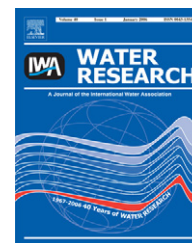


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Effect of anionic and nonionic surfactants on the kinetics of the aerobic heterotrophic biodegradation of organic matter in industrial wastewater

Ewa Liwarska-Bizukojc^{a,*}, René Scheumann^b, Anja Drews^b,
Ute Bracklow^b, Matthias Kraume^b

^aDepartment of Environmental Engineering, Technical University of Lodz, Al. Politechniki 6, 90-924 Lodz, Poland

^bDepartment of Chemical Engineering, Berlin University of Technology, Strasse des 17. Juni 135, 10623 Berlin, Germany

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ABSTRACT

While using the contemporary mathematical models for activated sludge systems, it is necessary to describe quantitatively the kinetics of microbiological processes and to characterise substrate (wastewater components in the influent) as well as biomass (activated sludge). In this paper, the kinetic parameters of the aerobic biodegradation of organic matter in wastewater containing synthetic surfactants in an activated sludge system were determined and discussed. Also, the composition of the tested wastewater was estimated and expressed as COD fractions. Five synthetic surfactants, three anionic and two nonionic, of different chemical structure were investigated. Each of them was tested separately and dissolved in wastewater to obtain a concentration of 50 mg l^{-1} , which can be found in some industrial wastewater. The presence of the elevated amount of synthetic surfactants in wastewater decreased the affinity of biomass to substrate. Nevertheless, maximum specific growth rates (μ_{\max}) of heterotrophic biomass exposed to wastewater containing surfactants were high but usually lower than μ_{\max} estimated for wastewater without surfactant. Surfactants, which contain a benzene ring, were the most likely to deteriorate wastewater treatment processes in the activated sludge systems.

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1. Introduction

In order to aid the design and operation of activated sludge systems, the software based on dynamic models belonging to the Activated Sludge Models is frequently used (ASIM, SYMOS). Activated Sludge Models (ASM1, ASM2-ASM2d,

ASM3) proposed by the IWA (formerly IAWPRC, then IAWQ) task group have shown to be a good compromise between the complexity of the activated sludge processes and the prediction of biological wastewater treatment under dynamic conditions (Henze et al., 1987; Gujer et al., 1999). However, a successful application of such modelling requires

*Corresponding author. Tel.: +48 42 631 35 98; fax: +48 42 631 35 17.

Abbreviations: μ_{\max} , maximum specific growth rate for heterotrophic biomass (d^{-1}); K_s , half-saturation constant for heterotrophic biomass ($\text{mg O}_2 \text{ l}^{-1}$); k_H , hydrolysis constant (d^{-1}); b_H , heterotrophic decay coefficient (d^{-1}); Y_H , yield coefficient for heterotrophic biomass (g COD g COD^{-1}); S_s , readily biodegradable substrate (% COD); X_s , slowly biodegradable substrate (% COD); S_I , soluble inert matter (% COD); X_I , suspended inert matter (% COD); X_{BH} , heterotrophic biomass (% COD); MBAS, methylene blue active substances

E-mail addresses: ewaliwar@p.lodz.pl, ewa.liwarska-bizukojc@p.lodz.pl (E. Liwarska-Bizukojc), rene.scheumann@tu-berlin.de (R. Scheumann), anja.drews@tu-berlin.de (A. Drews), ute.bracklow@tu-berlin.de (U. Bracklow), matthias.kraume@tu-berlin.de (M. Kraume).

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the estimation of kinetic and stoichiometric parameters as well as wastewater and activated sludge characterisation.

Wastewater characterisation can be performed with the help of physicochemical or biological methods. Taking into account that the ASMs are in general biologically defined models, the biological methods have found wider application than physicochemical tests (Petersen et al., 2003). Among biological methods, respirometry has turned into one of the most commonly used methods for the purpose of wastewater characterisation (Petersen et al., 2003; Lagarde et al., 2005). Respirometry is also a dominating method for the determination of kinetic and stoichiometric parameters. It is based on the measurement and interpretation of the transient oxygen uptake rate (OUR) of activated sludge. Kappeler and Gujer (1992) have shown that the estimation of most kinetic parameters and of the wastewater compositions is possible by measuring OUR in simple batch tests. Several studies have been dedicated to evaluate and verify the correctness of this methodology for model calibration (Novák et al., 1994; Spanjers and Vanrolleghem, 1995; Pollard et al., 1998). Finally, the methods based on batch respirometric experiments have been recommended by the authors of ASM and have become a standard tool for ASM calibration, especially in terms of kinetic parameters' estimation (Henze et al., 2002; Petersen et al., 2003).

