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COMPARISON OF ADVANCED OXIDATION PROCESSES FOR THE DESTRUCTION OF 2,4-DINITROPHENOL

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Abstract. Several advanced oxidation processes such as hydrogen peroxide photolysis, the Fenton treatment, photo-Fenton treatment, and ozonation combined with hydrogen peroxide and UV-radiation for the destruction of 2,4-dinitrophenol were studied. Advanced oxidation processes, especially the Fenton treatment, were found to be effective for the degradation of 2,4-dinitrophenol and removal of toxicity. According to the *Daphnia magna* acute toxicity test, advanced oxidation led to complete detoxification of 2,4-dinitrophenol. Also a high degree of nitrogen mineralization during advanced oxidation was achieved.

Key words: advanced oxidation processes, 2,4-dinitrophenol, destruction, toxicity, biodegradability, nitrogen mineralization.

INTRODUCTION

Nitrophenols are common components of industrial effluents and have been detected in urban and agricultural waste. 2,4-Dinitrophenol (2,4-DNP) is the most important of the six possible dinitrophenol forms. It is used as a wood preservative, for example, in the commercial product Triolit (80% NaF, 15% 2,4-DNP, 5% $Na_2Cl_2O_7$), in the production of 2,4-diaminophenol, in the medical treatment of obesity, and as a pesticide [1]. 2,4-DNP is also used as an intermediate to make dyes, photochemicals, and explosives and as an indicator for the detection of potassium and ammonium ions [2]. It may enter the environment from industrial discharges, spills, or possibly as a breakdown product of certain pesticides containing 2,4-DNP moieties [3]. 2,4-DNP exists as a yellowish crystalline solid, is soluble in water (5.6 g L^{-1} at 18 °C), and is volatile with steam [4]. It has strong acid properties; its pK_a value is 4.03 [3].

2,4-DNP is considered to be highly toxic to humans, with a lethal oral dose of 14 to 43 mg kg^{-1} [5]. The acute effects of 2,4-DNP in humans through oral exposure consist of nausea, vomiting, sweating, dizziness, headaches, and loss of weight [5]. Short-term animal tests, such as the LC_{50} (median lethal concentration) tests in rats, mice, and zooplankton (*Daphnia magna*), demonstrate its high acute toxicity. LC_{50} for mice, rats, and cats are 45, 30, and 75 mg kg^{-1}, respectively [6, 7]. LC_{50} for *Daphnia magna* is 4.1 mg L^{-1} in a 48-h test and 4.5 mg L^{-1} in a 24-h test [8]. Long-term oral exposure to 2,4-DNP in humans and animals has resulted in the formation of cataracts and skin lesions and has caused effects on the bone marrow, central nervous system, and cardiovascular system [5]. The available animal studies report fetal growth inhibition, but no birth defects in the offspring of animals fed 2,4-DNP [9].

In the natural environment, phenol derivatives are toxic and refractory pollutants. Moreover, phenols are only partly biodegradable and, therefore, they are not easily removed in biological wastewater treatment plants. That is why there is a need to develop effective methods for the degradation of these pollutants, either to less harmful compounds or to their complete mineralization.

Advanced oxidation processes (AOP), which involve the in situ generation of highly potent chemical oxidants such as the hydroxyl radical ($OH^{\bullet}$), have recently emerged as an important class of technologies for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water and air [10].

Recently the application of AOP for the treatment of phenols has been intensively studied. These studies have suggested a wide variety of AOP for the destruction of phenols, such as the Fenton and photo-Fenton treatments [11–13], hydrogen peroxide photolysis [14], combination of ozone with ultraviolet (UV) radiation [14–17], and also combination of sonolysis and ozonolysis [18]. These studies were mainly devoted to the degradation of phenol (oxybenzene) and chlorophenols.

