

## APPLICATION OF AOPs FOR THE REMOVAL OF NONYLPHENOL AND SHORT-CHAIN NONYLPHENOL ETHOXYLATES FROM WATER AND WASTEWATER EFFLUENT

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### ABSTRACT

The aim of this work was the application of Advanced Oxidation Processes for the removal of nonylphenol (NP) and short-chain nonylphenol ethoxylates (NP1EO and NP2EO) from aqueous solution and from the final effluents of a municipal wastewater treatment plant.

Heterogeneous photocatalysis mediated with TiO<sub>2</sub> suspension and oxidation with ozone were tested. Both techniques were found to be very effective for the removal of the compounds from the aqueous solution as well as from the wastewater effluent. The percentage of removal was greater than 90%. The reduction of dissolved organic carbon (DOC) was monitored during ozonation in order to assess the degree of mineralization.

The photocatalytic oxidation of the compounds followed first-order kinetics with good correlation coefficients. Pseudo-first order and second order kinetic models were applied in the case of oxidation with ozone. Correlation coefficient values were higher when data were fitted in second order models. The reaction rates were higher during the oxidation of aqueous solution in all cases.

**Keywords:** AOPs, nonylphenol, heterogeneous photocatalysis, ozonation

### 1. Introduction

The main advantage of the Advanced Oxidation Processes in comparison with the rest of the chemical and biological methods of water and wastewater treatment, is that they are “environmental friendly” methods. The pollutants are neither being transferred from one phase to other, as it happens during the chemical treatment nor big quantities of sludge is produced, like in the biological treatment methods.

Heterogeneous photocatalysis utilizes catalytic processes which take place in semiconductor suspensions (TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, CdS) in the presence of natural or artificial light, which can completely oxidize various organic and inorganic pollutants, without further environmental impacts (Tsimas, 2007). The technique is imitating the self-cleaning ability of nature with the help of the atmospheric oxygen and the solar radiation. The use of the catalyst accelerates the cleaning process over lots of orders of magnitude.

The use of ozone as chlorine alternative in the disinfection of water has increased significantly at the end of the 1970s when trihalomethanes and other organohalogenated compounds were identified in the drinking water as chlorination by-products (Beltran, 2003).

Nonylphenol polyethoxylates are considered to be endocrine disrupting compounds (Ying *et al.*, 2002). Toxicity and estrogenic activity is increasing with the shortening of the ethoxylate chain (Bennie *et al.*, 1998). They are often detected in the final effluents of sewage treatment plants, with nonylphenol being the most abundant, (Bennie *et al.*, 1998; Sekela *et al.*, 1999; Korner *et al.*, 2000), due to their persistence and inefficiency of third-stage treatment.

The effluent discharges pose a major environmental risk to the natural and human environment. In Greece, they have been detected in different stages of the wastewater treatment process

(Stasinakis *et al.*, 2008; Gatidou *et al.*, 2007; Yiantzi *et al.*, 2010), as well as in industrial wastewater (Pothitou and Voutsas, 2008).

In the present work, both methods (heterogeneous photocatalysis and oxidation with ozone were tested) for their ability in removing nonylphenol (NP) and short-chain nonylphenol ethoxylates (NP1EO and NP2EO) from aqueous solution and from the final effluents of a municipal wastewater treatment plant. The reduction of DOC, the decrease in the pollutants' concentration and the kinetic parameters were determined for each method.

## 2. Materials and methods

### 2.1. Wastewater samples

Grab samples were collected from the effluent of Municipal wastewater treatment plant of Chania (Crete, Greece). The samples were collected in amber glass bottles and were analyzed immediately in order to determine their quality characteristics and the compounds of interest. In each sample pH, chemical oxygen demand (COD) and total suspended solids (TSS) were determined. Chemical oxygen demand and total suspended solids were measured according to standard methods 5220D and 2540D, respectively (APHA, 1999).

For the determination of DOC a Total Organic Carbon Analyzer (Shimadzu, 5000A) was used. In the samples of the chlorinated secondary effluent the inorganic and organic carbon was found to be in the same level, so TOC was considered equal to the non purgeable organic carbon (NPOC). NPOC was measured after acidification of the sample with 2N HCl solution and air diffusion to the sample for 10 min.

