growth processes in activated sludge has resulted in Batstone et al. (2002) also using Monod equations in a model for anaerobic treatment processes and several authors using Monod-type equations to describe biological growth within biofilm models for wastewater treatment (Wanner and Reichert, 1996; Rittmann and McCarty, 2001).

The Monod equation – expressed in the form shown in Equation (1) - is empirical but has the same form as the Michaelis-Menten equation for enzyme kinetics (Monod, 1949). It has a characteristic shape that is useful for describing biological processes as it approximates a maximum growth rate with zero order kinetics at high substrate concentrations (when $S >> K_s$) and first-order kinetics at low concentrations (when $S << K_s$).

$$r_g = \mu_{\max}\frac{S}{K_S + S}X \tag{1}$$

where, r_g = growth rate (mg/L/day)

$\mu_{\max}$ = maximum specific growth rate (1/day)
S = substrate concentration (mg/L)
K_s = half-saturation coefficient, or affinity coefficient (mg/L)
X = biomass concentration (mg/L)

The half-saturation coefficient (or substrate "affinity coefficient"), K_s, plays a critical role in defining the concentration at which the kinetic rate will become substrate-limited to half of the maximum rate. At substrate concentrations lower than K_s, there is a strong linear dependency of the specific growth rate on the substrate concentration and the growth rate can be approximated by Equation (2) which is a first order rate equation with respect to S.

$$r_g \approx \frac{\mu_{\max}X}{K_S}S \tag{2}$$

Where, $\mu_{\max}X/K_S$ is constant.

Models used to design wastewater treatment plants that are required to achieve low effluent concentrations need to consider carefully half-saturation coefficients as they influence strongly biokinetic rates and therefore the ability of the design to achieve low concentrations. They are critical also in model predictions where multiple parallel or linked biological reaction processes are considered. Lackner and Smets (2012) showed that the values for oxygen affinity coefficients $K_{O,AOB}$ and $K_{O,NOB}$ were key to determining the extent of nitritation for ammonia removal in two different 1-dimensional biofilm models.

1.2. The significance of half-saturation coefficients in biological nutrient removal

A process model of a biological nutrient removal system that is operated to achieve very low effluent concentrations is likely to provide model predictions that are less accurate due to uncertainty in the K_S values. For instance, a denitrification process that needs to achieve a low effluent nitrate (NO_3) or total nitrogen concentration requires a model whose effluent predictions start to depend more on Monod half saturation terms (in the case of denitrification, that of available carbon substrate (K_S) and of residual NO_3 K_{NO_3} values, respectively) and less on the maximum specific growth rate ($\mu_{\max}$). The specific growth rate and in turn, the specific substrate removal rate, is strongly dependent on the half saturation coefficient at low substrate concentrations. Half saturation parameters in process models are routinely adjusted to better mimic final effluent concentrations rather than being independently determined and thus remain unverified. Hauduc et al. (2011) conducted a questionnaire of 28 modeling practitioners and reviewed literature values for the kinetic constants they used in ASM1 and other activated sludge models. They found that for ASM1 the half-saturation coefficients for soluble biodegradable carbon substrate and nitrate for heterotrophic organisms and ammonia for autotrophic nitrifying organisms had the highest variance, whereas other parameters such as the maximum specific growth rates and yield coefficients had a low variance.

1.3. Half-saturation coefficients as variables, not constants

Some researchers have noted that half-saturation coefficients are not constant but that they appear to be linked to the maximum specific growth rate. Lobry et al. (1992) cites a list of 14 references where data show K_s increasing with $\mu_{\max}$ and they suggest modifying the Monod expression by replacing K_s with $\mu_{\max}/k$ (where k is a different constant). The theoretical basis for their modified model is challenged by Gyllenberg (1993), however the evidence for some form of relationship between K_s and $\mu_{\max}$ still remains in the literature. Healey (1980) suggested that the ratio of maximum specific growth rate/K_s is a useful indicator of nutrient advantage for organisms at low substrate concentrations which may provide a better justification for modifying the Monod expression to account for the relationship between K_s and maximum specific growth rate.

The purpose of this study was to develop a method that was used to determine a relationship between maximum substrate removal rate and half saturation coefficient for nitrate in the denitrification process.

2. Materials and methods

2.1. Overall procedure

The following 4 step procedure was developed to investigate the dependency of half-saturation coefficients on the maximum rate:

1. Using a batch reactor under strictly controlled environmental conditions and with substrate initially in excess, measure the process rate continuously until all substrate is used up.