Only a few studies using AOP for the destruction of 2,4-DNP have been published. Lipczynska-Kochany [19, 20] indicated that photolysis in the presence of hydrogen peroxide and the Fenton (dark) reaction are effective in oxidizing aqueous 2,4-DNP. Stover et al. [21] studied the effect of ozone on the biodegradability of 2,4-DNP and found that ozone increases slightly the biodegradability of 2,4-DNP. Tanaka et al. [22] studied the photocatalytic degradation of 2,4-DNP in aqueous TiO_2 suspension and reported a significant decomposition of 2,4-DNP.

The present study was focused on the destruction of 2,4-DNP with O_3, O_3/H_2O_2, $O_3/UV/H_2O_2$, UV/H_2O_2, and Fenton and photo-Fenton oxidation processes. Preliminary oxidation experiments with the selected AOP were followed by a comparative assessment of their performance in terms of the kinetic parameters of 2,4-DNP removal in water, possible toxicity of the reaction by-products, and the impact on the biodegradation of 2,4-DNP.

MATERIALS AND METHODS

2,4-DNP, purchased from Aldrich Co, was of analytical grade. The solutions were prepared dissolving 2,4-DNP in twice-distilled water. The initial concentration of 2,4-DNP in all experiments was 0.4 mM. Solutions were treated at different pH values. The adjusting of pH was done with 0.1 and 1.0 N solution of H_2SO_4 or 0.1 and 1.0 N NaOH.

The ozonation experiments were carried out in semicontinuous bubble column with a volume of 0.8 L (18 cm high and 8.0 cm in diameter). A mixture of ozone gas and air produced by a laboratory ozone generator was bubbled through the aqueous solution of nitrophenol. In all experiments the ozone concentration in the feed-gas was kept at 0.50 ± 0.02 mg L^{-1} (if not mentioned differently) and the gas flow rate at 1.0 L min^{-1}. The initial and residual concentrations of ozone in the gas phase were measured using a Specord UV/VIS (Carl Zeiss, Jena, GDR) spectrophotometer (λ = 258 nm). The volume of fresh 2,4-DNP solution in the reactor was 0.6 L. The UV-radiation intensity of the low pressure UV-lamp located inside the bubble column in the quartz tube as measured with potassium ferrioxalate actinometry [23] was 0.758 ± 0.006 μEinstein s^{-1}.

In the Fenton and photo-Fenton treatment the pH was adjusted to 3.0. A standard procedure consisted of treating 0.7 L of fresh 2,4-DNP solution in the cylindrical glass reactor with magnetic stirring. Fe^{2+} and H_2O_2 at concentrations of 0.4 and 4 mM, respectively, were used in these experiments. The reaction was stopped by adding 10% aqueous solution of Na_2SO_3. The UV-radiation intensity measured with potassium ferrioxalate actinometry [23] was 3.315 ± 0.104 μEinstein s^{-1} (a 10 W OSRAM lamp was located inside the bubble column in the quartz tube). Photolysis in the presence of hydrogen peroxide was carried out under the same conditions. All experiments were carried out at 20 ± 1 °C.

The concentration of hydrogen peroxide was measured spectrophotometrically (Specord UV/VIS) at 410 nm as a complex with Ti^{4+} [24].

After the Fenton and photo-Fenton treatment of the solutions their pH values were adjusted to approximately 9.0 using 40% NaOH. In the basic medium iron ions precipitated and after that they were filtered through a paper (blue ribbon) filter. Total iron residual concentration was measured in the treated and filtered solutions according to [25].

The progress in the degradation of 2,4-DNP was followed with a high performance liquid chromatograph (“Millichrom”, USSR) equipped with a UV-spectrophotometer (190–360 nm). A reverse phase column, filled with 5 μm Separon C18 (Chemapol, Czechoslovakia), was 64 mm in length and 2.0 mm in diameter. The isocratic method with a solvent mixture of 50% acetonitrile and 0.2% of acetic acid in water with a flow rate of 100 μL min^{-1} was used. The retention time for 2,4-DNP was 3.2 min under the experimental conditions and the detection wavelength was 260 nm.

The concentration of nitrate ions formed as a result of nitrogen mineralization of 2,4-DNP was measured with ion chromatography [26].