In cases where preservation of the samples was necessary, formaldehyde solution was added (1 ml/100 ml of sample). Formaldehyde has been suggested in order to prevent biological degradation of the compounds of interest, if their analysis was not performed on the day of sampling (Shao *et al.*, 2002; Lee *et al.*, 1998).

### 2.2. Quantitation of the analytes

For the separation and quantitation of the short-chain nonylphenol ethoxylates (NP1EO, NP2EO) and nonylphenol (NP), reversed-phase high performance liquid chromatography with fluorescence detector was used. A Hewlett Packard 1100 series HPLC with SUPELCO<sup>TM</sup> LC 18 (15cm length X 4.6mm ID X 5 $\mu$ m film thickness) equipped with a fluorescence detector operating at 305 nm and 227nm (emission and excitation wavelength respectively). The mobile phase consisted of A: acetonitrile and B: H<sub>2</sub>O. The elution program was gradient with a flow rate of 0.5 mL min<sup>-1</sup> from 90% to 100% A (Neamtu and Frimmel, 2006).

### 2.3. Photocatalytic oxidation of short-chain nonylphenol ethoxylates

For the laboratory experiments during the photocatalytic oxidation a cylindrical glass reactor which was placed on a magnetic stirrer was used. (Figure 1).



**Figure 1.** Laboratory apparatus for photocatalytic oxidation reactions

For the oxidation of the NPnEOs (n=0-2), TiO<sub>2</sub> was used, which was selected due to its advantages (Gogate and Pandit, 2004) in comparison with other catalysts. It was used as a

suspension in aqueous solution or in spiked wastewater chlorinated effluent sample. The aqueous solution was prepared in Milli-Q water with a total final concentration of the NPnEOs  $750 \mu\text{g l}^{-1}$ . The wastewater sample which was used in the test was a filtered effluent of the third stage treatment (chlorination tank), spiked with the analytes ( $1000 \mu\text{g l}^{-1}$ ). For 300 ml of the samples, 30 mg of  $\text{TiO}_2$  was added.

The system was operated as a semi-batch reactor and all the parameters (contact time,  $\text{TiO}_2$  concentration, matrix effects) that affect the process were examined. An experiment was performed for determining the removal of the compounds from aqueous solution only with the use of solar radiation.

#### 2.4. Oxidation of short-chain nonylphenol ethoxylates with ozone

The ozone generator which was used in the experimental procedure is shown in Figure 2.



Figure 2. Ozone generator apparatus



Figure 3. Ozonation reactor and KI traps

Gaseous oxygen was transferred to an ozone generator (OZONIA PLANT LTD). A mixture of oxygen and ozone was ended in a semi-batch reactor (1 l volume). This type of reactor was operated in a semi-continuous mode, i.e., a stream of ozone was continuously added to the water sample through a stone diffuser. The gas inside the reactor was mixed with a magnetic stirrer. The surplus ozone stream leaving the reactor passed through glass traps containing 2% potassium iodide (KI) solution (Figure 3).

The experimental tests were performed with aqueous solution and spiked wastewater chlorinated effluent sample (700 ml sample volume). The aqueous solution was prepared in Milli-Q water with the addition of NPnEOs reagents. The oxidation was performed with 3000 and  $1500 \mu\text{g l}^{-1}$  initial concentration and 15 and 20 mg  $\text{l}^{-1}$  applied ozone doses.

The effect of the applied ozone dose on the removal of NPnEOs from the samples and the reaction kinetics were studied. In the wastewater effluent samples the decrease in the DOC concentration was also determined.

