

Removal of nonylphenol by pulsed corona discharge in water

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Abstract: Degradation of technical mixture of nonylphenol by the pulsed corona discharge in water has been investigated. It was shown that non-thermal plasma generated by the discharge can effectively remove nonylphenol from water. Degradation of nonylphenol followed first order kinetics. The removal efficiency was dependent on the solution conductivity, while a higher degree of degradation was obtained with higher conductivity. Oxidation of nonylphenol by OH radical attack was proposed as possible mechanism of degradation by the discharge in water.

Keywords: Nonylphenol, corona discharge in water, hydroxyl radical, HPLC.

1. Introduction

Nonylphenol (Fig. 1) is a synthetic substance, which does not occur naturally in the environment. It is mainly involved in technical nonylphenol ethoxylate mixtures, non-ionic surfactants, which are afterwards released to the environment through wastewater or industrial treatment plant. During the water treatment, nonylphenol ethoxylates are in aerobic conditions degraded back to nonylphenols, which persist mainly in sewage sludge, due to their physico-chemical properties, such as low solubility in water and high hydrophobicity. Nonylphenol is manufactured by alkylating phenol with variously branched nonenes (propylene trimers). Depending on the composition of nonene, the technical mixture of nonylphenol consists of isomeric compounds with differently branched nonyl chain. Some authors also tried to identify these isomers and describe their toxic impact on the environment, even though it is almost impossible due to very similar chemical and physical properties.

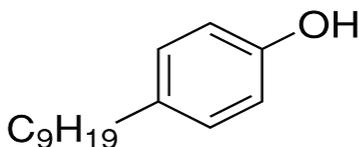


Fig. 1 Chemical structure of nonylphenol.

Nonylphenol was classified as an endocrine disrupter. These compounds have an ability to interact with the endocrine system of animals and humans and interfere with reproduction and natural development processes, where the disrupting power is shown to be connected with the structure of nonylphenol isomer. In order to protect the environment, the use and production of nonylphenol was banned in EU countries in 2004 and further regulations were applied. However, significant concentrations are still found in the effluent from

wastewater treatment plants and in river waters; therefore, some tertiary treatment before the release into water recipient should be taken into account.

Lenz *et al.* studied behaviour of nonylphenol in water system supply and found out that chlorination by NaClO leads to a creation of more toxic by-products, but suggested ClO₂ and ozonization as an appropriate method of nonylphenol removal [1]. Neamtu *et al.* used photodegradation of nonylphenol using UV-irradiation, but assumed that oxidation rate can be increased only in the presence of H₂O₂ and Fe(III). They also identified phenol, 1,4-dihydroxybenzene and 1,4-benzoquinone as intermediate products of photodegradation through an HPLC method [2].

In this work we have tried to remove nonylphenol from water solution using pulsed corona discharge generated directly in water. These discharges have been recently successfully used to degrade many organic compounds (e.g., chlorophenols, trichloroethylene, biphenyls, etc.) [3,4], since non-thermal plasma initiated by these discharges produces various chemically reactive species such as radicals (OH, H, O) and molecular species (H₂O₂, O₂, H₂, O₃), which are capable of diminishing undesirable xenobiotics from water. In the present study preliminary results on the effects of underwater pulsed corona discharge on degradation of nonylphenol in water are presented. Reactor of needle-to-plate electrode geometry is used. Comparison of removal efficiency of nonylphenol from water by the discharge for two solution conductivities (100 and 500 μS/cm) is made. Possible mechanism of nonylphenol degradation by the pulsed corona discharge in water is proposed.

2. Experimental

The reactor used for generating of the pulsed corona discharge with needle-to-plate electrode geometry in water was described in detail in previous work [5]. Briefly,

needle electrode, made of tungsten rod, was in the distance of 52 mm from the second electrode and almost totally insulated from surrounding water by Teflon insulator. A pulsed high voltage applied to the needle was provided by a pulse power supply. All experiments were conducted with fixed applied voltage of 27 kV, pulse repetition frequency of 70 Hz and charging capacitance of 7 nF. The only parameter changed was the solution conductivity. The reactor vessel was cooled during the whole experiment by a water circulating system to avoid heating of the solution and maintain isothermal conditions of about 16°C. The experiments were made in solutions initial conductivities of 100 and 500 $\mu\text{S}/\text{cm}$. The conductivity of aqueous solutions was prepared by the addition of dilute sulfuric acid to deionized water. The pH of the solutions was 2.8 after sulfuric acid addition. The volume of the treated solution was 1300 ml.

