Fate of nonylphenol polyethoxylates and nonylphenoxy acetic acids in an anaerobic digestion process for sewage sludge treatment

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Abstract Many environmental problems caused by endocrine disruptors (EDs) have been reported. It is reported that EDs flow into sewage treatment plants, and it has been pointed out that these may be shifted from the wastewater treatment process to the sludge treatment process. Little is known about the fate of EDs accumulated in sewage sludge, so we carried out a study to clarify the fate of EDs in sewage sludge treatment processes, especially in an anaerobic digestion process. In this study, nonylphenol (NP) was selected as a target ED. Nonylphenol ethoxylates (NPnEO) or nonylphenoxy acetic acids (NPnEC), which were the precursor of NP, were added to an anaerobic digestion process, and mass balance was investigated. The following results were obtained from the anaerobic digestion experiments. (1) NP1EO was injected to an anaerobic digestion testing apparatus that was operated at a retention time of approximately 28 d and a temperature of 35 °C with thickened sludge sampled from an actual wastewater treatment plant. Approximately 40% of the injected NP1EO was converted to NP. (2) NP1EC was injected to an anaerobic digestion testing apparatus with thickened sludge. As a result, almost all injected NP1EC was converted to NP. When NP2EC was injected, NP2EC was not converted to NP until the 20th day.

Keywords Anaerobic digestion; endocrine disruptors; nonylphenols

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Introduction

In recent years, there have been many reports on environmental problems caused by endocrine disruptors (EDs) discharged as trace chemicals in many countries. In Japan, the Ministry of Construction carried out a national survey on the EDs pollution of river waters and treated wastewater in FY1998 (MOC, 1999). Some trace chemicals suspected to be EDs were detected at almost all surveyed points, and relatively higher concentrations were found in treated wastewater. A further survey was carried out by the Ministry of Land, Infrastructure and Transport in FY2000, and showed that the removal ratios of these EDs in the wastewater treatment process were 70–99% (MLIT, 2001). These results suggest the possibility that EDs are either decomposed or shifted to sludge by treatment processes at sewage treatment plants.

On the other hand, little is known about the fate of EDs in the sewage sludge treatment process. Therefore, it is necessary to clarify the fate of EDs in every treatment process in sludge treatment processing at wastewater treatment plants. In particular, it is said that nonylphenol (NP) that is one ED is produced by the decomposition of nonylphenol polyethoxylates (NPnEO) that are used as a surfactant (Giger *et al.*, 1984; Ahel *et al.*, 1994). This decomposition process is summarised in Figure 1. Under aerobic conditions, shortening the chain of the NPnEO, formation of nonylphenoxy acetic acids (NPnEC) and shortening the chain of NPnEC are carried out and nonylphenol-mono-ethoxylate (NP1EO) and nonylphenol carboxylate (NP1EC) are generated (Ahel *et al.*, 1994). Then,

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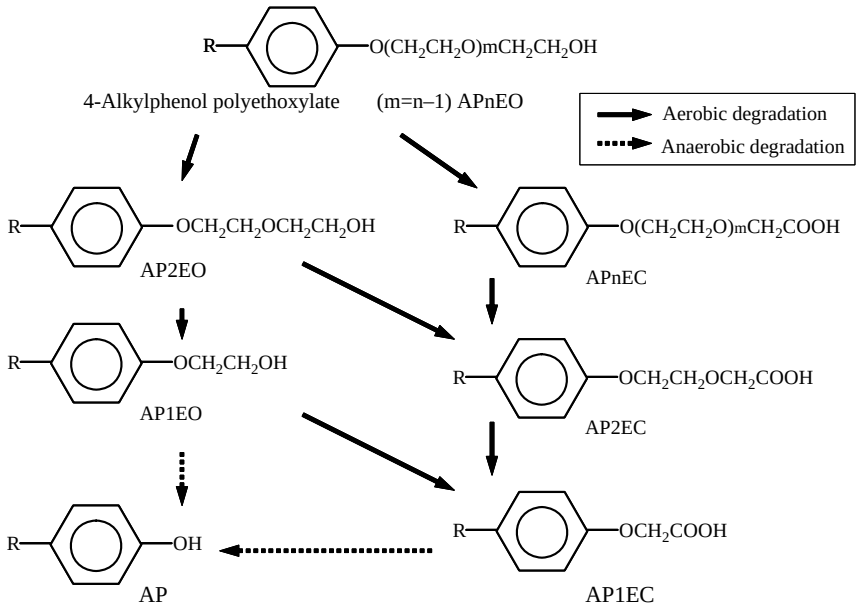

