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Modelling biodegradation of nonylphenol ethoxylate in acclimated and non-acclimated microbial cultures

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A B S T R A C T

The biodegradation and inhibition kinetics of a commercial nonylphenol ethoxylate formulation were modelled for an activated sludge system fed with a synthetic substrate and nonylphenol ethoxylate mixture. Kinetic and stoichiometric coefficients of the proposed activated sludge model were obtained by employing on-line respirometry. Experimental as well as model results confirmed that nonylphenol ethoxylate exhibited non-competitive inhibition on the hydrolysis process with a coefficient of 150 mg/L on the basis of COD and negatively influenced biomass growth through a competitive inhibition mechanism with a coefficient of 500 mg/L on the basis of COD, when the biomass was not acclimated. Upon acclimation of the activated sludge system, the inhibition concentration for non-competitive inhibition on hydrolysis was increased to 5000 mg/L, practically showing no inhibition, and the coefficient of competitive inhibition increased to 450 mg/L, corresponding to a significant decrease in the inhibitory effects of NPEO on growth.

1. Introduction

Nonylphenol ethoxylates, (NPEOs) are cleaning agents that belong to the larger group of compounds called alkylphenol ethoxylates (APEOs). NPEOs are produced in huge quantities for use in many different industrial sectors including industrial laundering, textile processing (wetting and scouring), pulp and paper processing, paint and resin formulation, oil and gas recovery, steel manufacturing, pest control and power generation. As an example in textile industry NPEOs are mostly applied in the concentration range of 0.5–1.0 g/L as a wetting agent in the textile fabric preparation stage. Their organic carbon contribution to the ultimate, combined textile effluent is around 400–500 mg/L in terms of COD. More recently, many countries, large corporations, environmental protection agencies and scientific entities have classified metabolites of NPEOs and other APEOs as toxic, since they enter the aquatic and terrestrial environment at concentrations and/or conditions that might have immediate or long-term harmful impacts (Renner, 1997; APE Research Council, 2001; Environment Canada, 2002; EU, 2002; US EPA, 2004). In a review by Servos (1999), acute toxicity of nonylphenol (NP), the NPEO breakdown product, to fish, aquatic invertebrates and algae was reported to occur in the range of concentrations from 17 to 3000 μg/L. Levels for no observable effect during chronic exposure to NP in fish and invertebrates were reported at levels as low as 6 and 3.7 μg/L, respectively (Servos, 1999). In the same study, the examples of NP acting as an estrogen mimic in fish are given for concentrations as low as 10 μg/L. The predicted no-effect concentration for NP is reported as 1 μg/L or even lower e.g. European Union risk assessment used 0.33 μg/L (Toxicology Environmental Consulting Ltd., 2002). A lot of companies even voluntarily stopped using APEO-based chemicals in their application and massive productions as it has been recognized that their use has proven to create long-term concerns and potential risks for the ecosystem (Procter and Gamble, 2005). On the other hand, APEO are still being used in several industrial applications where they have not been replaced yet by another alternative chemical due to technical as well as economical reasons. The prices of the main alternatives (alcohol ethoxylates, glucose-based surfactants) to NPEO have been, on average, ~20–40% higher than NPEO (Toxicology Environmental Consulting Ltd., 2002).

It has been postulated that primary NPEO biodegradation at wastewater treatment plants produces metabolites that are generally speaking more lipophilic, toxic, persistent and estrogenic when compared to the mother compound (Thiele et al., 1997; Bokern and Harms, 1997; Servos, 1999; EU, 2002). The generally accepted biodegradation pathway was proposed by Ahel et al. (1994) and begins with the simultaneous ω-oxidation of the ethoxy chain and the α-, β-, or ω-oxidation of the alkyl chain prior to ether hydrolysis (Di Corcia et al., 2000). The metabolites formed are short chain APEOs which are subsequently transformed to the corresponding alkyl phenol polyethoxylates as well as carboxyalkylphenol polyethoxylates under aerobic and to alkyl phenols under anaerobic conditions

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Nomenclature

S_S	readily biodegradable substrates in synthetic substrate, mg COD/L
X_S	slowly biodegradable substrates in synthetic substrate, mg COD/L
C_{NPEO}	NPEO in the bulk liquid, mg COD/L
$S_{S,NPEO}$	readily biodegradable substrate generated after the breakdown of NPEO and formed after the hydrolysis of slowly biodegradable portion of NPEO, mg COD/L
$S_{H,NPEO}$	slowly biodegradable portion of NPEO after breakdown of NPEO, mg COD/L
$S_{I,NPEO}$	non-biodegradable portion of NPEO, mg COD/L
S_P	soluble metabolic products, mg COD/L
X_H	heterotrophic biomass, mg COD/L
Y_H	heterotrophic growth yield, g COD/g COD
I_{NC}	function for non-competitive inhibition of hydrolysis, –
I_C	function for competitive inhibition of growth, –
$K_{I,NC}$	inhibitor concentration for 50% rate reduction, mg COD/L
$K_{I,C}$	inhibitor concentration for 50% affinity coefficient increase, mg COD/L
f_{ES}	fraction of metabolic products, g COD/g COD
$f_{I,NPEO}$	non-biodegradable fraction of NPEO, g COD/g COD
α	readily biodegradable fraction of NPEO produced through adsorption/oxidative cleavage, g COD/g COD
k_{OCL}	first-order adsorption/oxidative cleavage coefficient, d^{-1}
b_H	endogeneous decay coefficient, d^{-1}
k_h	hydrolysis rate coefficient of synthetic substrate, d^{-1}
K_X	half-saturation coefficient for the hydrolysis of synthetic substrate, g COD/g COD
μ_H	rate of heterotrophic growth on synthetic substrate mixture, d^{-1}
K_S	half-saturation coefficient for synthetic substrate mixture, mg COD/L
$k_{h,NPEO}$	hydrolysis rate coefficient of NPEO, d^{-1}
$K_{X,NPEO}$	half-saturation coefficient for the hydrolysis of NPEO, g COD/g COD
$\mu_{H,NPEO}$	rate of heterotrophic growth on NPEO, d^{-1}
$K_{S,NPEO}$	half-saturation coefficient for NPEO, mg COD/L