The stock solution of nonylphenol was prepared by dissolving technical mixture of nonylphenol (CAS No. 84852-15-3) in distilled water. Due to very low solubility of nonylphenols in water (~ 5 mg/l at 20 °C [6]), droplet of nonylphenol (~ 15 mg) was transferred by glass pipette to 5 litres of deionized water and mixed five days prior using for the experiments to allow nonylphenol completely dissolve in water. The initial concentration of nonylphenol in water was 3 mg/l (0.136 mmol/l).

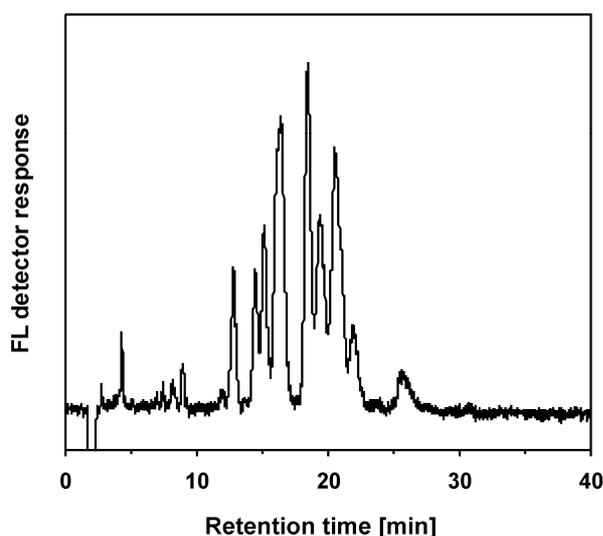


Fig. 2 Chromatogram of HPLC analysis of technical mixture of nonylphenol.

Analyses of nonylphenols were performed on a Shimadzu LC-10Avp HPLC system equipped with a 5 μm Hypercarb column (100×4.6 mm; Thermo Scientific Inc.). A 5 μm Hypercarb guard column (10×4.6 mm; Thermo Scientific Inc.) was used in-line with the analytical column. The columns were thermostated at 35°C. An isocratic method with a solvent mixture of 60% (v/v) acetonitrile and 1% (v/v) acetic acid in deionized water was used with a flow rate

of 0.8 ml/min. Detection of nonylphenols was performed using fluorescence detector set at 222 nm excitation and 304 nm emission wavelengths. A sample injection volume was 40 μl . Quantitative analyses of nonylphenol were based on peaks retention times and calibration method with standard solutions. Fig. 2 shows a typical chromatogram of HPLC analysis of nonylphenol technical mixture obtained using above described method.

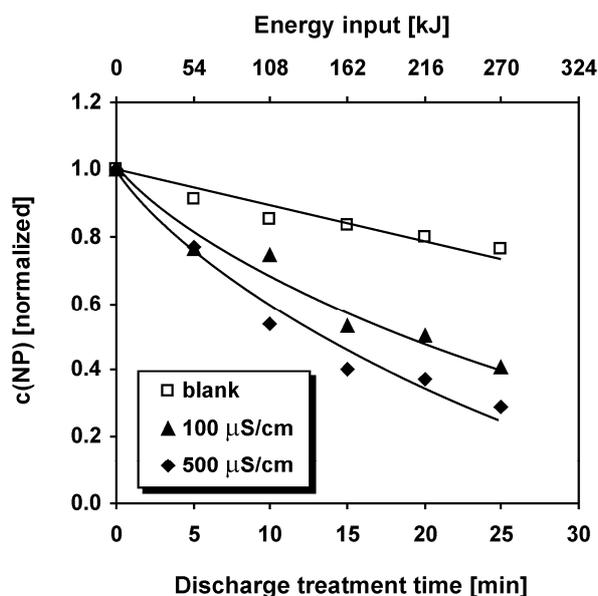


Fig. 3 Degradation of nonylphenol by corona discharge in water of solution conductivity 100 (\blacktriangle) and 500 $\mu\text{S}/\text{cm}$ (\blacklozenge), sorption losses of nonylphenol in reactor (\square).

3. Results and discussion

Fig. 3 shows comparison of the degradation of nonylphenol induced by the pulsed corona discharge performed in aqueous solutions of 100 and 500 $\mu\text{S}/\text{cm}$. Both experiments were made under the same experimental conditions ($U=27$ kV, $f=70$ Hz, $P=180$ W). In addition, Fig. 3 shows decrease in nonylphenol concentration determined in the reactor after the same time period as were performed experiments but without discharge (i.e. losses of nonylphenol in the reactor that were not caused by the action of the discharge). It is apparent that the losses caused by adsorption of nonylphenol in the discharge reactor are significant. Overall, these losses accounted about 25% of total nonylphenol removal from the discharge reactor. It should be noted that nonylphenols adsorb more or less on all types of surfaces and materials, which cannot be completely eliminated. Therefore, although we replaced some parts of the reactor with materials that were more susceptible to nonylphenol sorption, it was not possible to absolutely avoid sorption of nonylphenols in the reactor. Therefore, sorption losses of nonylphenols have to be taken into account.

