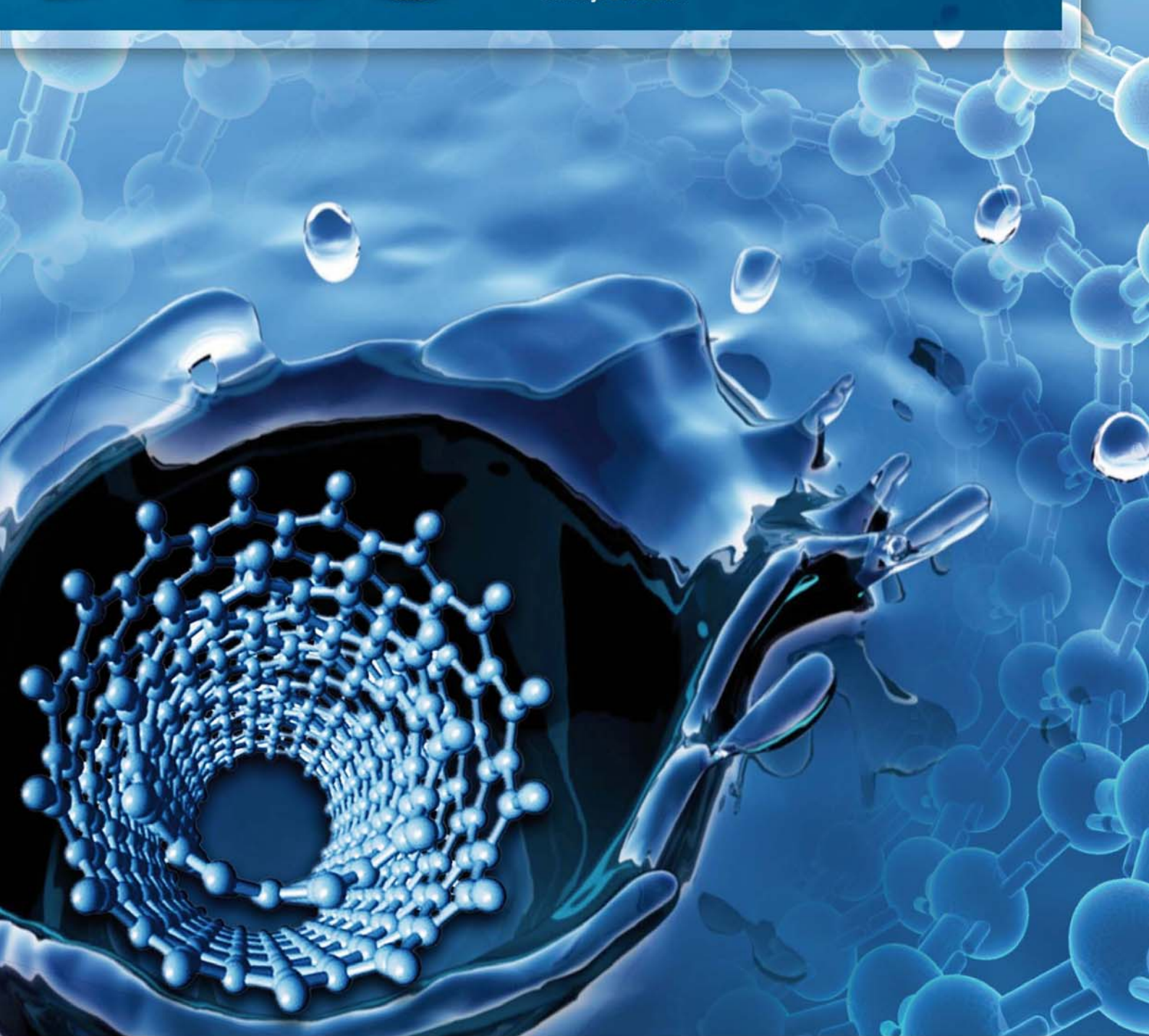


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## Photochemical degradation of nonylphenol in aqueous solution: The impact of pH and hydroxyl radical promoters