Acute toxicity of the treated 2,4-DNP solutions to *Daphnia magna* (Cladocera, Crustacea) was studied. The *Daphnia* clone used was of Finnish origin (*Daphnia magna* EF) from the North Savo Regional Environmental Centre in Kuopio, Finland. 2,4-DNP was treated so that at least 90% conversion of the initial 2,4-DNP to products was achieved. The living conditions were kept optimal and a 24-h toxicity test was carried out according to [27]. EC_{50} (median effective concentration) and their 95% confidence limits were calculated on the basis of the experimental data for both initial and treated solutions.

The chemical oxygen demand (COD) was determined by the closed reflux titrimetric method [25]. In addition, the initial and treated solutions of 2,4-DNP were analysed to determine the 7-day biochemical oxygen demand (BOD_7) [25]. Dissolved oxygen was measured before and after incubation with MARVET JUNIOR oxygen analyser Model MJ97.

RESULTS AND DISCUSSION

Changes in the initial concentration of 2,4-DNP during hydrogen peroxide photolysis and the Fenton and photo-Fenton reactions are shown in Fig. 1. Half-lives and 90% conversion times for the degradation of 2,4-DNP calculated from the degradation curves are presented in Table 1. The degradation of 2,4-DNP followed mainly a pseudo-first order kinetics in our experiment. The regression analysis of the concentration curves versus reaction time indicated that the decomposition rate of 2,4-DNP can be described by a pseudo-first order kinetics with respect to the 2,4-DNP concentration:

$$dC_{2,4\text{-DNP}}/dt = -k_1 C_{2,4\text{-DNP}},$$

where k_1 is the pseudo-first order rate constant.

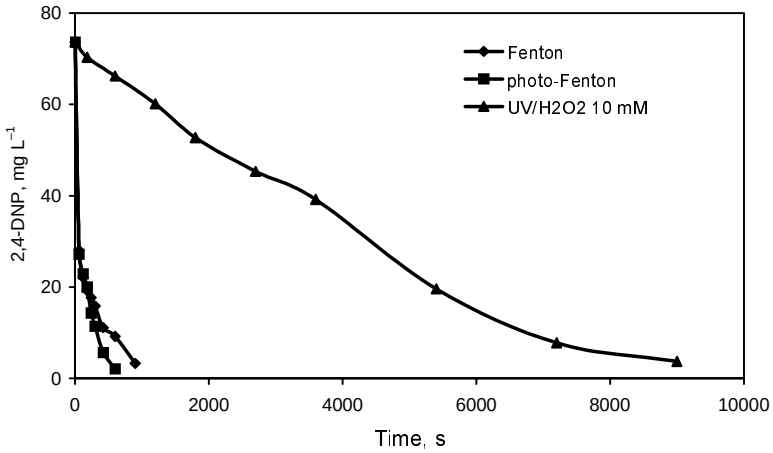

Fig. 1. Degradation of 2,4-DNP by the Fenton and photo-Fenton treatments and hydrogen peroxide photolysis at pH 3.0.

Table 1. Degradation of 2,4-DNP in 0.4 mM aqueous solution by the Fenton treatment, photo-Fenton treatment, and hydrogen peroxide photolysis: half-lives ($T_{1/2}$) and 90% conversion times ($T_{90\%}$) of 2,4-DNP

AOP	$T_{1/2}$, s	$T_{90\%}$, s
Photo-Fenton (0.4 mM Fe^{2+}/4 mM H_2O_2/UV)	40	380
Fenton (0.4 mM Fe^{2+}/4 mM H_2O_2)	40	700
UV/H_2O_2 (10 mM)	3800	7200

2,4-DNP was degraded at a high rate by the Fenton reaction (see Fig. 1). Our results demonstrated that UV radiation improves the performance of the Fenton reagent system quite significantly, and at the same concentrations of hydrogen peroxide, photo-Fenton reaction led to a more rapid decomposition of 2,4-DNP than that observed during the Fenton reaction. The addition of UV radiation to the Fenton reaction led to a 2-fold decrease in the 90% conversion time (from 12 to 6 min). Still, the application of the more complicated and therefore costly method is not reasonable, because more than 90% degradation in the Fenton treatment was reached in several minutes. The degradation of 2,4-DNP with hydrogen peroxide photolysis involved a very long reaction time if compared with the Fenton and photo-Fenton reactions, so that 90% destruction of 2,4-DNP required 2 hours of treatment.