Fig. 3 shows that concentration of nonylphenol decreases exponentially with the treatment time under both solution conductivities. Thus, the removal of nonylphenol by the discharge could be described by the first order kinetics with respect to nonylphenol concentration as

$$\ln \frac{c}{c_0} = -k_0 t \quad (1)$$

where c_0 and c are the concentrations of nonylphenol at times 0 and t (mol/l), respectively, k_0 is a pseudo-first order rate constant (1/s) and t is the treatment time (s). The results for nonylphenol removal (reduced for adsorption losses) expressed in the form of first order plots are shown in Fig. 4.

Consequently, using pseudo-first order rate constant k_0 energy yield G of nonylphenol removal has been calculated as

$$G = \frac{0.63 c_0 V}{P t_{37}} = \frac{0.63 k_0 c_0 V}{P} \quad (2)$$

where G has been defined as the number of moles of nonylphenol removed from the solution by factor of e (i.e. to 37 % of the initial concentration c_0) by energy of 1 J supplied to the system (mol/J), V is solution volume (l), P is power input applied to the discharge reactor (W) and t_{37} is the time required for 63% nonylphenol conversion that corresponds under assumption of first-order kinetics to inverted value of k_0 (i.e., $t_{37} = 1/k_0$) [3].

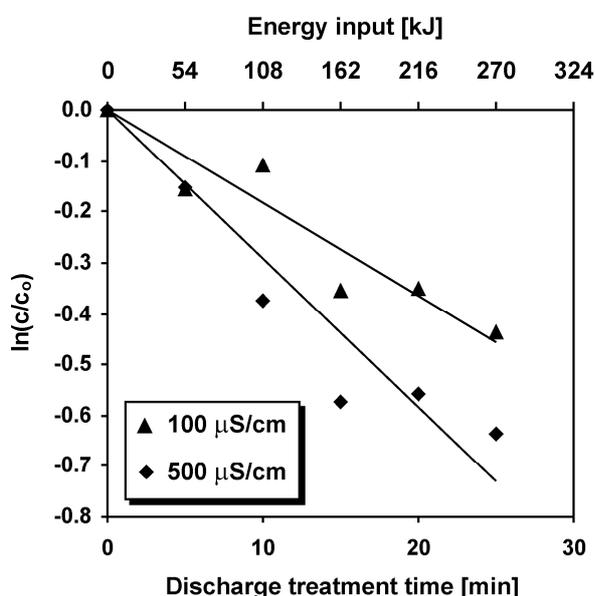


Fig. 4 First order plot of degradation of nonylphenol by discharge in water of conductivity 100 and 500 $\mu\text{S}/\text{cm}$.

Fig. 4 shows that degradation of nonylphenol proceeded faster with higher solution conductivity. Pseudo-first order rate constant of $3.05 \times 10^{-4} \text{ s}^{-1}$ was

determined for conductivity of 100 $\mu\text{S}/\text{cm}$ compared to $4.87 \times 10^{-4} \text{ s}^{-1}$ for conductivity of 500 $\mu\text{S}/\text{cm}$. This corresponds to energy yields of 1.89×10^{-11} and $3.02 \times 10^{-11} \text{ mol}/\text{J}$ for the solution conductivity 100 and 500 $\mu\text{S}/\text{cm}$, respectively. This is a little bit unexpected result since the yield of chemical activity of the discharge in water generally decreases with increasing solution conductivity as it that was observed in previous works (see [4] and reference therein). In these works plasmachemical activity of the discharge is largely attributed to the oxidation of organic compounds by OH radicals. Since, the production of OH radicals by the discharge is decreasing with increasing solution conductivity this results into a decreasing removal efficiency of organic compounds by the discharge with higher solution conductivity. However, more recently Lukes *et al.* [7] have observed a catalytic effect of tungsten, when used as high voltage electrode, on the plasmachemical efficiency of the discharge in water. They found that due to erosion of tungsten electrode in the discharge tungstate ions WO_4^{2-} are released into water during the discharge treatment time period. WO_4^{2-} ions can induce catalytic process with hydrogen peroxide that is generated by the discharge. This process leads to the production of additional oxidation species (such as atomic oxygen), which can contribute to the degradation of organic compounds by the discharge in water. Since erosion of high voltage electrodes by the discharge in water significantly increases with the solution conductivity [8] this leads to the increasing importance of $\text{WO}_4^{2-}/\text{H}_2\text{O}_2$ catalytic process and thus to a higher plasmachemical activity of the discharge in water generated using tungsten electrodes. Therefore, a higher removal of nonylphenol that was observed in this work for solution conductivity of 500 $\mu\text{S}/\text{cm}$ compared to that of 100 $\mu\text{S}/\text{cm}$ is more likely result of contribution of tungstate-catalyzed oxidation of nonylphenol by H_2O_2 to the total degradation of nonylphenol by the discharge at 500 $\mu\text{S}/\text{cm}$.