Aleksandr Dulov\*, Niina Dulova, Marina Trapido

*Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia*

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### Abstract

The degradation of nonylphenol (NP) in aqueous solution with UV, H<sub>2</sub>O<sub>2</sub>/UV, and Fenton/photo-Fenton processes was studied. The efficacy of direct and hydrogen peroxide photolysis proved to be dependent on the pH value. The addition of H<sub>2</sub>O<sub>2</sub> to UV treatment improved NP degradation. The application of UV photolysis and the H<sub>2</sub>O<sub>2</sub>/UV system at pH 7 resulted in low pseudo first-order rate constants at 10<sup>-4</sup> sec<sup>-1</sup>. In the experiments at elevated pH values the pseudo-first order rate constants increased to 10<sup>-3</sup> sec<sup>-1</sup>. The efficacy of the Fenton process was lower in comparison with UV and hydrogen peroxide photolysis. The addition of UV irradiation to the H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> system substantially improved NP degradation efficacy. In terms of performance, the photo-Fenton process was similar to the H<sub>2</sub>O<sub>2</sub>/UV process. The most favourable process for complete nonylphenol degradation considering both operational cost and treatment efficacy was H<sub>2</sub>O<sub>2</sub>/UV at pH 11 and 250 µmol/L H<sub>2</sub>O<sub>2</sub>.

**Key words:** AOPs; endocrine disrupting compound; photo-Fenton process; photolysis; UVC radiation

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### Introduction

The presence of compounds with estrogenic properties in the environment has become a subject of major concern throughout the world. Among the various endocrine disrupting compounds (EDCs), nonylphenol (NP) has been classified as a significant endocrine disruptor capable of interfering with the hormonal system of numerous organisms and acting as an estrogen mimic. NP is produced in large volumes, and it is mainly used as a chemical intermediate for the production of nonylphenol ethoxylates (NPEs). NPEs are efficient non-ionic surfactants used in a wide variety of industrial applications and consumer products, such as domestic liquid laundry detergents, industrial liquid soaps and cleaners, cosmetics, paints, and as dispersing agents in pesticides and herbicides. Most of the extensively used NPEs are discharged to the sewer system and directed into the wastewater treatment plants.

Although NPEs are highly treatable in conventional biological treatment facilities, effluent from wastewater treatment plants is one of the major sources of NPs, which are primary NPEs biodegradation products, due to incomplete removal and degradation of these pollutants (Ahel et al., 1994a; Soares et al., 2008). NP is known

to be persistent in the aquatic environment, moderately bioaccumulative, and extremely toxic to aquatic organisms (Soares et al., 2008). Due to harmful effects of NP, its production and use is restricted in the European Union since 2003 and the limits for NP in water bodies are set at 2 µg/L (Bertanza et al., 2011).

The advanced oxidation processes (AOPs) involving ozone, hydrogen peroxide, UV photolysis, the Fenton process, etc., have been widely studied for the treatment of persistent organic pollutants (such as EDCs) and proved to have potential for complete degradation of the target compound as well as its degradation products (Lee et al., 2003; Irmak et al., 2005; Ning et al., 2007; Bertanza et al., 2011). The degradation of NP in aqueous medium by AOPs, such as photocatalytic processes with TiO<sub>2</sub> and ZnO (Ike et al., 2002; Babaeia et al., 2011), natural and simulated sunlight photolysis (Ahel et al., 1994b; Neamțu and Frimmel, 2006; Gao et al., 2010), sonolysis (Yim et al., 2003; Ince et al., 2009), and ozonation (Ning et al., 2007) has been reported. The effective removal of NP was demonstrated for adsorption on activated carbon (Choi et al., 2005). Additionally, combined biological and chemical (ozonation) treatment has been studied for real wastewater treatment plant effluents contaminated with NP and resulted in estrogenic activity abatement and reduction of target

\* Corresponding author. E-mail: [alexandr.dulov@gmail.com](mailto:alexandr.dulov@gmail.com)

compound concentration (Bertanza et al., 2011). However, no previous works have been found in the literature on the removal of NP by UVC photolysis, the H<sub>2</sub>O<sub>2</sub>/UVC system and Fenton-based processes with UVC radiation.

In the present study the degradation of NP using UVC photolysis, hydrogen peroxide photolysis, and Fenton/photo-Fenton processes was investigated. The efficiencies of various oxidation processes on NP removal from aqueous solution were compared.

## 1 Experimental

### 1.1 Chemicals and materials

Nonylphenol (C<sub>15</sub>H<sub>24</sub>O, CAS Nr. 104-40-5, molecular weight 220.4 g/L, pK<sub>a</sub> 10.7 (Ince et al., 2009)) was purchased from Sigma-Aldrich; acetonitrile (99.8%, isocratic grade for HPLC) was obtained from Baker. All the other chemicals of analytical grade were used without further purification.

