Oxidation of nonylphenol ethoxylates in aqueous solution by UV-C photolysis, H₂O₂/UV-C, Fenton and photo-Fenton processes: are these processes toxicologically safe?
Akin Karci, Idil Arslan-Alaton and Miray Bekbolet

ABSTRACT
UV-C, H₂O₂/UV-C, Fenton and photo-Fenton treatment of a nonylphenol polyethoxylate (NP-10) were comparatively studied, primarily focusing on the acute toxicity of degradation products. Formic, acetic and oxalic acids were all identified as the degradation products of NP-10; however, the sole common carboxylic acid was found to be formic acid for the studied treatment processes. The percent relative inhibition towards Vibrio fischeri increased from 9% to 33% and 24% after 120 min-UV-C and H₂O₂/UV-C treatment, respectively. Complete NP-10 and 70% of its total organic carbon (TOC) content was removed by the photo-Fenton process, which ensured the fastest removal rates and lowest inhibitory effect (8% after 120 min treatment). The acute toxicity pattern being observed during H₂O₂/UV-C and photo-Fenton treatment positively correlated with temporal evolution of the identified carboxylic acids, whereas unidentified oxidation products were the most likely origin of the acute toxicity in UV-C photolysis.

INTRODUCTION
Alkylphenol ethoxylated nonionic surfactants, having an annual worldwide production of 500,000 tons, are being commonly used as detergents, wetting agents, dispersants, emulsifiers, solubilizers and foaming agents (Ying et al. 2002). Among them, nonylphenol ethoxylates (NPEOs) are by far the most widely employed, encompassing more than 80% of the world market. As a consequence of their extensive production and consumption, high concentrations of these substances are being discharged into wastewater treatment plants or released directly into receiving water bodies. NPEOs are unstable in sewage treatment plants and in the aquatic environment and transformed to mainly nonylphenol ethoxy acetic acid, nonylphenoxo acetic acid and nonylphenols under aerobic conditions (Cailleaud et al. 2007). However, NPEOs are rather slowly biotransformed into nonylphenols, nonylphenol monoethoxylates and nonylphenol diethoxylates under anoxic conditions. These metabolites are known to be more toxic than the mother pollutant and recognized as potential endocrine disruptors (Petrovic et al. 2003). Furthermore, these products are more lipophilic and biorecalcitrant than the parent NPEOs, leading to an additional problem of bioaccumulation (Brand et al. 1998). Because of the above-mentioned facts, the use of alkylphenol ethoxylates in household cleaning products and industrial applications has been restricted in some European countries (Renner 1997). However, they are still being detected at high concentrations in wastewater treatment plant influents in Europe and the USA (Loyo-Rosales et al. 2007; González et al. 2007; Céspedes et al. 2008).

Advanced oxidation processes (AOPs) characterized by the formation of free radicals, including hydroxyl radicals (HO·), can be considered as promising alternatives to conventional biological treatments for the elimination of organic and inorganic pollutants found in water and wastewater at acceptable rates (Arslan-Alaton et al. 2010). Although the number of treatability publications dealing with AOPs has increased rapidly, the major limitations of AOPs for their full-scale application, i.e. their relatively high capital and operating costs as well as the possibility of the formation of oxidation products more toxic than the
mother compound(s), have not been overcome yet (Fatta-Kassinos et al. 2011; Rizzo 2011). In order to avoid potential risks caused by oxidation products, control of these treatment processes by toxicity test protocols is an essential task. Laboratory toxicity tests are also useful tools in determining the treatment time after which the effluent becomes biocompatible without complete mineralization, thus saving treatment time and cost (Oller et al. 2011).

Investigations have already demonstrated that AOPs can be used to successfully degrade NPEOs in aqueous systems (de la Fuente et al. 2010; Nagarnaik & Boulanger 2011; Olmez-Hanci et al. 2011). However, bioanalytical tools including toxicity tests have never been used to comparatively evaluate the ecotoxicological safety of different AOPs applied for the degradation of aqueous NPEOs. Moreover, although the prediction of toxicity on the basis of advanced oxidation products of NPEOs can be a potentially valuable tool in ecological risk estimation, there are still not any scientific data available on this research topic.