Nevertheless, since nonylphenol removal by the discharge could be described by the first order kinetic (Fig. 4) this suggests that degradation of nonylphenol is mainly dependent on the action of oxidation agent(s) that is/are produced at constant (zero-order) rate by the discharge (such as OH, H or O radicals, H_2O_2 , H_2 , O_2 etc.). It is apparent that among them OH radical is the most likely species to take place in degradation of nonylphenol by the discharge. However, it is also possible that atomic oxygen produced by $\text{WO}_4^{2-}/\text{H}_2\text{O}_2$ catalytic process might be involved in the oxidation of nonylphenol.

Fig. 5 shows a proposed scheme for possible mechanism of nonylphenol oxidation by hydroxyl radical. Since OH· radical reacts with aromatic hydrocarbons predominantly by the electrophilic addition on the C=C double bonds at aromatic ring, initially OH adducts

nonyldihydroxycyclohexadienyl radicals (NDHCD·) (2) are formed. In the presence of oxygen NDHCD· radical may form organoperoxy radical. The decay of such transients leads largely through the elimination of HO₂· radical to the hydroxylated products of nonylphenol, i.e. 2-hydroxy-4-nonylphenol (3) or also to the direct fragmentation of aromatic ring of nonylphenol. The isomeric distribution of the hydroxylated products depends on the orientation of the OH· radical attack on the aromatic ring, which is directed by the phenol substitution. In case of nonylphenol, OH· attack on bisubstituted aromatic ring is directed to the *ortho*-position with respect to the OH group due to the stronger directory effect of this group than that of alkyl group.

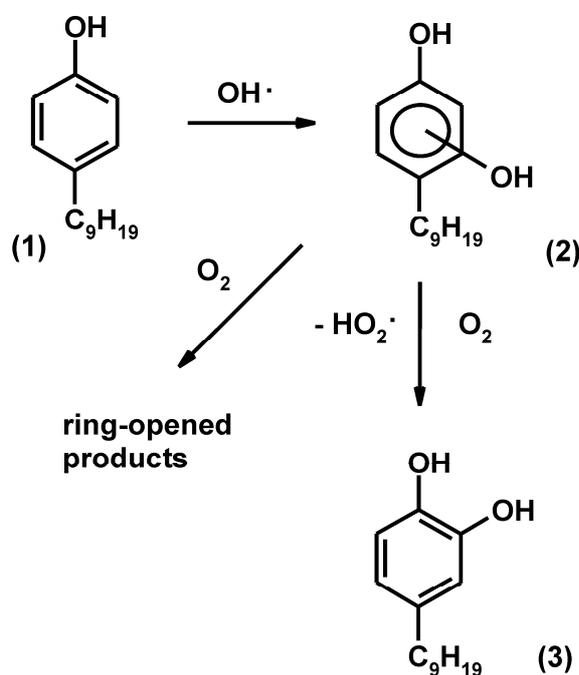


Fig. 5 Proposed scheme of oxidation of nonylphenol by OH radical attack.

Thus, 2-hydroxy-4-nonylphenol should be the main primary oxidation by-product of nonylphenol degradation by the pulsed corona discharge in water. However, to prove existence of this product in the reaction mixture of nonylphenol was not successful yet. One reason is that technical mixture of nonylphenol consists of many different nonylphenol isomers (about 22 isomers are known [9]). Porous graphitic carbon chromatography [10] that was used in this work allows high degree of separation of nonylphenol technical mixture, which is much better compared to classical C18 silica packed columns (8 peaks were separated from nonylphenol mixture using Hypercarb column, see Fig. 2). However, there are no standards available on the market for individual nonylphenol isomers as well as for proposed

nonylphenol degradation by-product. This limits possibility to further evaluate mechanisms of plasmachemical degradation of nonylphenol induced by the corona discharge in water.

4. Conclusion

The results presented in this paper showed that nonylphenol can be removed by pulsed corona discharge in water. Degradation was tested at two different solution conductivities. It was shown that with higher solution conductivity the rate of nonylphenol removal increases. This might be due to presence of tungstate ions released from tungsten high voltage electrode in water, which might be also involved in the oxidation of nonylphenol by WO₄²⁻/H₂O₂ catalytic process. OH radical attack was proposed as possible mechanism of nonylphenol degradation by the discharge. Further experiments will be made to better understand the reaction mechanism, influence of discharge on individual isomers of nonylphenol and to find possible byproducts

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