A stock NP solution of 4.54 mmol/L was prepared in 100 mL methanol and stored in the dark at 4°C. Test solutions with initial NP concentration of 20 μmol/L were prepared by dilution of the stock in twice-distilled water. The solution was stirred for several hours to ensure complete NP dissolution. Sodium hydroxide and sulphuric acid aqueous solutions were used for pH adjustment.

### 1.2 Experimental procedure

A mercury low-pressure OSRAM lamp with an energy input of 10 W located in a quartz tube inside the reactor was used as an UVC (thereinafter UV) source. The incident UV radiation photon flux at 254 nm measured by potassium ferrioxalate actinometry (Gordon and Ford, 1972) was 5.52 ± 0.38 μEinstein/sec. The constant temperature (22 ± 1°C) in the reactor was maintained using a cooling jacket.

All Fenton-based process trials were carried out in batch mode and in non-buffered solutions. NP solutions were treated in a 1-L cylindrical glass reactor with permanent agitation for a period of 120–180 min; samples were withdrawn at pre-selected time intervals. The classic Fenton reaction (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) was initiated by adding H<sub>2</sub>O<sub>2</sub> (100–500 μmol/L) to NP solution (pH 3) containing a known amount of Fe<sup>2+</sup> ion. The molar ratio of H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> was kept invariable at 10:1, which is optimal according to Tang and Huang (1997). The H<sub>2</sub>O<sub>2</sub> concentration in the photo-Fenton experiments was in the range of 50–500 μmol/L; the pH value of the stock solution was adjusted to 3 or 7.

The direct UV photolysis and H<sub>2</sub>O<sub>2</sub>/UV experiments were carried out in the same reactor (1 L of stock NP solution in a glass reactor with a permanent agitation speed for a period of 30–180 min). The pH value of the stock solution was 7 or 11. The H<sub>2</sub>O<sub>2</sub> concentration varied from 50 to 500 μmol/L.

Additionally, the experiments on NP oxidation with non-catalyzed H<sub>2</sub>O<sub>2</sub> were conducted in the same reactor

and treatment conditions as the respective Fenton-based treatment trials.

### 1.3 Analytical methods

NP concentrations were quantified by means of a CLAS MPm (Labio Ltd.) high performance liquid chromatograph equipped with a MAG 0 (1.5 × 50 mm) Biospher PSI 100 C18 (particle size, 5 μm) microcolumn and UV/Vis detector SAPHIRE. The isocratic method with a solvent mixture of 80% acetonitrile and 0.3% of acetic acid in water was applied. Samples were analyzed at a flow rate of 70 μL/min and an absorbance wavelength of 210 nm. The concentration of NP was determined by using the standard chemical to fit the retention time.

The total iron concentration in the solution was quantified with the phenanthroline method (APHA, 2005). The initial H<sub>2</sub>O<sub>2</sub> concentration in stock solutions was determined spectrophotometrically by measuring the absorption of H<sub>2</sub>O<sub>2</sub> at 254 nm using Helion-β UV/Vis (Thermo Electron Corporation). The residual H<sub>2</sub>O<sub>2</sub> concentration was measured by the spectrophotometric method with Ti<sup>4+</sup> (Eisenberg, 1943).

## 2 Results and discussion

### 2.1 UV photolysis and H<sub>2</sub>O<sub>2</sub>/UV process

Nonylphenol absorbs mainly at lower wavelengths (in the range of 200–210 nm); its absorbance almost ceases at approximately 250 nm. Therefore, degradation of NP by the UV photolysis with the application of a low pressure lamp was expected to be slow.

The efficacy of NP removal was controlled by measuring the residual concentration of the target compound. The nonylphenol degradation followed a pseudo first-order kinetic law and may be described with regard to the compound concentration:

$$\frac{dC_{\text{NP}}}{dt} = -k_1 \times C_{\text{NP}}$$

where,  $k_1$  is the pseudo first-order rate constant. The  $-k_1$  constants were calculated from the slopes of the straight lines by plotting  $\ln(C/C_0)$  as a function of time  $t$ , through linear regression.

Similarly to some other phenols, it was presumed that deprotonated NP reacts about an order of magnitude faster than the protonated compound. The fraction of the dissociated species depends on the dissociation constant and on the pH of the aqueous media. Therefore, the impact of pH on the nonylphenol degradation by the UV photolysis was studied.