Considering all these data gaps in the scientific literature, degradation of aqueous nonylphenol decaethoxylate (NP-10), an NPEO being frequently employed in textile preparation (desizing, mercerizing and scouring) processes, was studied with a focus on changes in the acute toxic effect in relation to the measured and unidentified transformation products. The H2O2/UV-C, Fenton and photo-Fenton AOPs were investigated as potential treatment processes for NP-10 due to their well-known reaction kinetics and mechanism. Although not an AOP, UV-C photolysis was also included in the study due to the availability of UV-based systems in many water utilities and the potential effectiveness of such UV systems for the treatment of chemical contaminants. Experiments were first conducted to assess the ability of the selected treatment processes to degrade and mineralize aqueous NP-10 based on parent compound and total organic carbon (TOC) removals as also affected by the initial H2O2 and Fe2+ concentrations. Under established experimental conditions, the studied treatment processes were compared for temporal evolution of formic acid to gain an insight into their potential to produce simple-structured aliphatic carboxylic acids which are refractory in nature. Finally, acute toxic effects towards the marine photobacteria Vibrio fischeri were monitored during application of the studied treatment processes in parallel to temporal changes of the measured carboxylic acids (formic, acetic and oxalic acids) and unidentified transformation products. V. fischeri was chosen as the target species due to its high sensitivity towards a wide range of environmental pollutants (Radjenović et al. 2009).

MATERIAL AND METHODS

Materials

NP-10 (average number of ethylene oxide units = 10) was obtained from a local chemical company and utilized without further purification. Methanol (CH2OH, Merck, Germany), sodium sulphate anhydrous (Na2SO4, Merck, Germany) and methanesulfonic acid (CH3SO3H, Sigma-Aldrich, USA) were used to prepare the mobile phases for high performance liquid chromatography (HPLC) analysis. All other chemicals and reagents were at least of analytical grade and purchased from Merck (Germany). Aqueous NP-10 reaction solutions were prepared daily by dilution of the stock solution of 2 g L\(^{-1}\) with distilled water except for oxidation product and acute toxicity analyses where a stock solution of 4 g L\(^{-1}\) was used. For the preparation of the mobile phases for HPLC analysis, doubly distilled water with a conductivity of 0.055 μS cm\(^{-1}\) was used (Arium 611UV, Sartorius AG, Germany).

Photoreactor and UV-C light source

The batch-operated photoreactor used in all experiments was a 3,250 mL capacity, cylindrical stainless steel tube (length: 84.5 cm; diameter: 8.0 cm). A 40 W low pressure mercury vapour lamp located in a quartz sleeve in the centre of the photoreactor was employed as the UV-C light source. The reaction solution was circulated inside the photoreactor at a flow rate of approximately 170 mL min\(^{-1}\) by means of a peristaltic pump. The incident radiation intensity at 253.7 nm was determined by means of H2O2 actinometry (Nicole et al. 1990) as 1.4 × 10\(^{-5}\) Einstein L\(^{-1}\)s\(^{-1}\).

Experimental procedures

For the baseline experiments, aqueous NP-10 solutions were prepared at a concentration of 50 mg L\(^{-1}\) (76 μM), while a concentration of 100 mg L\(^{-1}\) (150 μM) was selected for oxidation product quantification and acute toxicity analyses. The initial pH of the reaction solutions was adjusted to pre-determined values by using H2SO4 and NaOH solutions at varying concentrations and no attempt was made to control pH throughout the experiments. Appropriate amounts of H2O2 (35%, w/w) were added to pH-adjusted NP-10 solutions in a single-step in order to achieve an initial concentration range of 1 mM to 10 mM H2O2.
the addition of H$_2$O$_2$ to the aqueous NP-10 solution at predetermined concentrations, the photoreactor was filled with the aqueous NP-10 solution by means of the peristaltic pump and UV-C-irradiated to initiate the H$_2$O$_2$/UV-C process. In the Fenton and photo-Fenton experiments, FeSO$_4$·7H$_2$O from 180 and 360 mM stock solutions was added at the final step to the photoreactor which was loaded with the previously acidified and H$_2$O$_2$-introduced samples. The Fenton reaction started as soon as FeSO$_4$·7H$_2$O was introduced into the photoreactor, whereas turning the UV-C lamp on simultaneously to the addition of the Fe$^{2+}$ source was recognized as the starting point of the photo-Fenton process. For each Fenton- and photo-Fenton-treated sample withdrawn from the photoreactor at predetermined time intervals, the reaction was quenched with the addition of 1 N or 10 N NaOH solution and precipitated iron in the form of ferric hydroxide was further separated from the mixture using 0.45 μm regenerated cellulose syringe filters (Sartorius, Germany). The pH-adjusted NP-10 solution without H$_2$O$_2$ included was also loaded into the photoreactor and UV-C-irradiated to compare the treatment efficiency of UV-C photolysis for degradation and detoxification of aqueous NP-10 with those achieved by the studied AOPs.