The results of the present study demonstrated significantly higher degradation rates of 2,4-DNP in the Fenton treatment and hydrogen peroxide photolysis than those presented by Lipczynska-Kochany [20]. According to the latter the 2,4-DNP half-life in the Fenton treatment was 13 min and in H_2O_2 photolysis 200 min whilst in the present study the half-lives were less than 1 and 63 min, respectively. The reason is that a very low concentration of the catalyst was used by Lipczynska-Kochany [20] in the Fenton treatment (hydrogen peroxide: catalyst ratio of 230:1). According to the results obtained by our earlier studies [28] the degradation rates of some other nitrophenols in the Fenton reaction were significantly higher when relatively higher Fe^{2+} concentrations were used. No reasons are presented in [20] for the application of such unfavourable ratios of chemicals. Usually hydrogen peroxide:catalyst ratios from 10:1 to 40:1 are recommended as optimal for the Fenton treatment [29, 30]. In terms of hydrogen peroxide photolysis the difference in 2,4-DNP degradation rate between the data in [20] and those obtained in the present study may be explained with different UV-radiation intensities applied – the intensity was 17 times lower in [20].

The residual iron can be removed by alkalization of the solution. Iron is precipitated at pH $\geq$ 9.0 in the form of $Fe(OH)_3$. The residual concentration of total iron after alkalization and subsequent filtration was much lower than the initial concentration of Fe^{2+} added (0.4 mM) and did not exceed the value of 0.0061 mM.

The present study of ozonation and ozonation combined with UV-radiation and hydrogen peroxide for the degradation of 2,4-DNP showed that 2,4-DNP can be successfully degraded with all these methods. The decrease in the 2,4-DNP concentration in these experiments can be described by the pseudo-first order

kinetics (r^2 = 0.953–0.998), and the corresponding apparent rate constants k_1 were used for the estimation of the reaction rates (see Table 2).

Table 2. Pseudo-first order rate constants (k_1, s^{-1}) of 2,4-DNP degradation, squared correlation coefficients (r^2), and ozone consumption (Z, mM of ozone per 1 mM of 2,4-DNP degraded) for AOP

AOP	pH 2.5	pH 9.5	Z, pH 2.5	Z, pH 9.5
O_3	$k_1 = 0.865\times10^{-4}$ $r^2 = 0.988$	$k_1 = 1.15\times10^{-4}$ $r^2 = 0.993$	3.65 ± 0.21	2.92 ± 0.25
O_3/UV	$k_1 = 1.13\times10^{-4}$ $r^2 = 0.992$	$k_1 = 1.07\times10^{-4}$ $r^2 = 0.992$	3.36 ± 0.22	2.88 ± 0.21
O_3/H_2O_2 (1 mM)	$k_1 = 1.13\times10^{-4}$ $r^2 = 0.989$	$k_1 = 1.24\times10^{-4}$ $r^2 = 0.991$	2.03 ± 0.08	2.52 ± 0.16
O_3/H_2O_2 (2 mM)	$k_1 = 1.36\times10^{-4}$ $r^2 = 0.972$	$k_1 = 1.12\times10^{-4}$ $r^2 = 0.953$	2.31 ± 0.07	2.62 ± 0.09
O_3/H_2O_2 (4 mM)	$k_1 = 1.55\times10^{-4}$ $r^2 = 0.995$	$k_1 = 0.821\times10^{-4}$ $r^2 = 0.995$	1.68 ± 0.06	2.60 ± 0.21
O_3/H_2O_2 (10 mM)	$k_1 = 1.39\times10^{-4}$ $r^2 = 0.996$	–	1.87 ± 0.41	–
$O_3/UV/H_2O_2$ (2 mM)	$k_1 = 1.78\times10^{-4}$ $r^2 = 0.992$	$k_1 = 1.52\times10^{-4}$ $r^2 = 0.982$	1.42 ± 0.26	2.05 ± 0.29
$O_3/UV/H_2O_2$ (4 mM)	$k_1 = 2.26\times10^{-4}$ $r^2 = 0.998$	$k_1 = 2.01\times10^{-4}$ $r^2 = 0.986$	1.33 ± 0.15	2.06 ± 0.11
$O_3/UV/H_2O_2$ (8 mM)	$k_1 = 3.52\times10^{-4}$ $r^2 = 0.980$	$k_1 = 3.22\times10^{-4}$ $r^2 = 0.986$	0.98 ± 0.09	1.17 ± 0.13

