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Technical Note

Removal of surfactants nonylphenol ethoxylates from municipal sewage-comparison of an A/O process and biological aerated filters

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HIGHLIGHTS

- The A/O process exhibits improved performance in comparison to the BAF process.
- Adsorption plays the dominant role in the removal of NP*n*EOs from municipal sewage.
- The long-chain NP*n*EOs undergo biodegradation in the aerobic unit.

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ABSTRACT

The concentrations of nonylphenol ethoxylates (NP*n*EO, $n = 1$ to 2) and nonylphenol (NP) in water and sludge samples were measured from a full scale sewage treatment plant (STP) with an Anaerobic/Oxic (A/O) and a Biological Aerated Filter (BAF) process. The A/O process was found to exhibit improved performance in comparison to the BAF process. Mean values of NP, NP1EO and NP2EO concentrations in influents from the STP were similar, ranging from 1.8 to 2.0 $\times 10^3$ ng L^{-1}. In the A/O process, the removal efficiency of NP, NP1EO and NP2EO from the aqueous phase was 78%, 84%, and 89%, respectively. In contrast, the removal efficiencies of NP, NP1EO, and NP2EO were relatively lower for the BAF process, at 55%, 76%, and 79%, respectively. High concentrations of NP, NP1EO and NP2EO detected in the sludge samples had a maximum value of 2.7 μg g^{-1} dw, which indicates that improvement in the overall elimination of NP, NP1EO and NP2EO may be associated with adsorption by the sludge. To further investigate the fate of NP, NP1EO and NP2EO in the STP, our research assessed the degradation characteristics of NP by calculating its transformational loss in the STP. The results demonstrate that the quantity of NP measured in the effluent from the oxic unit increased by 32%, which indicates that NP1EO and NP2EO may undergo degradation in the oxic conditions.

1. Introduction

Short-chain nonylphenol ethoxylates (NP*nEO*, $n = 1$ to 2) and nonylphenol (NP) have been detected at relatively high concentrations in sewage influents, ranging from 0.69 to 280 μg L^{-1} (Maguire, 1999; Loyo-Rosales et al., 2007). Numerous investigations have demonstrated that the short-chain NP*n*EO have estrogenic properties and are more toxic to aquatic organisms than long-chain NP*n*EO (Soares et al., 2008). Due to the hydrophobic nature of these compounds, they are apt to adsorb onto solid particles. Consequently, higher concentrations, ranging from 50 to 200 μg g^{-1} dw, can be detected in sewage sludge and sediments (Ventura et al., 1989; Ahel et al., 1994; Planas et al., 2002). Some research findings suggest that removal efficiency of NP*n*EO in conventional activated sludge reactors can range from 74% and 97%, with membrane-assisted treatment being even more effective and reliable than conventional biological treatments (Terzic et al., 2005). However, most studies focus on concentrations in effluents and receiving waters, or the NP*n*EO removal efficiency in the sewage treatment plants (STPs). There are few studies that have analyzed the fate and behavior of short-chain NP*n*EO in specialized individual treatment units and there are few comparisons of the removal performance of short-chain NP*n*EO for different advanced treatment processes.

The anaerobic/oxic (A/O) process, which consists of a sequential anaerobic and aerobic stage for the biological phosphorus removal. The A/O process has been widely used for sewage treatment in both urban and rural areas and is favored for its high efficiency and low energy consumption (Farabegoli et al., 2009). Alternatively, Biological Aerated Filters (BAFs) are an attached biomass process, which are associated with superior economical upgrading of the technology (Ding et al., 2006; Farabegoli et al., 2009). The

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BAF contains granular media that supplies biofilm with a large superficial area per unit volume. Although the potential of A/O and BAF processes in removing dissolved organic compounds are well documented, it remains unknown whether they are able to effectively mineralize nonylphenolic contaminants. Determining the effectiveness of the technology is important to truly evaluate the applicability and potential of the technologies in terms of eliminating certain persistent pollutants.

In the present study, the relative concentrations and fate of NP, NP1EO and NP2EO in a full-scale sewage wastewater plant equipped with A/O and BAF processes have been compared. The aim of the study is to assess the viability and efficiency of A/O and BAF processes in the elimination of short-chain NP*n*EO, and to compare their performance. The results will contribute to understanding and assessing the behavior and transformation of short-chain NP*n*EO in sewage treatment processes, and thereby improve the work efficiencies of STPs.

2. Materials and methods

2.1. Standards and regents

A Standard solution of NP (purity > 95%) was purchased from Sigma–Aldrich (Taufkirchen, Germany). NP1EO and NP2EO were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Seven standardized solutions were produced from these solutions by further dilution with iso-octane. High purity pesticide analytical grade solvents (acetone, methanol, ethyl acetate and iso-octane) were purchased from J.T. Baker, USA. Carbon-free, deionized water (DI water) was obtained from a NANO pure system (Barnstead International, Dubuque, IA).

