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Fate and degradation kinetics of nonylphenol compounds in aerobic batch digesters

*Seçil Ömeroğlu, F. Dilek Sanin**

Department of Environmental Engineering, Middle East Technical University, Ankara 06800, Turkey

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ABSTRACT

Nonylphenol (NP) compounds are toxic and persistent chemicals that are not fully degraded either in natural or engineered systems. Current knowledge indicates that these compounds concentrate in sewage sludge. Therefore, investigating the degradation patterns and types of metabolites formed during sludge treatment are important for land application of sewage sludge. Unfortunately, the information on the fate of nonylphenol compounds in sludge treatment is very limited. This study aims to investigate the biodegradation patterns of nonylphenol diethoxylate (NP2EO) in aerobic batch digesters. For this purpose, two NP2EO spiked and two control laboratory aerobic batch digesters were operated. The spiked digester contained 3 mg/L NP2EO in the whole reactor content. The compounds of interest (parent compound and expected metabolites) were extracted with sonication and analyzed by gas chromatography-mass spectrometry (GC–MS) as a function of time. Results showed that, following the day of spike, NP2EO degraded rapidly. The metabolites observed were nonylphenol monoethoxylate (NP1EO), NP and dominantly, nonylphenoxy acetic acid (NP1EC). The mass balance over the reactors indicated that the total mass spiked was highly accounted for by the products analyzed. The time dependent analysis indicated that the parent compound degradation and daughter product formation followed first order kinetics. The digester performance parameters analyzed (VS and COD reduction) indicated that the spike of NP2EO did not affect the digester performance.

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1. Introduction

Sewage sludge is the by-product of wastewater treatment plants (WWTPs), and, increasing number of WWTPs globally results in the increase of sewage sludge produced. Although sewage sludge contains beneficial nutrients, it also has organics and odor containing substances and hosts pathogens and viruses. For this reason sewage sludge must be treated properly before being discarded. Aerobic and anaerobic digestions are the most commonly applied treatment methods on sewage sludge to mitigate these undesirable characteristics. For final disposal/reuse landfilling, incineration and agricultural use are the possible approaches widely used worldwide. From these alternatives, land application is preferred in a number of countries since sewage sludge is rich in organics and beneficial nutrients (Aparicio et al., 2007 and Santos et.al., 2007). Besides these advantages however, sewage sludge also concentrates some unwanted synthetic organic contaminants and land application may provide a route for these chemicals to enter the food chain (Abad et al., 2005). Nonylphenol (NP) compounds are among these

* *Corresponding author*. Tel.: +90 312 210 26 42.
E-mail address: dsanin@metu.edu.tr (F.D. Sanin).
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synthetic organic contaminants and recently they are in the focus of interest due to their toxic, carcinogenic and endocrine disrupting properties. Even in short term exposures, they result in severe effects such as eye/skin irritation and respiratory diseases (Cox, 1996). Carcinogenic effect of NP compounds was accidentally discovered first in a study on human breast cancer cells where NP compounds leaking from the material of the plastic tubes resulted in the multiplication of cancer cells rapidly (Soto et al., 1991). In addition to the carcinogenic effect, NP compounds are among the endocrine disrupting chemicals (EDCs) since they mimic oestrogen hormone due to their similarity to 17-β-ostradiol (Warhurst, 1995). In fact, the main reason behind the multiplication of breast cancer cells was the oestrogen mimicking ability of NP.

Presence of NP compounds in environment is purely anthropogenic. Due to their surface active properties, they are being used in domestic (personal care products, detergents, etc.), industrial and commercial formulations (wetting and dispersing agents, textile production, metal finishing, etc.) (CEPA, 1999). Due to their widespread use, they eventually reach WWTPs and from there they are released into the environment (Soares et al., 2008). Since they are not highly biodegradable, they are typically discharged into the receiving bodies before being fully degraded. NP compounds are persistent in environmental systems and highly hydrophobic (high log K_{ow}), which make them pretty insoluble and tend to stick on organic surfaces such as soil, sediment and sewage sludge (Nielsen et al., 2000).

