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Modelling and experimental investigation of activated sludge VOCs adsorption and degradation

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ABSTRACT

This article deals with role and importance of adsorption in the activated sludge substrate degradation. This process is typically described according to the Monod–Michaelis–Menten (M–MM) kinetics, which is based on the assumption that the substrate has been pre-adsorbed on flocs in order for the biochemical reaction to take place. However, the simple and generalised use of M–MM equation in wastewater treatment modelling could be misleading in describing some specific scenarios, where substrate in the liquid phase is not in equilibrium with substrate inside the flocs and, in general, when adsorption and kinetic rates are not comparable. This can occur in numerous process configurations, during plant start-up, when substrate peaks or significant fluctuations are met, in batch processes. An experimental test has been carried out with the aim to investigate the characteristics of the adsorption mechanism and its relationship with the stored mass degradation. Direct application of M–MM kinetics failed in fitting the experimental data. External transport and Glueckauf and Coates particle-phase diffusion relations have been adopted to study substrate transfer to active sites. Andrews and Busby model has then been applied and an excellent accordance with the experimental data has been found. As a final aim of the work, transition from adsorption-to-kinetics has been modelled, which has shown to be very effective for a full understanding of phenomena.

1. Introduction

Activated sludge processing is a mature technology, which has been extensively studied and applied. Municipal and industrial wastewaters are successfully treated and polluting load is reduced below the regulation limits. However, due to the complexity and to the nature of activated sludge, management of wastewater treatment plant can pose some potential issues and design failures are not infrequent. In addition, when specific chemical substances are to be removed, treatment process parameters, such as mass transfer and kinetic terms, can be very different from those associated to municipal wastewater. Substrate degradation is a complex phenomenon, consisting of liquid diffusion, liquid-to-solid transfer, particle phase diffusion, adsorption, desorption as has been analysed and modelled by Williamson and McCarty (1976). The understanding of the characteristics of each mechanism is fundamental. Monod–Michaelis–Menten (M–MM) reaction is generally assumed as representative of the overall phenomena, whereas role of floc adsorption has to be specifically considered. Frequently, the extreme simplicity of the design procedure differs dramatically from the reality. An excellent approach to overcome these difficulties was presented by Andrews and Busby (1975), whose structured sludge model identifies a sequential order of stages, and distinguishes mass storage and adsorption from degradation kinetics. The importance of role and potential of activated sludge adsorption has been analysed in many recent works. Standard ISO 18749:2004 specifies a screening test method for the determination of the degree of adsorption of substances

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Nomenclature

a	parameter in equation solving
a_p	outer-surface interfacial area per unit volume
b	parameter in equation solving
c	parameter in equation solving
COD	chemical oxygen demand
$\mathcal{D}$	ester diffusivity in pure water
d_p	particle diameter
$\mathcal{D}_p$	particle phase diffusivity
f_s	maximum storable fraction of MLVSS
G_0	free energy
HGLH	Hougen–Watson Languimur–Hinshelwood
K	constant for yield coefficient
K_a	M–MM constant
K_a	Andrews and Busby saturation constant
K_i	specific decay rate of active mass
K_s	saturation constant
k_a	adsorption constant
k_d	desorption constant
k_p	Glueckauf and Coates mass transfer coefficient
k_s	attachment mass transfer coefficient
k_{sl}	external transport transfer coefficient
MLVSS	mixed-liquor volatile suspended solids
M–MM	Monod Michaelis–Menten
m_o	moles of oxygen needed to oxide 1 mol of substrate
N	substrate flux
N_{SH}	Sherwood number
P	number of adsorption sites
r	generic radius
r_a	attachment rate
r_{ad}	adsorption rate
r_d	M–MM substrate degradation rate
r_i	inert mass formation rate
r_s	active mass synthesis rate
S	substrate concentration
S_0	initial substrate concentration
S_i	substrate at particle outer surface
t	time
X_a	active mass concentration
X_{a0}	initial active mass concentration
X_i	inert mass concentration
X_s	substrate solid-phase concentration
X_s^*	substrate solid-phase concentration in equilibrium with S_i
X_{smax}	asymptotic solid-phase concentration
X_t	total mixed-liquor volatile suspended solids concentration
Y_Δ	mass per unit energy
Y_i	inert mass formed per unit mass of active mass converted
Y_{O_2}	mass of cell per mass of consumed oxygen
Y_s	yield coefficient
Γ	integration constant
θ_a	fraction of active centres occupied by substrate
θ_{ae}	fraction of active centres occupied at equilibrium
μ_a	maximum specific rate for conversion of stored mass
μ_{max}	M–MM maximum degradation rate
Ψ_p	correction factor

on to activated sludge or primary sludge in a wastewater treatment plant. In two articles Chu and Chen (2002a,b) have studied the adsorption of Basic Yellow 24 dye on activated sludge biomass. In the first part of the study they found that kinetics of adsorption followed a first order mechanism, controlled by film diffusion. The experimental results included in the second article indicate that there is a boundary layer surrounding the biomass particles and that adsorption process is mainly controlled by intra-particle diffusion. Pérez et al. (2005) have discussed role of diffusion in flocculated and granular sludge and have presented a specific analytical approach to describe the biofilm behaviour. Smith et al. (2009) have studied in detail the properties and the factors which influence the adsorption properties of activated sludge and have provided a clear picture of its characteristics and importance. Stevens-Garmon et al. (2011) examined the removal mechanism of trace organic compounds during activated sludge treatment and found similar characteristics of different sludge type. The excellent adsorbing capacity of sewage-sludge has been studied and enhanced by Anfruns et al. (2011) with specific reference to VOC removal. Zhang et al. (2014), in a recent article, have confirmed the specific role of activated sludge adsorption with respect to the substrate.

This paper specifically focuses on the activated sludge adsorption in substrate degradation. On the basis of some experimental findings and following Williamson and McCarty biofilm model, Andrews and Busby approach has been adopted with reference to the general interface and intra-particle substrate mass transfer transport equations in order to adequately explain the experimental data and to model the adsorption-to-degradation transition in activated sludge water treatment.

1.1. *Objective and methodology*

The objective of this article is to identify and to study role and importance of substrate adsorption on to activated sludge in the overall removal and degradation process. Ethyl acetate has been added to an activated sludge sample collected from a municipal/semi-industrial treatment plant and liquid samples have been taken and analysed for the ester concentration at regular time intervals. The results have been compared to the findings obtained through M–MM equation and the discrepancy has been investigated by analysing the liquid-to-solid substrate transport and the intra-particle diffusion. To this purpose, the linear driving force relation of Glueckauf and Coates (1947) has been applied and related to the Andrews and Busby model (1975). Comparison to the experimental data has quantified the relevance of external and intra-particle diffusion. Finally, combination of adsorption and degradation kinetics has been modelled and interpreted against the test data.

2. Biochemistry of ethyl acetate

2.1. *Oxidation*

Ethyl acetate is subject to the preliminary action of hydrolytic enzymes. Esterase splits esters into an acid and an alcohol (Bailey and Ollis, 1986):

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH \tag{1}$$