### 3. Results and Discussion

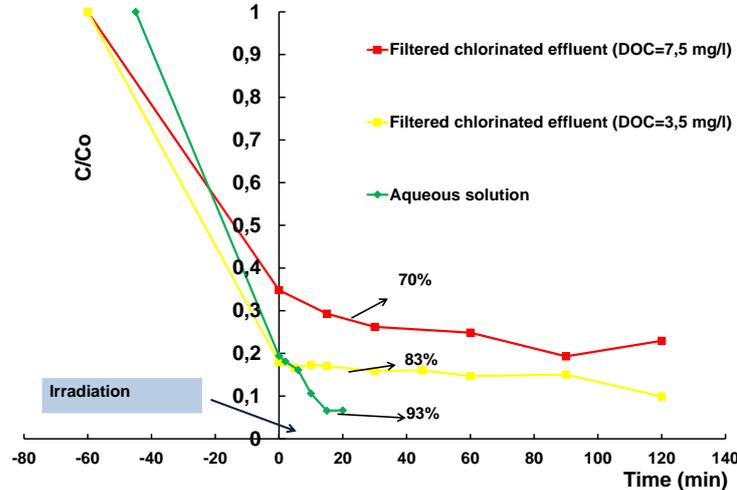
#### 3.1. Photocatalytic oxidation of NPnEOs with $\text{TiO}_2$

The 80% of the initial concentration of the compounds in aqueous solution was adsorbed to the catalyst in the dark in 5 min. Equilibrium was reached after 45 min with the adsorption of the 87% of their initial concentration. The optimum  $\text{TiO}_2$  dose which was used in the experimental tests was  $100 \text{ mg l}^{-1}$ .

After 20 min of exposure to the solar light the 67% of the compounds which have been remained in the solution had been removed, which means that the initial concentration of the solution has been decreased by 93%. In the wastewater samples the removal of the concentration in the solution was 44%, while the 80% of the initial concentration has been removed after 90 min of exposure.

### 3.1.1. Matrix effects

For the study of the effect of the sample matrix to the removal of NPnEOs during photocatalytic oxidation aqueous solution ( $750 \mu\text{g l}^{-1}$ ) and spiked chlorinated wastewater effluent samples ( $1000 \mu\text{g l}^{-1}$ ) were used in the tests. The DOC content in the wastewater samples was 7.5 and  $3.5 \text{ mg l}^{-1}$ . The results are presented in Figure 4.



**Figure 4.** Matrix effects in the photocatalytic oxidation of NPnEOs ( $n=0-2$ ,  $[\text{TiO}_2]=100 \text{ mg l}^{-1}$ )

### 3.1.2. Photocatalytic reaction kinetics

The photocatalytic oxidation of NPnEOs in aqueous solution followed first order kinetics with a reaction rate coefficient  $k=0.0562 \text{ min}^{-1}$ . In spiked wastewater effluent samples ( $7.5$  and  $3.5 \text{ mg l}^{-1}$  DOC), the data fitted in a first order kinetic model as well. The reaction rate coefficients were found to be  $0.058 \text{ min}^{-1}$  and  $k= 0,0049 \text{ min}^{-1}$ . In all cases, the correlation coefficients were greater than 0,9.

The reaction rate constants which have been calculated by Ike *et al.* (2002), for the photocatalytic oxidation of aqueous solution with UV/ $\text{TiO}_2$ , were in the same order of magnitude ( $0,062$  for NP and  $0,044$  for NP1EO).

## 3.2. Oxidation of NPnEOs with ozone

### 3.2.1. Matrix effects and DOC removal

For the study of the matrix effects in the oxidation of NPnEOs with ozone, semi-batch experimental tests were performed for two different applied ozone doses  $15$  and  $20 \text{ mg l}^{-1}$  (ozone concentration in the feeding mixture). The initial concentration of NPnEOs in the aqueous solution and the spiked wastewater sample (chlorinated effluent) was  $1500 \mu\text{g l}^{-1}$ . The results are presented in Figure 4.

The DOC in the sample was  $7.7 \text{ mg l}^{-1}$ . After 180 min of contact time 44% of the initial concentration was removed when  $15 \text{ mg l}^{-1} \text{ O}_3$  was applied and 47% when the dose was increased ( $20 \text{ mg l}^{-1}$ ). Obviously, the removal of the dissolved organic carbon was not depended to contact time, or ozone dose. This means that oxidation with ozone did not lead to mineralization of the compounds. The percentage of the organic matter in the sample was transformed, thus DOC concentration was kept in high levels.