NP compounds do not degrade fully during wastewater treatment. Additionally, their degradation leads to the formation of metabolites that are equally resistant and hazardous. Therefore, the degradation mechanisms of NP compounds must be fully investigated. NP compounds are mostly in the form of nonylphenol polyethoxylates (NPnEOs) in domestic, industrial and commercial formulations. The information on the biodegradation of NP compounds in wastewater treatment state that biodegradation starts with the attack of microorganisms to eliminate ethylene oxide chain of NPnEOs (CEPA, 1999). As the number of ethylene oxide units decreases, NPnEOs are converted into nonylphenol diethoxylate (NP2EO) and nonylphenol monoethoxylate (NP1EO). From this point on, the degradation differs under aerobic and anaerobic conditions (Ying et al., 2002). Under aerobic conditions, NP2EO and NP1EO are converted into nonylphenoxy ethoxy acetic acid (NP2EC) and nonylphenoxy acetic acid (NP1EC). However, under anaerobic conditions NPnEOs are converted to NP2EO, NP1EO and NP, whereas NP2EC and NP1EC formation are not observed. Another difference is that under aerobic conditions the rate of degradation is faster compared to anaerobic degradation (Ahel et al., 1994; CEPA, 1999; Soares et al., 2008). The schematic representation of aerobic and anaerobic degradation of NPnEOs during biological wastewater treatment is presented in Fig. 1.

NP compounds being in the focus of scientific groups this much and the findings on health effects, have alarmed the governments to take precautions. First, the use of NP compounds was banned in household detergents in United Kingdom in 1976 (La Guardia et al., 2003). Then many countries started to either limit or completely ban the use of NP compounds. These substances have been included in the hazardous substances list of EU (Directive 2000/60/EC) (DG, 2000a) and OSPAR commissions. Although they are banned in most of the European countries, these substances are still in use in South American and Asian countries (Soares et al., 2008).

Although NP compounds are banned or limited in use for the last couple of decades, their persistent nature described above makes them remain on organic surfaces such as soil, sediment and sewage sludge for a long time once they enter. Considering that the agricultural use of sewage sludge is a popular and widespread application, sewage sludge must also be monitored and tested for suitability for this family of compounds (Aparicio et al., 2007). A limit for NP compounds in land applied sewage sludge is set for the sum of NP, NP1EO and NP2EO, which is represented as NPE, in many countries such as Denmark, Sweden, Spain and Turkey (Aparicio et al., 2007; DG, 2001; MoEU, 2010). European Union, in Working Document on Sludge-3rd Draft, proposed a limit value for NPE as 50 mg/kg dry solids (ds) and this value has been accepted by most of the member countries with few exceptions. For instance, in Spain the limit value 50 mg/kg ds for NPE was recognized as it is, whereas in Denmark, this limit value was first decreased to 30 mg/kg ds in 2000 and then to 10 mg/kg in 2002 (DG, 2001).

Even though a degradation mechanism was suggested based on the behavior of nonylphenols in aqueous systems and despite the possible risks posed by these chemicals in land application of sewage sludge, a through mechanistic research for sludge digesters have not been conducted. The motivation of this study rests on this fact. The objective of this research is to investigate the biodegradation mechanisms and degradation kinetics of NP compounds during anaerobic sludge digestion. For this purpose, the fate of a model compound, NP2EO, was monitored in 3.2 L laboratory scale aerobic batch digesters containing 3 mg/L NP2EO. In order to achieve 3 mg/L NP2EO concentration within the whole reactor content, 9 mg of NP2EO in acetone was injected into the reactors. The transformation of NP2EO into metabolites such as NP, NP1EO and NP1EC were followed by measuring the concentrations of the compounds in solid and liquid phases of sludge using gas chromatography-mass spectrometry (GC–MS). Once the product concentrations are determined, kinetics of degradation was examined.

2. Materials and methods

2.1. Chemicals and standards

The standards solutions of NP, NP1EO and NP2EO (analytical standard, 5 μg/mL in acetone) were supplied from Fluka, Sigma Aldrich Co. LLC, USA (Product# 32,889, 32,895, 32,899, respectively). The standard solution of NP1EC (10 ng/μL in acetone) was purchased from Dr. Ehrenstorfer GmbH, Germany (Product# LA15631020AC). The solid NP2EO (purity 99.0%, 10 mg) used to spike the reactors were obtained from Dr. Ehrenstorfer GmbH, Germany (Product# C15631010). The N,O-Bis(trimethylsilyl)trifluoroacetamide and the catalyst TMCS (trimethylchlorosilane) (BSTFA + TMCS, 99:1 Sylon BFT