(Jonkers et al., 2001; Zhang et al., 2008; Montgomery-Brown et al., 2008). It is estimated that at least 60–65% of all nonylphenolic compounds that have entered sewage treatment are discharged into the environment, mainly in the form of acidic and neutral degradation products (Ahel et al., 1994). For instance, NPEOs are easily degraded to their main metabolite, e.g. NP under anaerobic conditions, that is known to disrupt normal hormonal functioning in the body (Dachs et al., 1999; Johnson and Sumpter, 2001) and thus is considered as an *endocrine disrupting chemical* (EDC). Moreover, the formation of NP cannot be ruled out under oxic conditions, since some scientific evidence has been reported recently (Montgomery-Brown et al., 2008). NPEOs may undergo complete primary biodegradation in the presence of oxygen; oxidation is attributed to the degradation of the alkyl chain, but little evidence is observed for degradation of the aromatic ether bond (Scott and Jones, 2000).

It is important to predict the removal kinetics of APEOs including NPEO in order to effectively control and enhance the treatment performance of biological treatment facilities for chemicals with slow and incomplete biodegradation characteristics. As a matter of fact, it is an urgent need to describe and formulate the biodegradation rate of surfactants by means of suitable mechanistic models capable of predicting the behaviour of complex substrates whose inhibitory effect is attributable to the degradation of their metabolites rather than the mother pollutant (NPEO). Recent models incorporate two major conceptual developments that have provided major achievement in the interpretation of biodegradation kinetics (i) they include a number of COD fractions as model components with different biodegradation characteristics; (ii) they use dissolved oxygen concentration (S_O) as a model component which allows to express the oxygen uptake, (OUR), as a significant process rate (Henze et al., 2002). This way, calibration of the selected model with the experimental OUR profile is generally used to obtain the COD fractions and kinetic coefficients characterizing the biodegradation of the tested substrate (Cokgor et al., 2007, 2009a). Such models have now been developed and widely used based on the pioneering work of Henze et al. (1987), who proposed the first multi-component mechanistic model, commonly known as ASM1. Toxic and inhibitory effects of different compounds and xenobiotics can also be determined by the use of respirometric methods (Insel et al., 2006; Jurado et al., 2009). In addition, it is also possible to assess the degradability of inhibitory organics through on-line respirometric measurements (Stasinakis et al., 2008). Although the toxic or inhibitory levels of industrial pollutants were successfully identified in previous studies (Meric et al., 2003; Orhon et al., 2010) by employing different biodegradation test protocols like ISO 8192 (2007) and using respirometry, the concept and mechanisms of inhibitory effects have been incorporated into activated sludge modelling only recently (Cokgor et al., 2009b; Karahan, 2010). Identification of inhibition mechanisms and their effect on different biochemical processes taking place in biological treatment is crucially important especially for commercially important surfactants like LAS or NPEO, since increasing levels of these compounds enter municipal activated sludge treatment systems (EU, 2002).

In this context, the present study was primarily focused on investigating the biodegradation kinetics of a commercially important NPEO in continuously-fed fill and draw reactors sustained at steady-state, simulating an activated sludge treatment system under typical conditions for industrial effluents bearing NPEO formulations. The evaluation was based for the first time on a modelling approach providing numerical information on the biodegradation kinetics and inhibitory effects of NPEO in a way that is compatible with other wastewaters and similar chemicals. In the first stage of this study, sewage sludge was gradually acclimated to aqueous NPEO equivalent to 500 mg/L COD, which is a typical concentration that can be found in industrial wastewater streams, for a period of 8 months. In the second stage, a series of biodegradation experiments were conducted where acclimated and non-acclimated biomass was exposed to a mixture of synthetic substrate and NPEO, mainly to elucidate the effect of NPEO addition and acclimation on the biodegradation rates. A multi-component model specifically structured to reflect the characteristics of NPEO was used for this purpose. The model was calibrated with the experimental oxygen uptake rate profiles for the assessment of (i) possible inhibitory impacts of NPEO and (ii) the effect of acclimation of the microbial culture on the biodegradation characteristics of NPEO.

2. Methods

2.1. Materials

NPEO (NP-10; 660 g/mol; $(C_2H_4O)_{10}\,C_{15}H_{24}O$; CAS No.: 26027-38-3) was of commercial grade and supplied by Eksoy Chemicals