Figure 1 Decomposition of nonylphenol polyethoxylates (based on Ahel *et al.*, 1994) AP: Nonylphenol, R: C9H19

under anaerobic conditions, NP1EO or NP1EC decomposes to NP (Ahel *et al.*, 1994). Understanding the role of the anaerobic digestion process is important to clarify the fate of NP in sludge treatment process. In this study, NP1EO, NP1EC, and NP2EC were spiked to laboratory trial digesters that simulate the anaerobic digestion process of a sewage sludge treatment system in order to clarify the material balance of NP and its precursors in the process.

Methods

Test methods

NP1EO, NP1EC and NP2EC were spiked respectively to anaerobic digesters supplied with thickened sludge sampled from an actual sewage treatment plant and the response was observed.

Figure 2 shows outlines of a test apparatus. Figure 3 shows a real view of apparatuses. Thickened sludge was injected into an approximately 5 L glass vessel from above. The volume of the injected thickened sludge was 200 mL and the same volume of

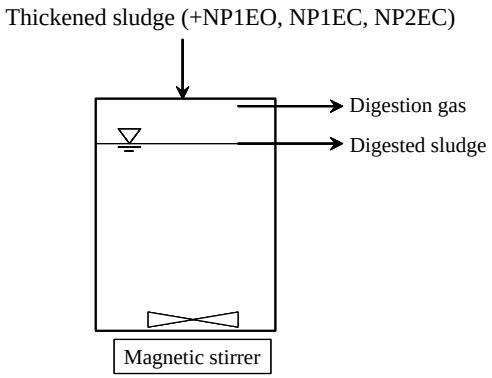

Figure 2 Outlines of an anaerobic digestion test apparatus

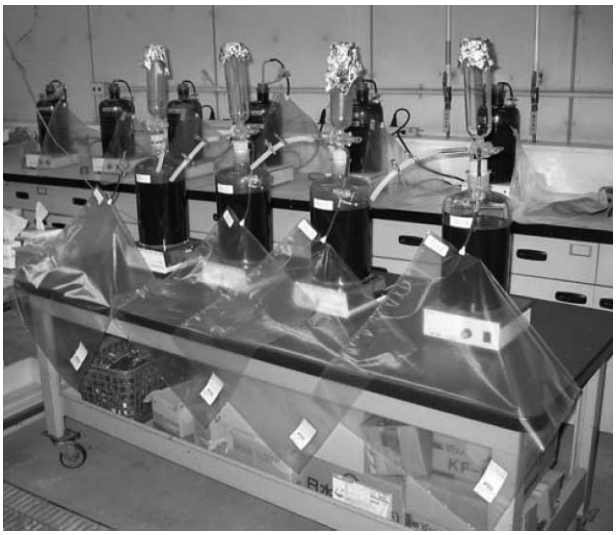

Figure 3 Anaerobic digestion test apparatuses

digested sludge was removed, every day excluding holidays. The volume of digested sludge in each glass vessel was 4 L. Thus, average retention time was approximately 28 d. The test was performed at a temperature of 35 °C to simulate the mesophilic digestion.

During the test, the glass vessel was covered with aluminium foil to shut out the light.

The thickened sludge sampled at a wastewater treatment plant was basically a mixture of gravity thickened sludge made of primary sludge and mechanical thickened sludge made of excess activated sludge.