### 3.2.2. Study of the reaction kinetics during the oxidation of NPnEOs with ozone

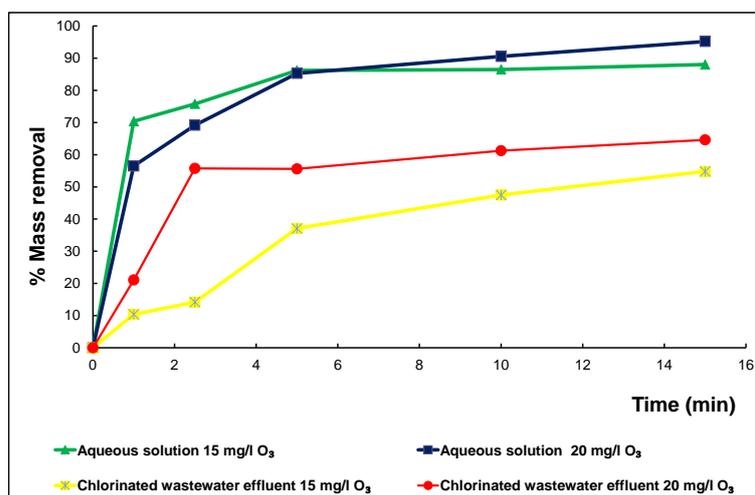
In the case of the oxidation of short chain nonylphenol ethoxylates with ozone the experimental data were simulated with pseudo-first and second order kinetic models.

Pseudo-first order kinetics: The reaction rate was calculated considering that the ozone is in great excess during the ozonation (its concentration is practically constant), so the reaction rate coefficient was determined based on the pollutant's consumption. The rate of the removal of the compounds is described by equation (1)

$$\frac{d[C_{\text{NPnEOs}}]}{d[t]} = k[O_3][C_{\text{NPnEOs}}] \quad (1)$$

from which equation 2 is derived

$$\ln \frac{[C_0]}{[C]} = k[O_3]t \quad (2)$$



**Figure 4.** Matrix effects on the oxidation of NPnEOs (n=0-2) with ozone

The slope is equal to the reaction rate constant multiplied by ozone concentration. By changing the ozone concentration, the coefficient is determined. In any case, it represents the observed reaction rate constant ( $k_{\text{obs}}$ ). Since the reaction rate is also depended on the ozone concentration, the breakdown constant will be calculated by equation 3

$$k_{\text{obs}} = k_{\text{NPnEOs}} \times [O_3] \quad (3)$$

where  $k_{\text{NPnEOs}}$  is the breakdown rate constant of the pollutants ( $M^{-1} \text{ min}^{-1}$ ) and its value depends on the applied ozone dose.

Second-order kinetics: The reaction rate for the removal of NPnEOs during ozone oxidation is calculated using equation (4)

$$-\frac{d[C_{\text{NPnEOs}}]}{d[t]} = k[C_{\text{NPnEOs}}]^2 \quad (4)$$

The reaction rate constants for the pseudo-first and second order kinetic models are summarized in Table 1.

**Table 1.** Kinetic parameters for the oxidation of NPnEOs with ozone

Sample	Applied ozone dose ( $\mu\text{M}$ )	Pseudo-first order kinetics			Second order kinetics	
		$k_{\text{obs}}$ ( $\text{min}^{-1}$ )	$k_{\text{NPnEOs}}$ ( $M^{-1} \text{ min}^{-1}$ )	$R^2$	$k_2$ ( $l \mu\text{g}^{-1} \text{ min}^{-1}$ )	$R^2$
Aqueous solution	312.5	0.0402	128.64	0,8267	$3 \times 10^{-4}$	0.9637
Aqueous solution	416	0.4059	159.86	0,7499	$4 \times 10^{-4}$	0.9746
Spiked wastewater sample	312.5	0.0201	64.32	0,9611	$4 \times 10^{-5}$	0.9728
Spiked wastewater sample	416	0.0389	93.51	0,9234	$7 \times 10^{-5}$	0.9624

In the case of pseudo-order kinetic model, the reaction rate constants are of the same order of magnitude for the aqueous solution as well as for the wastewater sample. Their values are different and they increase when the applied ozone dose increases. The breakdown of the compounds is faster when there is no organic matter in the sample.

In the case of second-order kinetic model, the reaction rate constants are one order of magnitude higher for the aqueous solution in comparison with the ones for the wastewater sample.

The correlation coefficients values are better when the data are fitted into second-order kinetic curves.