It was observed that pH has significant influence on the degradation of nonylphenol during the application of the UV photolysis (Table 1). Nonylphenol removal was faster in alkaline medium. This is probably due to the fact that in alkaline medium the molar absorption coefficients of

**Table 1** 90% conversion times ( $T_{90\%}$ ) and the pseudofirst-order rate constants ( $k_1$ ) of NP degradation with different treatment methods.

Treatment method	pH	H <sub>2</sub> O <sub>2</sub> (μmol/L)	$T_{90\%}$ (min)	$k_1$ ( $\times 10^{-4}$ sec <sup>-1</sup> ) ( $r^2 > 0.985$ )
UV photolysis	7	–	97	3.96 ± 0.12
	11	–	29	13.20 ± 0.33
H <sub>2</sub> O <sub>2</sub> /UV	7	50	80	4.77 ± 0.14
	7	100	60	6.41 ± 0.21
	7	500	38	10.20 ± 0.25
	11	50	20	19.40 ± 0.36
	11	100	16	23.70 ± 0.41
	11	250	12	31.70 ± 0.55
H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup>	3	100	>180	–
	3	200	120	–
	3	500	>180	–
H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> /UV	3	50	60	–
	3	100	45	–
	3	500	>180	–
	7	50	60	–
	7	100	50	–
	7	500	40	–

the molecule are slightly higher than at acidic and basic pH values (Neamtu and Frimmel, 2006). Differences in the quantum yields at the two pH values would lead to different rate constants as well. The 90% conversion times ( $T_{90\%}$ ) for the UV photolysis at pH 7 and pH 11 were 97 and 29 min, respectively. The pseudo-first order rate constant for the experiment at pH 11 was  $(13.2 \pm 0.33) \times 10^{-4}$  sec<sup>-1</sup>, which was three times higher than the rate constant for trial at pH 3.

Photo-degradation can occur by the direct absorption of radiation (direct photolysis) or by reaction with reactive intermediates (e.g. hydroxyl radicals) that are intensively generated when irradiation is combined with a strong oxidant, e.g. hydrogen peroxide (hydrogen peroxide photolysis). In general, addition of free radical promoters enhances the efficiency of the UV photolysis when irradiated substances have relatively low values of quantum yield and the molar absorption coefficient, as in the case of NP. In the present study, different concentrations of H<sub>2</sub>O<sub>2</sub> were tested to increase the efficacy of the UV photolysis.

As compared to single UV photolysis, the addition of H<sub>2</sub>O<sub>2</sub> to UV treatment improved NP degradation substantially and was dependent on the added H<sub>2</sub>O<sub>2</sub> concentration (Table 1). The addition of 50, 100 and 500 μmol/L of H<sub>2</sub>O<sub>2</sub> (pH 7) resulted in  $T_{90\%}$  of 80, 60 and 38 min, respectively. Similarly to the direct photolysis, NP degradation rate in the H<sub>2</sub>O<sub>2</sub>/UV system was considerably dependent on the pH of the solution. The pseudo first-order rate constants for the H<sub>2</sub>O<sub>2</sub>/UV process at pH 11 were  $(19.4 \pm 0.36) \times 10^{-4}$ ,  $(23.7 \pm 0.41) \times 10^{-4}$ , and  $(31.7 \pm 0.55) \times 10^{-4}$  sec<sup>-1</sup> after the addition of 50, 100 and 250 μmol/L of H<sub>2</sub>O<sub>2</sub>, respectively.

The results of blank H<sub>2</sub>O<sub>2</sub> oxidation trials indicated no degradation of NP at all studied concentrations.

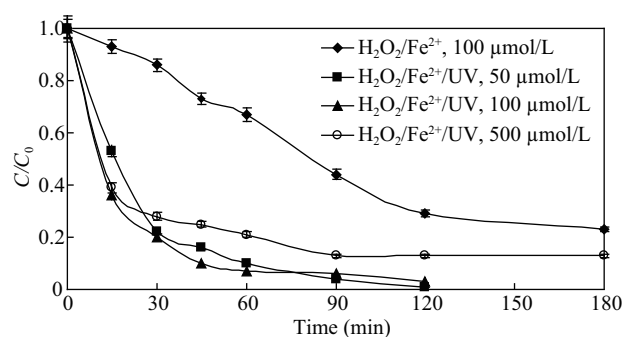
## 2.2 Fenton and photo-Fenton process

Kinetic constants' values were not calculated for the Fenton-based processes because the data did not fit any kinetic model.  $T_{90\%}$  values for the degradation of NP calculated from the degradation curves are presented in Table 1.