The NP1EO additive was made by dissolving 500 μg of NP1EO (Hayashi Pure Chemical Ind. Ltd.) in 100 μL of methanol. This additive was added to the thickened sludge, then quickly injected to the apparatus with the sludge. This test started after digested sludge was acclimatised for approximately 6 months.

The addition of the NP1EC and NP2EC (Hayashi Pure Chemical Ind. Ltd.) started approximately 50 d after the start of acclimatisation when the pH of digested sludge and the volume of produced digestion gas had stabilised. The NP1EC or NP2EC additive was made by dissolving 500 μg of each pure substance in 100 μL of methanol, and this additive was injected to vessel with thickened sludge.

For comparison purposes, another specimen was made by adding the same volume of methanol.

Analysis method

NP and NPnEO were analysed because a method of analysing NPnEC in sludge has not been established.

The sludge was extracted using the pressurised fluid extraction method reported by Minamiyama *et al.* (2002). The extraction time was 30 min because large amounts of NP1EO were recovered from the thickened sludge at preliminary examination.

The NP and NP1EO were detected using HPLC (Waters 2690, Fluorescence Detector: Waters 474, Column: Inertsil Ph 5 μm, inner diameter 4.6 and 150 mm long).

When a recovery test of the NP and NP1EO spiked to the digested sludge was performed during the digestion test, the recovery rate was between approximately 80 and 117%.

Figure 4a shows a chromatogram of NP and NPnEO standards. Figure 4b shows a chromatogram of NPnEC standards whose concentrations were the same as NP and NPnEO standards. Because peaks of NPnEC were negligible, NPnEC were not interfering substances for analysing NP and NPnEO.

Results and discussion

Fate of NP1EO in an anaerobic digestion process

The ratio of the carbon converted to the digestion gas was between 31 and 34% of the carbon in the injected sludge. Fifty to 53% of the carbon in the injected sludge was removed from the vessel with digested sludge. Over all, approximately 86% of injected carbon was recovered.

Figure 5 shows the test results. The residual NP1EO in the week after the start of the test was 22 to 26% of the NP1EO that was spiked, and later, this ratio declined as the quantity of residue tended to decline after approximately 50 d. The average daily NP1EO decomposition rate at the beginning of the test and on approximately the fiftieth day were approximately 7 μg/(g-dry·day) and approximately 10 μg/(g-dry day) respectively.

The increase of NP caused by the addition of the NP1EO remained at a quantity equivalent to approximately 40% of the NP1EO that was spiked. It was revealed that 60% of NP1EO in the anaerobic digestion process was decomposed or in a changed form other than NP or NPnEO.

Fate of NP1EC and NP2EC in an anaerobic digestion process

Figure 6 shows the test results. In the test with NP1EC spiked, the concentration of NP in the test apparatus increased. The quantity of increased NP throughout the test period was