– not determined.

General changes in the concentration of ozone in the inlet and outlet feed-gas during ozonation in the basic medium are shown in Fig. 2. Besides the changes in the concentration of 2,4-DNP and pH values, the formation of NO_3^- was followed. The initial pH of the solution decreased by 5.9 units during ozonation due to the formation of a significant amount of acidic by-products. Total nitrogen mineralization of 2,4-DNP was achieved (see Fig. 2).

The effect of pH on the degradation of 2,4-DNP with ozonation is shown in Fig. 3, which indicates a slight dependence of the degradation rate of 2,4-DNP on the pH. It is quite different from the results of the ozonation of some other phenols [12] where a significant dependence of the ozonation rate on the pH was observed.

The degradation rates of 2,4-DNP in O_3/UV treatments were quite similar to those observed in ozonation at pH 9.5 and somewhat higher than at pH 2.5 (see Table 2). A possible reason for this phenomenon is the significant UV-absorptivity of dinitrophenol at λ = 254 nm, which diminishes the part of UV radiation absorbed by ozone for $OH^\bullet$ radical formation. Also, no significant differences in the ozone consumption were observed in the O_3/UV treatment and non-accompanied ozonation at both pH values. These results are in good agreement with the results reported previously for 2,4-dichlorophenol [12].

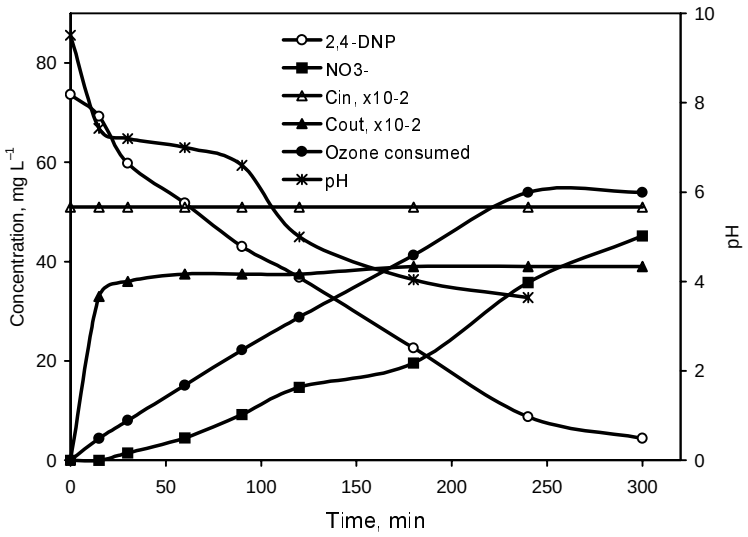

Fig. 2. Changes in the concentration of 2,4-DNP, ozone in the inlet and outlet feed-gases, ozone consumed, nitrate ion, and pH during ozonation at the initial pH 9.5.