The experiments of the Fenton treatment (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) of NP were performed as preliminary trials for subsequent assessment of the efficacy of the photo-Fenton treatment. The results of NP degradation in the Fenton system indicated dependence of the treatment efficacy on the H<sub>2</sub>O<sub>2</sub> concentration. Thus, the increase in H<sub>2</sub>O<sub>2</sub> dose from 100 to 200 μmol/L intensified the degradation of the target compound (Table 1). In general, the Fenton system efficacy was lower than in the case of UV and hydrogen peroxide photolysis. The moderate NP removal by the Fenton reagent under the conditions used in this study can be explained by an effective scavenging of the hydroxyl radicals by the elevated concentrations of H<sub>2</sub>O<sub>2</sub> used (Neyens and Baeyens, 2003).

The addition of UV radiation to the Fenton system resulted in the improvement of NP removal (Table 1, Fig. 1). Similarly to hydrogen peroxide photolysis, the efficacy of the photo-Fenton process proved dependent on H<sub>2</sub>O<sub>2</sub> concentrations. The  $T_{90\%}$  of photo-Fenton experiments at pH 3 after addition of 50 and 100 μmol/L of H<sub>2</sub>O<sub>2</sub> were 60 and 45 min, respectively. Further increase in the H<sub>2</sub>O<sub>2</sub> concentration up to 500 μmol/L indicated a decrease in the NP degradation efficacy. This fact can be explained by the scavenging effect of H<sub>2</sub>O<sub>2</sub> at the high concentration used (Neyens and Baeyens, 2003). The influence of pH on the degradation of the target compound during photo-Fenton was more obvious at the elevated H<sub>2</sub>O<sub>2</sub> concentration, and consequently at higher iron concentrations (Figs. 1 and 2). Thus, the results of 500 μmol/L H<sub>2</sub>O<sub>2</sub> application at pH 3 and pH 7 demonstrated similarity of the efficacy of the photo-Fenton process oxidation with the Fenton system and hydrogen peroxide photolysis, respectively, indicating difference in NP oxidation at acidic and neutral pH values.

Although the efficacy of the photo-Fenton process was higher than that of the Fenton system, the result of NP degradation indicated no considerable improvement compared to the hydrogen peroxide photolysis (Fig. 2).

**Fig. 1** NP degradation by Fenton and photo-Fenton treatment at pH 3.

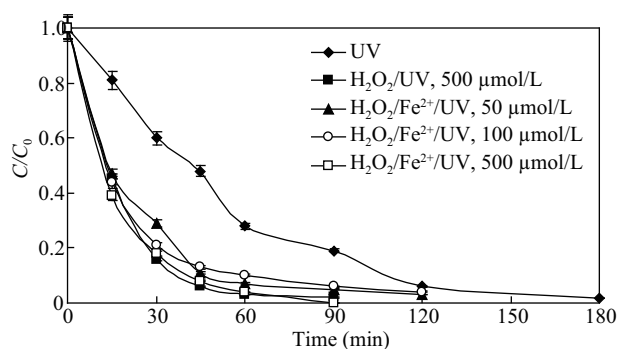


Fig. 2 NP degradation by the photo-Fenton treatment, UV and hydrogen peroxide photolysis at pH 7.

Therefore,  $\text{H}_2\text{O}_2/\text{UV}$  process without iron admixture may be recommended for NP removal, as it does not improve the overall degradation efficacy.

### 2.3 Operational costs of treatment

In order to assess the economical feasibility of different treatment schemes for NP  $T_{90\%}$  conversion time, the operational costs were calculated. The cost estimation and methodology were based on the calculation made by Munter et al. (2006).

The data obtained from the laboratory experiments allowed us to make approximate calculations of operating costs comprising the energy required for ozonation, UV photolysis, and chemicals. Doses of ozone and  $\text{H}_2\text{O}_2$  injected to the studied samples were used in calculations without presumption of re-circulation of non-consumed chemicals. The specific energy requirement for ozone production from air was 20 kWh/kg  $\text{O}_3$ ; the estimated unit energy cost was 0.1 €/kWh. In the Fenton-based process, the cost of  $\text{H}_2\text{O}_2$  was 0.9 €/kg, calculated as 100%;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  price was 0.13 €/kg. For sodium hydroxide and sulphuric acid used for pH adjustment, average current prices of chemicals on the Estonian market were taken as

a basis. Treatment cost calculations in €/m<sup>3</sup> are presented in Table 2.