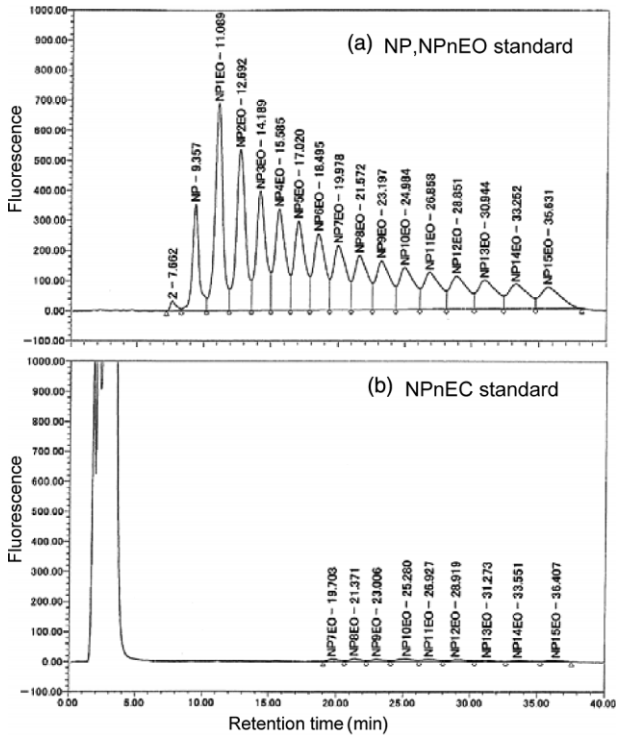

Figure 4 NPnEC were not interfering substances for analysis of NP, NPnEO

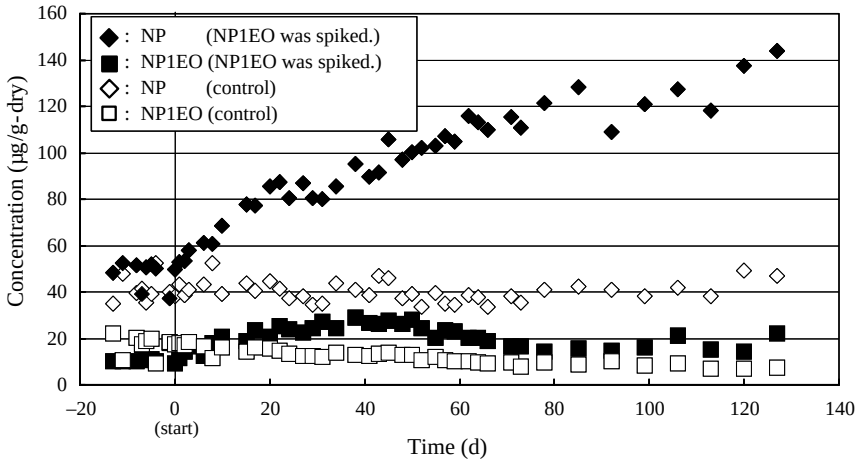

Figure 5 Decomposition of NP1EO and generation of NP in anaerobic digestion process

almost equivalent to 100% of the NP1EC that was spiked. This clarifies that almost all the NP1EC that was added became NP.

In the test with NP2EC spiked, the concentration of NP did not change during the test period. Therefore, it is assumed that there is a small possibility that NP is produced from NP2EC in an anaerobic digestion process.

NPnEO and NPnEC in anaerobic process

According to the experimental results, approximately 40% of the spiked NP1EO and almost all spiked NP1EC were converted to NP in an anaerobic digestion process. These results suggest that under anaerobic digestion at a temperature of 35 °C, the formation of NP from NP1EO or NP1EC is almost unavoidable. In order to decrease the concentration of NP in sewage sludge in the sludge treatment process, NP decomposition must be performed using an aerobic process such as a composting process. It is necessary to study methods to control NPs in composting process.

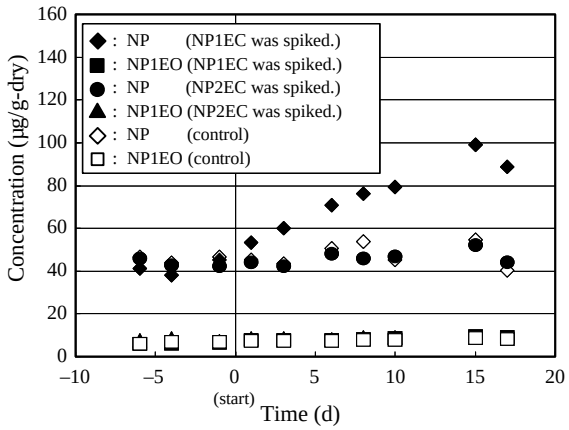

Figure 6 Generation of NP in the anaerobic digestion process (NPnEC was spiked)

Conclusions

It is reported that EDs flow into sewage treatment plants, and it has been pointed out that these may be shifted from the wastewater treatment process to the sludge treatment process. Little is known about the fate of EDs accumulated in sewage sludge, so we carried out a study to clarify the fate of EDs in sewage sludge treatment processes, especially in an anaerobic digestion process.

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