2.2. STP

The STP investigated in this study, located in Harbin, Northeast China, primarily treats domestic sewage, as well as a small proportion of industrial wastewater. The STP was configured such that after the primary settling tank wastewater passed through a secondary A/O process (with a capacity of 1.6×10^5 m^3 d^{-1}) or BAF process (with a capacity of 4.0×10^4 m^3 d^{-1}), which were operated in parallel. The process flow of the STP studied is illustrated in Fig. 1.

2.3. Site descriptions and sampling procedures

Grab wastewater samples were collected from all stages of the treatment process. All samples were collected by a vessel precleaned with acetone. The samples were transported to the International Joint Research Center for Persistent Toxic Substances laboratory and immediately stored at 4 °C. Extraction was carried out within 24 h once the samples was collected. To prevent biological degradation, formaldehyde (1 vol%) was added to water samples.

Sludge samples were collected from the primary and secondary settling tanks and the anaerobic and oxic tanks of the A/O system and stored in aluminum boxes which had been pre-cleaned with acetone. The sludge samples were centrifuged (4000 rpm, 5 min) to separate the NP*n*EO associated with the liquid (supernatant) and solid (total minus supernatant) phases. The solid samples were then ventilated, completely air-dried for more than one week, and ground to powder.

2.4. Extraction and analysis

Caliper solid-phase extraction coupled with Waters C18 cartridges were used to concentrate the water samples. Prior to extraction, the water samples were acidified to pH = 2–3 with HCl (v:v, 1:1) to ensure protonation of the NP*n*EO metabolites. Conditioning of the cartridge was performed in sequence using 10 mL of ethyl acetate, 10 mL of methanol, and 10 mL of DI water, following which 500 mL of the acidified water sample (filtrated by 0.45 μm glass fiber filter) was passed through the cartridge. The flow rate of the equipment was maintained at approximately 10 mL min^{-1}. The cartridges were then allowed to dry under nitrogen gas for 25 min. To ensure the complete elution of the target compounds a further 15 mL ethyl acetate was passed through the column. The samples were then evaporated under nitrogen gas to a volume 1 mL, and transferred to GC vials.

Sludge samples were treated by Soxhlet extraction for 24 h using dichloromethane and methanol (v:v, 1:1). After rotary-evaporation to 4 mL, extracts were cleaned using silica chromatography (consisted of 10 g silica gel, and topped with 2.5 cm of anhydrous sodium sulfate), which was eluted with 30 ml of ethyl acetate and hexane (v:v, 1:1). Elutriates were solvent exchanged into iso-octane by rotary-evaporation and concentrated under a gentle stream of ultra-high purity nitrogen.

After pretreatment, pyrene-D10 was added to all the water and sludge samples as an internal standard. NP*n*EO concentrations were determined by gas chromatography-negative ion chemical ionization mass spectrometry using an Agilent 6890 GC-5975N mass selective detector equipped with splitless injection.

2.5. Quality assurance/quality control

Blank samples consisting of DI water containing a labeled recovery standard were processed along with every seven sample extraction round. Relative recovery values were then calculated from these samples. The recovery of blank samples ranged from 65% to 106% (mean 83 ± 10%). Recovery values for all the NP*n*EO compounds ranged from 90% to 135%, with a mean value of 104 ± 7%. Blank contamination were also assessed from two field blanks and two laboratory blanks, and all of the NP*n*EO congeners in the blank samples were below the detection limit.

3. Results and discussion

3.1. Concentration and removal of NP, NP1EO and NP2EO by the A/O process

The concentrations of NP, NP1EO and NP2EO detected in wastewater samples taken from different positions of A/O processes are presented in Fig. 2. Operation of the A/O process achieved effective elimination of NP and NP*n*EO from sewage. Influent concentrations of NP, NP1EO and NP2EO were similar, ranging from 1.8 to 2.0×10^3 ng L^{-1}, however the effluent concentrations of NP, NP1EO and NP2EO measured from the grit chamber, increased from approximately 1.9×10^3 ng L^{-1} to 2.5, 4.4, 2.1×10^3 ng L^{-1}, respectively. A possible cause for the increased concentrations is the sludge backflow that occurs from the primary settling tank to the grit chamber. $\log K_{ow}$ values for NP, NP1EO and NP2EO are relatively high (4.48, 4.17, and 4.21, respectively) (Ahel and Giger, 1993), it can be hypothesized that a large amount of NP, NP1EO and NP2EO would be adsorbed by sludge in the primary settling tanks. After undergoing treatment by the biological units (anaerobic tank and oxic tank), NP, NP1EO and NP2EO concentrations reduced to below those observed in the influent, and after the treatment by the secondary settling unit, the concentrations of NP, NP1EO, and NP2EO further decreased to 0.44, 0.28, 0.2×10^3 - ng L^{-1}, respectively.

In the A/O process, the removal efficiency of NP, NP1EO, and NP2EO from the aqueous phase was 78%, 84%, and 89%, respec-