Synthetic surfactants are extensively used in households as well as in industrial processes. Most of the surfactants consumed nowadays are anionic or nonionic surfactants (Petrovic and Barceló, 2004). Biodegradation and environmental impact of anionic and nonionic surfactants have been the subject of substantial research for many years (Perez et al., 1996; Rozzi et al., 1999; Cserháti et al., 2002; Carvalho et al., 2004; Ying, 2006). So far, the quantitative description of the kinetics of synthetic surfactants' microbiological decomposition has been presented only in a few studies (Zhang et al., 1999; Carvalho et al., 2001).

The main aim of this work was to describe and discuss the kinetics of the aerobic heterotrophic biodegradation of

organic matter in wastewater containing the most commonly used anionic and nonionic surfactants of different chemical structure at elevated concentration (50 mg l^{-1}). Thus, the kinetic and stoichiometric parameters for such activated sludge processes were determined with the help of respirometric methods. Additionally, wastewater containing synthetic surfactants was characterised in terms of the COD fractions.

2. Materials and methods

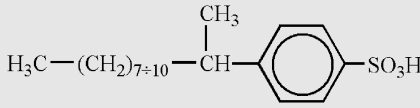
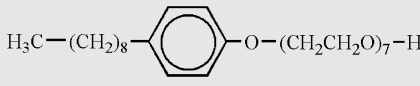
2.1. Surfactants

Five different surfactants, three anionic (A1, A2, A3) and two nonionic (N1, N2), were tested. All the surfactants studied are very popular and extensively used as detergents and emulsifiers (Petrovic and Barceló, 2004). Each of them had a different chemical structure and was investigated individually. Systematics and chemical formulae of the surfactants tested are given in Table 1. The initial surfactant concentration in wastewater was identical for all surfactants and equal to 50 mg l^{-1} . This concentration was higher than in typical municipal wastewater and corresponded with the surfactant content in some industrial wastewater. The concentration of anionics in industrial wastewater reaches 300 mg l^{-1} , whereas nonionics exceed 30 mg l^{-1} (Zhang et al., 1999; Petrovic and Barceló, 2004). What is more, in wastewater coming from tannery, textile, pulp and paper industries, the amounts of anionics or nonionics even close to the critical micelle concentration were detected (Zhang et al., 1999).

2.2. Wastewater

Synthetic wastewater with or without addition of one of the surfactants tested was the substrate used in the batch

Table 1 – Characteristic of wastewater tested

Code	Surfactant chemical name	Group of surfactants	Structural formula	Average COD _{tot} of wastewater ($\text{mg O}_2 \text{ l}^{-1}$)
A1	Sodium dodecyl sulphate (SDS)	Alkyl sulphates (AS)	$\text{H}_3\text{C} - (\text{CH}_2)_{11} - \text{O} - \text{SO}_3\text{Na}$	735
A2	Sodium alkylbenzene sulphonate	Linear alkylbenzene sulphonates (LAS)		735
A3	Sodium alkyltrioxyethylene sulphate	Alkylpolyoxyethylene sulphates (AES)	$\text{H}_3\text{C} - (\text{CH}_2)_{11+13} - \text{O} - (\text{CH}_2\text{CH}_2\text{O})_{10} - \text{H}$	725
N1	Decaoxyethylene alkyl ether	Alcohol ethoxylates (AE)	$\text{H}_3\text{C} - (\text{CH}_2)_{11+13} - \text{O} - (\text{CH}_2\text{CH}_2\text{O})_{10} - \text{H}$	740
N2	Nonylphenylheptaoxyethylene glycol ether	Alkyl phenol ethoxylates (APE)		710
Control	–	–	–	750

Chemical name and structure of surfactant, total COD of wastewater.

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