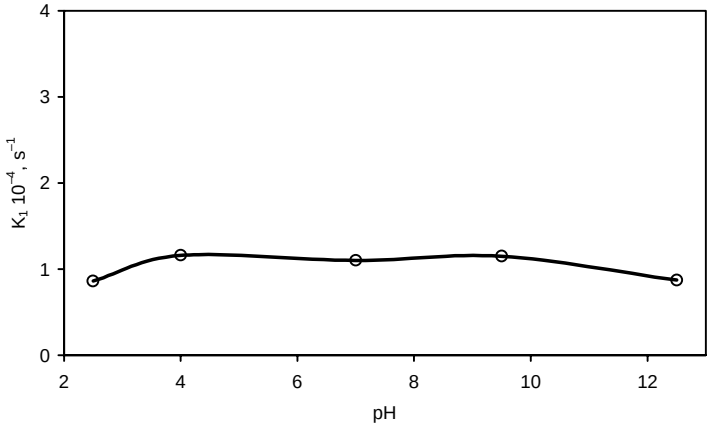

Fig. 3. 2,4-DNP degradation rate in ozonation versus the pH.

In the O_3/H_2O_2 treatment various hydrogen peroxide amounts were added to the reaction mixture. Acceleration of 2,4-DNP degradation was observed under certain treatment conditions. Figure 4 indicates that beyond a certain hydrogen peroxide concentration no further enhancement of the performance occurs. In the acidic medium the degradation rate was higher than in non-accompanied ozonation at the same pH value with the admixture of H_2O_2 from 1 to 4 mM. At the pH value of 9.5 some acceleration of the degradation of 2,4-DNP was observed only with the H_2O_2 dose of 1 mM. The introduction of 2–4 mM H_2O_2 did not enhance the degradation rate at pH 9.5 compared with ozonation, and

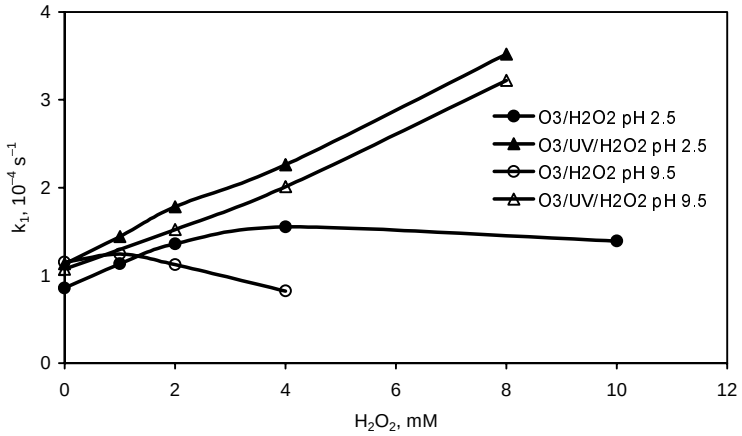

Fig. 4. First-order apparent rate constant (k_1) of 2,4-DNP degradation versus hydrogen peroxide concentration in O_3/H_2O_2 and $O_3/UV/H_2O_2$ treatments at different pH values.

even a significant deceleration was noticed. Thus, H_2O_2 admixture exceeding the optimum dose may decrease the reaction rate of the target compound with excess of H_2O_2 acting as a radical scavenger. The application of O_3/H_2O_2 treatment enabled to achieve a reduction in the ozone specific consumption as compared with non-accompanied ozonation (see Table 2). The admixture of H_2O_2 made possible a 40–50% reduction in ozone consumption when 2,4-DNP was treated in the acidic medium. The reduction in ozone consumption in the basic medium was insignificant, not exceeding 10%.

2,4-DNP degradation can be accelerated by applying a combination of $O_3/H_2O_2/UV$. Like in the previous case, the effects were definitely more significant at low pH values (see Table 2). The degradation rate of 2,4-DNP with $O_3/H_2O_2/UV$ process was definitely dependent on the concentration of H_2O_2. Figure 4 shows that the increasing of the hydrogen peroxide concentration from 2 to 8 mM clearly intensified the degradation rate of 2,4-DNP in the $O_3/H_2O_2/UV$ treatment in both media. For example, the apparent rate constant of 2,4-DNP degradation at H_2O_2 admixture of 8 mM was twice as high as that at 2 mM. Moreover, the 2,4-DNP degradation rate in the $O_3/H_2O_2/UV$ treatment was the highest among all combinations that included ozone. Ozone specific consumption could be also reduced in the $O_3/H_2O_2/UV$ treatment as compared with ozonation and other combinations (Table 2). H_2O_2 admixture of 8 mM in the $O_3/H_2O_2/UV$ treatment enabled to reduce ozone consumption to about 1 mM of ozone per 1 mM of 2,4-DNP degraded in both media. This was the lowest value for all processes under study.