**Analytical procedures**

NP-10 and its aliphatic oxidation products (formic, acetic and oxalic acids) were monitored by HPLC (Agilent 1100 Series, Agilent Technologies, USA) equipped with a diode array (DAD) and fluorescence detector (FLD). A Novapack C18 (150 mm × 3.9 mm, Waters, USA) reversed phase column was used for the separation of NP-10, while the carboxylic acids were separated on an Acclaim OA (250 mm × 4 mm, Dionex, USA) organic acid column. NP-10 analysis was performed using FLD and a mobile phase consisting of methanol:water (80:20, v/v) at a flow rate of 1.0 mL min$^{-1}$. The column temperature, injection volume and excitation and emission wavelengths were set at 20 °C, 100 μL, 230 nm and 290 nm, respectively. For the analysis of carboxylic acids by means of DAD, a buffer solution consisting of 100 mM Na$_2$SO$_4$ adjusted to pH 2.65 with methanesulfonic acid was used as the mobile phase at a flow rate of 0.60 mL min$^{-1}$. The column temperature, injection volume and detection wavelength were set at 30 °C, 50 μL and 210 nm, respectively. External calibration based on the peak areas was used to determine NP-10 and carboxylic acid concentrations in the samples. The detection limits for NP-10, formic acid and acetic acid determined as the signal-to-noise ratio (S/N) of 3.0 were found as 0.047, 2.5 and 1.4 mg L$^{-1}$.

The TOC of the samples was monitored on a Shimadzu VPCN carbon analyzer (Japan) equipped with an autosampler. An Orion (USA) 720$^+$ model pH-meter was used for pH measurements. The molybdate-catalyzed iodometric method (Official Methods of Analysis 1980) was employed to follow the residual H$_2$O$_2$ in the treated samples.

Acute toxicity tests were carried out using a lyophilized preparation of *V. fischeri* (NRRL B-11177) in a commercial assay kit marketed as BioTox$^+$ (Finland) according to the ISO 11348-3 test protocol (ISO 2008). The test is based on the inhibition of the bioluminescence of *V. fischeri*, which was calculated from the decrease in light emission after 15 min exposure time. In order to eliminate its positive effect on the toxicity test results, any unreacted H$_2$O$_2$ remaining in the samples was catalytically decomposed with catalase made from *Micrococcus lysodeikticus* (Fluka, Switzerland) after adjusting the sample pH to 7.0. The details of the procedure have been described elsewhere (Karci et al. 2012).

**RESULTS AND DISCUSSION**

H$_2$O$_2$/UV-C, Fenton and photo-Fenton baseline experiments

In the first part of the study, baseline experiments were conducted to explore the ability of H$_2$O$_2$/UV-C, Fenton and photo-Fenton processes to oxidize aqueous NP-10. Within this scope, preliminary sets of H$_2$O$_2$/UV-C and photo-Fenton experiments were first conducted to determine the most appropriate reaction conditions for the effective treatment of NP-10. Kinetics of NP-10, TOC and H$_2$O$_2$ disappearance upon H$_2$O$_2$/UV-C oxidation at an initial H$_2$O$_2$ concentration of 10 mM as given in Figure 1(a) revealed that the initially-added H$_2$O$_2$ was completely consumed at the end of 90 min treatment and proved that the residual H$_2$O$_2$ concentration is the major limiting factor for the H$_2$O$_2$/UV-C process. As can be clearly seen from the insert in Figure 1(a), the decay of NP-10, TOC and H$_2$O$_2$ via the H$_2$O$_2$/UV-C process all followed pseudo-first-order kinetics with regression coefficients ($R^2$) of above 0.99. The combination of H$_2$O$_2$ with UV-C light greatly enhanced the removal rate of NP-10, even at the lowest studied H$_2$O$_2$ concentration of 1 mM as compared to direct UV-C photolysis ($k_{NP-10} = 0.014$ min$^{-1}$), although the mineralization was still poor at this lowest H$_2$O$_2$
concentration (10% TOC removal) as can be seen from Figure 1(b). From the experimental results it became evident that although total conversion of NP-10 was achieved at all investigated \(H_2O_2\) concentrations, increasing the \(H_2O_2\) concentration to 10 mM resulted in both NP-10 removal rate and mineralization enhancement from 0.41 to 0.69 \(min^{-1}\) and from 10 to 97%, respectively, at the end of the treatment period.