Due to more effective NP degradation at basic pH values, the operational costs of experiments performed at pH 11 were lower than at acidic and neutral pH values. For example, the treatment cost of UV photolysis at pH 11 and pH 7 were 0.83 and 2.66 €/m<sup>3</sup>, respectively, and the cost of  $\text{H}_2\text{O}_2/\text{UV}$  (50  $\mu\text{mol/L}$   $\text{H}_2\text{O}_2$ ) treatment at pH 11 and 7 was 0.51 and 1.93 €/m<sup>3</sup>, respectively. On the other hand, low concentration of chemicals used in the treatment processes under the conditions studied resulted in a low operational cost of the processes with the fastest NP removal. In general, the cost of UV radiation constituted a major part in the overall operational costs of all photo-treatment processes.

The cost of the most efficient process  $\text{H}_2\text{O}_2/\text{UV}$  at pH 11 and 250  $\mu\text{mol/L}$   $\text{H}_2\text{O}_2$  ( $T_{90\%}$  12 min) was 0.28 €/m<sup>3</sup>. The cheapest treatment was the Fenton process, but due to low efficacy it cannot be considered as the main NP degradation technique. The operational cost of the photo-Fenton process (that was also more efficient than the classical Fenton process) was at least 10 times higher than the cost of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  system. For example, NP degradation by the photo-Fenton and the Fenton process at 100  $\mu\text{mol/L}$   $\text{H}_2\text{O}_2$  resulted in 1.19 and 0.10 €/m<sup>3</sup>, respectively. Taking into consideration all above-mentioned facts, the optimal treatment method of NP regarding the operational cost and treatment efficacy was  $\text{H}_2\text{O}_2/\text{UV}$  at pH 11 and 250  $\mu\text{mol/L}$   $\text{H}_2\text{O}_2$ .

### 3 Conclusions

In the current study the efficacy of photo-AOPs for NP degradation was evaluated. NP removal by the direct and hydrogen peroxide photolysis proved pH dependent. The addition of  $\text{H}_2\text{O}_2$  to the UV system substantially improved the degradation of NP. The increase in the  $\text{H}_2\text{O}_2$  dose from

Table 2 Operational costs of treatment schemes for  $T_{90\%}$  of NP.

Treatment method	pH*	$\text{H}_2\text{O}_2$ ( $\mu\text{mol/L}$ )	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (€/m <sup>3</sup> )	$\text{H}_2\text{O}_2$ (€/m <sup>3</sup> )	UV (€/m <sup>3</sup> )	Total (€/m <sup>3</sup> )
UV photolysis	7	–	–	–	2.66	2.66
	11	–	–	–	0.73	0.83
$\text{H}_2\text{O}_2/\text{UV}$	7	50	–	0.0015	1.93	1.93
	7	100	–	0.0031	1.69	1.69
	7	500	–	0.015	0.84	0.86
	11	50	–	0.015	0.41	0.51
	11	100	–	0.0031	0.31	0.41
	11	250	–	0.0077	0.17	0.28
$\text{H}_2\text{O}_2/\text{Fe}^{2+}$	3	100	0.00036	0.0031	–	0.10
	3	200	0.0072	0.0061	–	0.11
	3	500	0.0018	0.015	–	0.12
$\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$	3	50	0.0018	0.0015	1.45	1.55
	3	100	0.00036	0.0031	1.09	1.19
	7	50	0.00018	0.0015	1.21	1.21
	7	100	0.00036	0.0031	1.45	1.45
	7	500	0.0018	0.015	0.97	0.99

\* pH regulation in average 0.1 €/m<sup>3</sup>.

50 to 500  $\mu\text{mol/L}$  intensified the degradation of the target compound in the  $\text{H}_2\text{O}_2/\text{UV}$  process. The application of the hydrogen peroxide photolysis at pH 11 and at  $\text{H}_2\text{O}_2$  dose 250  $\mu\text{mol/L}$  demonstrated the highest NP removal rate ( $(31.7 \pm 0.55) \times 10^{-4} \text{ sec}^{-1}$ ). The results of NP degradation by the photo-Fenton process revealed similarity in terms of performance with the hydrogen peroxide photolysis. The optimal treatment method of NP regarding operational costs and treatment efficacy was  $\text{H}_2\text{O}_2/\text{UV}$  (250  $\mu\text{mol/L}$   $\text{H}_2\text{O}_2$ ) treatment at pH 11 with the respective cost of 0.28  $\text{€}/\text{m}^3$ .

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