#### 4. Conclusions

The removal of short-chain NPnEOs from aqueous solution and wastewater effluent is feasible with the use of Advanced Oxidation Processes (AOPs). Both during the photocatalytic oxidation as well as the oxidation of the compounds with ozone the total removal is greater than 90%.

The application of AOPs for the removal of nonylphenol ethoxylates can be used as a third stage treatment method in the wastewater treatment targeting in the elimination of environmental impact of the effluents in the aqueous environment.

#### References

- APHA, Standard methods for the examination of water and wastewater. 20<sup>th</sup> edition, APHA, AWWA & WEF, Washington, D.C (1999).
- Beltran F.J. (2003), Ozone–UV Radiation–Hydrogen Peroxide Oxidation Technologies, in *Chemical Degradation Methods for wastes and Pollutants*, edited by Matthew A. Tarr, Marcel Dekker, INC, New York
- Bennie D.T., Sullivan C.A., Lee H-B. and Maguire R.J. (1998), Alkylphenol polyethoxylate metabolites in Canadian sewage treatment plant waste streams, *Water Qual. Res. J. Canada*, **33**(2), 231–252.
- Gatidou G., Thomaidis N., Stasinakis A. and Lekkas T.D. (2007), Simultaneous determination of the endocrine disrupting compounds nonylphenol, nonylphenol ethoxylates, triclosan and bisphenol A in wastewater and sewage sludge by gas chromatography-mass spectrometry, *J. Chromat. A*, **1138**(1&2) 32–41.
- Gogate P.R. and Pandit A.B. (2004) A review of imperative technologies for wastewater treatment: I. Oxidative technologies at ambient conditions, *Advances in Environmental Research*, **8**, 501-551.
- Korner W., Bolz U., Suímuth W., Hiller G., Schuller W., Hanf V. and Hagenmaier H. (2000), Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany, *Chemosphere*, **40**, 1131–1142.
- Lee H-B. and Peart T.E. (1998), Occurrence and elimination of nonylphenol ethoxylates and metabolites in municipal wastewater and effluents, *Water Qual. Res. J. Canada*, **33**(3), 389–402.
- Lee H-B., Weng J., Peart T.E. and Maguire R.J. (1998), Occurrence of alkylphenoxyacetic acids in Canadian sewage treatment plant effluents, *Water Qual. Res. J. Canada*, **33**(1), 1–929.
- Neamtu M. and Frimmel F.H. (2006), Photodegradation of endocrine disrupting chemical nonylphenol by simulated solar UV-irradiation, *Science of the Total Environment*, **369**, 295-306
- Pothitou P. and Voutsas D. (2008), Endocrine disrupting compounds in municipal and industrial wastewater treatment plants in Northern Greece, *Chemosphere*, **73**(11), 1716–1723.
- Sekela M., Brewer R., Moyle G. and Tuominen T. (1999), Occurrence of an environmental estrogen (4-nonylphenol) in sewage treatment plant effluent and the aquatic receiving environment, *Wat. Sci. Technol.*, **39**(10–11), 217–220.
- Shao B., Hu J.Y. and Yang M. (2000), Determination of nonylphenol ethoxylates in the aquatic environment by normal phase liquid chromatography–electrospray mass spectrometry, *J. Chromat. A*, **950**, 167.
- Stasinakis A., Gatidou G., Mamais D., Thomaidis N. and Lekkas T.D. (2008), Occurrence and fate of endocrine disrupters in Greek sewage treatment plants, *Wat. Res.*, **42**(6&7), 1796–1804.
- Tsimas M. (2007), Simultaneous treatment of As(III) and humic acids with the use of heterogeneous photocatalysis, Maste Thesis, Technical Univeristy of Crete, Chania, Greece (*in Greek*).
- Yiantzi E., Psillakis E., Tyrovolas K. and Kalogerakis N. (2010), Vortex assisted liquid-liquid microextraction of octylphenol, nonylphenol and bisphenol-A, *Talanta*, **80**(5), 2057–2062.
- Ying G.-G., Williams B. and Kookana R. (2002), Environmental fate of alkylphenols and alkylphenol ethoxylates-a review, *Environ. Int.*, **28**, 215–226.