Findings from the photo-Fenton baseline experiments indicated that although the mineralization achieved even with the lowest \(Fe^{2+}\) concentration of 25 \(\mu M\) was higher than that obtained in the absence of \(Fe^{2+}\) within the first 30 min of treatment, TOC removal at all studied \(Fe^{2+}\) concentrations practically stopped after this treatment time due to the near-complete catalytic decomposition of \(H_2O_2\) by \(Fe^{2+}\) (Figures 2(a) and 2(b)). This finding suggested that UV-C photoreduction of \(Fe^{3+}\) was not sufficient to continue significant \(HO^+\) generation after complete exhaustion of \(H_2O_2\) in the photo-Fenton process. However, the role of UV-C irradiation in the photo-Fenton oxidation of NP-10 can be clearly realized from Figure 2(b), which delineates that the dark Fenton process accounts only for 5% of the overall TOC removal obtained by applying the photo-Fenton process. The improvement in mineralization achieved by the photo-Fenton process instead of classical Fenton oxidation was most probably due to the photoreduction of \(Fe^{3+}\) to \(Fe^{2+}\) in the photo-Fenton process, continuing the redox cycle as long as \(H_2O_2\) is available (Arslan-Alaton & Gurses 2004). Figure 2(b) also depicts that TOC removal efficiencies were positively affected by an increase in the initial \(Fe^{2+}\)
concentration, reaching the maximum value of 68% at an initial Fe$^{2+}$ concentration of 200 μM. Considering the above experimental findings, 10 mM H$_2$O$_2$ and 200 μM Fe$^{2+}$ were chosen for the forthcoming H$_2$O$_2$/UV-C, Fenton and photo-Fenton processes. Furthermore, for the next-level experiments, an initial NP-10 concentration of 100 mg L$^{-1}$ (150 μM) was selected in order to improve the analytical conditions for carboxylic acids and acute toxicity analyses, and hence, the treatment time was extended from 90 to 120 min.

**Carboxylic acid products**

Low molecular mass mono- and dicarboxylic acids appear as the ultimate organic intermediates in the oxidation schemes of many organic pollutants including NPEOs (Vinodgopal et al. 2001; Horikoshi et al. 2002). Their conversion into CO$_2$ and H$_2$O is considered as the rate-limiting step due to their refractory nature. Accordingly, the analysis of three selected carboxylic acids, namely formic, acetic and oxalic acids, was performed on NP-10 samples subjected to UV-C, H$_2$O$_2$/UV-C, Fenton and photo-Fenton treatment. Formic acid was found to be the common carboxylic acid product of all studied treatment processes, and hence, its evolution during degradation of aqueous NP-10 by UV-C, H$_2$O$_2$/UV-C, Fenton and photo-Fenton treatments is displayed in Figure 3. Formation of only a small concentration of formic acid at the end of 120 min UV-C and Fenton treatment (4.1 and 4.5 mg L$^{-1}$, respectively) verified the incomplete transformation and poor mineralization of NP-10 achieved by these treatment processes. On the other hand, the near-complete removal of NP-10 within the first 30 min of H$_2$O$_2$/UV-C and photo-Fenton treatments was accompanied by the generation of formic acid of 12 and 8.4 mg L$^{-1}$, respectively, which were significantly higher than the formic acid concentrations measured in UV-C and Fenton treatments (not detectable and 3.0 mg L$^{-1}$, respectively) after the same treatment time. The higher production of formic acid in the H$_2$O$_2$/UV-C oxidation as compared to the photo-Fenton process after 30 min treatment also correlated well with the pseudo-first-order rate coefficients for NP-10 removal quantified for these treatment processes (0.395 and 0.159 min$^{-1}$, respectively). However, additional elimination of formic acid from the aqueous phase during separation of the dissolved iron through precipitation and subsequent filtration in the photo-Fenton process could not be excluded. Formic acid concentration showed a second increase during application of the H$_2$O$_2$/UV-C and photo-Fenton processes starting from 60 min of the treatments where mineralization practically stopped due to the complete consumption of H$_2$O$_2$, but the re-increase was more pronounced in the H$_2$O$_2$/UV-C process. Results delineated that under the pre-established experimental conditions, the H$_2$O$_2$/UV-C and photo-Fenton processes could not ensure efficient disappearance of the generated formic acid whose residual

![Figure 3](https://iwaponline.com/wst/article-pdf/68/8/1801/472519/1801.pdf)
concentration after 120 min treatment was considerably higher in the former treatment process (13 mg L\(^{-1}\)) than in the latter one (2.7 mg L\(^{-1}\)).

**Acute toxicity results**

Changes in the relative inhibition towards \(V.\, fischeri\) during UV-C, \(\text{H}_2\text{O}_2/\text{UV-C},\) Fenton and photo-Fenton treatment of 100 mg L\(^{-1}\) (150 \(\mu\)M) NP-10 are depicted in Figure 4(a).

The temporal change of carbon equivalent of the measured carboxylic acids (formic, acetic and oxalic acids) and unidentified transformation products (difference between the TOC recorded in the system and the carbon equivalents of NP-10 and measured carboxylic acids) is also given in Figures 4(b) and 4(c) in order to discuss the resulting toxicity patterns in relation to the transformation products. The percent relative inhibition gradually increased from 9 to 33% throughout the course of UV-C photolysis which followed
the same trend as both formic acid, the only detected carboxylic acid in UV-C photolysis, and unidentified transformation products. It is evident that during UV-C treatment, NP-10 was transformed into more toxic degradation products which accumulated particularly within the first 60 min of photolysis. As can be followed from Figures 4(b) and 4(c), through the whole of UV-C photolysis, the carbon equivalent of unidentified transformation products was considerably higher than that of the measured carboxylic acids. Considering that the measured maximum concentration of formic acid in the UV-C treatment (4.1 mg L\(^{-1}\)) was far below its reported effective concentration (\(EC_{50}\) — concentration that reduces the intensity of light emitted by \(V.\ fischeri\) by 50% after 15 min contact time) of 160 mg L\(^{-1}\) (Zazo et al. 2007), unidentified transformation products were the most likely origin of the increasing acute toxic effect during UV-C photolysis of NP-10.

For the Fenton process, the acute inhibitory effect showed no significant change within the first 30 min of treatment, but notably increased to 24% after 60 min treatment. There was no clear relationship apparent between the transformation products and the toxicity pattern during the first 60 min of the Fenton treatment. Its slow kinetics was speculatively the reason for the observed increase in acute toxicity in the Fenton process. From 60 min of the Fenton process, the relative inhibition started to decrease and reached a value (9.9%) after 120 min treatment which was not practically different from that of the untreated NP-10.

The acute toxicity evolutions showed similar trends for the treatment of NP-10 with \(H_2O_2/UV-C\) and photo-Fenton processes. From Figure 4(a), it is evident that inhibition values first increased to 21 and 16% during the first 30 min of \(H_2O_2/UV-C\) and photo-Fenton processes, respectively, where nearly-complete elimination of the parent substance was achieved, and decreased thereafter. This toxicity increase at the initial stages of \(H_2O_2/UV-C\) and photo-Fenton processes has also been reported in other relevant studies (Parra et al. 2000; Neamtu et al. 2003), referring to the generation of first transformation products which exert a higher inhibitory effect than the original pollutant. The subsequent reductions in inhibition values to 10% and less than 2% after 60 min \(H_2O_2/UV-C\) and photo-Fenton treatments, respectively, coincide well with the time interval where significant TOC reductions were achieved (45 and 36% mineralization for \(H_2O_2/UV-C\) and photo-Fenton processes, respectively), explaining the removal of these early inhibitory oxidation products to some extent. However, a re-increase in the inhibitory effect was evident starting from 60 min of both photochemical AOPs. Considering that the carbon equivalent of unidentified transformation products decreased between 60 and 120 min of the \(H_2O_2/UV-C\) process and was almost unchanged in the photo-Fenton process within the same time interval (Figure 4(b)), the re-increase in acute toxicity towards the end of the \(H_2O_2/UV-C\) and photo-Fenton processes could be related to the slight increase in the carbon equivalent of the measured carboxylic acids including formic acid (Figure 4(c)).

Since unidentified transformation products also contributed to TOC measured after 120 min \(H_2O_2/UV-C\) and photo-Fenton processes, the assessment of any acute toxic effect from the detected carboxylic acids was still of major importance in order to conclude on their contribution to the overall toxicity. For this purpose, two synthetic samples containing the same concentrations of the detected carboxylic acids as the real samples taken after 120 min \(H_2O_2/UV-C\) and photo-Fenton processes (13 mg L\(^{-1}\) formic acid, 14 mg L\(^{-1}\) acetic acid and 1.4 mg L\(^{-1}\) oxalic acid for the \(H_2O_2/UV-C\) process; 2.7 mg L\(^{-1}\) formic acid and 14 mg L\(^{-1}\) acetic acid for the photo-Fenton process) were prepared and assayed for their toxic effects. The obtained findings indicated that the inhibition values observed in the synthetic samples were equivalent to 67 and 92% of the inhibition values measured in the real samples taken after 120 min \(H_2O_2/UV-C\) and photo-Fenton processes, respectively. These latter complementary results strongly suggested that the measured carboxylic acids were a major origin of the acute toxic effects observed after 120 min \(H_2O_2/UV-C\) and photo-Fenton processes.

As could be deduced from Figure 4(a), although similar trends were monitored for the evolution of acute toxicity during the application of \(H_2O_2/UV-C\) and photo-Fenton processes, the levels of inhibitory effects observed during photo-Fenton treatment were always below the levels obtained via \(H_2O_2/UV-C\) oxidation, speculatively due to the different chemical structure and concentration of the formed oxidation intermediates during these processes. More importantly, a residual toxicity (24% relative inhibition) higher than that of the original pollutant was observed in the reaction solution treated by the \(H_2O_2/UV-C\) process, whereas the relative inhibitory effect was practically unchanged (from 9 to 8%) after the photo-Fenton treatment. Again, it should be mentioned that the photo-Fenton process takes advantage of having the dual function of oxidation and coagulation in the treatment process, which might have a positive influence on the detoxification efficiency. Accordingly, the bioassay results indicated that the photo-Fenton process could be more safely applied for effective degradation of aqueous NP-10.
than the other examined treatment processes as assessed by the acute inhibitory effect towards *V. fischeri*. *V. fischeri* was very useful for obtaining a first idea of overall mixture toxicity resulting from the transformation of NP-10 by UV-C, H$_2$O$_2$/UV-C, Fenton and photo-Fenton treatment under pre-established experimental conditions. However, it should be underlined here that different test organisms may have different sensitivities to a given pollutant. Therefore, for a more comprehensive and reliable toxicity evaluation, a battery test with organisms from different trophic levels is highly recommended.

**CONCLUSIONS**

UV-C, H$_2$O$_2$/UV-C, Fenton and photo-Fenton treatment of NP-10 were comparatively studied focusing on the changes in acute toxicity in relation with degradation products. The degradation of NP-10 was accompanied by the formation of aliphatic carboxylic acids including formic, acetic and oxalic acids, formic acid being the common oxidation product of the studied treatment processes. A degree of the generated formic acid was observed persisting at the end of the H$_2$O$_2$/UV-C and photo-Fenton processes, whereas UV-C and Fenton treatments resulted in gradual accumulation of formic acid at very low rates.

The acute toxicity test results implied that the inhibitory effect towards *V. fischeri* observed after 120 min treatment was in the order UV-C > H$_2$O$_2$/UV-C > Fenton > photo-Fenton. The relative inhibition of NP-10, originally being non-toxic, increased after applying UV-C and H$_2$O$_2$/UV-C treatments. The inhibitory effect observed after the Fenton treatment was not practically different from that of the untreated NP-10, but the NP-10 removal achieved by this treatment process was rather poor. The photo-Fenton process ensured effective oxidation of NP-10 and produced an effluent which did not exert acute toxic effects. Temporal evolution of the acute toxic effect during application of the H$_2$O$_2$/UV-C and photo-Fenton processes positively correlated with that of the measured carboxylic acids. On the other hand, the inhibitory effect observed during UV-C treatment was speculated to be caused by the unidentified photolysis products which were generated at considerably higher concentrations than formic acid, the only detected carboxylic acid during UV-C photolysis.

This study delineated the importance of discussing the performances of different treatment processes for degradation of aqueous NPEOs from an ecotoxicological perspective. However, more studies should be done to clarify the toxicity profiles observed during advanced oxidation of NPEOs, using the capabilities of more sophisticated analytical techniques such as liquid chromatography-mass and tandem mass spectrometry (LC-MS, LC-MS$^2$). Additionally, since the presence of organic and inorganic species in the water matrix may cause synergy in toxic effects, replication of the presented study in real environmental samples is of major importance. Future work focusing on these issues is underway.

**REFERENCES**


First received 10 January 2013; accepted in revised form 10 June 2013