Some experiments were carried out at an increased ozone concentration in the feed-gas (1.52 ± 0.05 mg L^{-1}). These results are presented in Table 3. It was ascertained that a 3-fold increase of the ozone concentration in the feed-gas (from 0.5 to 1.5 mgO_3 L^{-1}) led to some acceleration of the 2,4-DNP destruction but did not influence the ozone consumption.

Table 3. Pseudo-first order rate constants (k_1) of 2,4-DNP degradation, squared correlation coefficients (r^2), and ozone consumption (Z, mM of ozone per 1 mM of 2,4-DNP degraded) at different concentrations of ozone in the feed-gas

AOP	Inlet concentration of ozone, mg L^{-1}			
	0.50 ± 0.01		1.52 ± 0.05	
	k_1, s^{-1} (r^2)	Z	k_1, s^{-1} (r^2)	Z
O_3	0.865×10^{-4} (0.988)	3.65 ± 0.21	2.51×10^{-4} (0.993)	3.51 ± 0.17
O_3/H_2O_2 (1 mM)	1.13×10^{-4} (0.989)	2.03 ± 0.22	3.17×10^{-4} (0.993)	2.24 ± 0.20
O_3/H_2O_2 (2 mM)	1.36×10^{-4} (0.972)	2.31 ± 0.07	3.61×10^{-4} (0.992)	2.23 ± 0.21

The influence of the AOP treatment on the biodegradability of 2,4-DNP was also studied. COD and BOD_7 values of the initial and treated 2,4-DNP determined according to [25] and BOD_7/COD values are listed in Table 4. The results of the study show that the products formed during the AOP treatment are much more biodegradable than 2,4-DNP. The initial 2,4-DNP solution had COD of 83 mg L^{-1} and BOD_7 of 32 mg L^{-1} (BOD_7/COD value of 0.4). Besides the fact that COD removal (65–24%) was lower than 2,4-DNP removal ($\geq 94\%$), it can be seen that an increase in the biodegradability of 2,4-DNP was achieved. The 2,4-DNP solution was completely biodegradable after ozonation and the Fenton treatment. The treatment with other combinations also enabled to improve the biodegradability of 2,4-DNP.

Table 4. BOD_7/COD ratio for treated solutions of 2,4-DNP (initial ratio 0.4)

AOP	2,4-DNP elimination, %	BOD_7/COD, final
UV/H_2O_2 (10 mM)	96	0.6
Fenton (0.4 mM Fe^{2+}/4 mM H_2O_2)	97	0.97
O_3; pH 7.0	95	1.0
O_3/UV; pH 2.5	96	0.8
O_3/UV; pH 9.5	94	0.5

The destruction of 2,4-DNP with ozonation, O_3/H_2O_2, $O_3/UV/H_2O_2$, UV/H_2O_2, and the Fenton and photo-Fenton oxidation processes was followed by the formation of nitrate ions. In different AOP nitrogen mineralization took place at different stages of the treatment (see Fig. 5). In the Fenton and photo-Fenton treatments and hydrogen peroxide photolysis nitrogen mineralization was very slow at the initial stage and accelerated at the final stage of 2,4-DNP destruction. In some processes, for example, O_3 (pH 12.5), O_3/H_2O_2 (pH 9.5), and $O_3/UV/H_2O_2$ (pH 2.5) nitrate ion was formed quite evenly during the 2,4-DNP destruction. In ozonation and O_3/H_2O_2 at pH 2.5 the formation of NO_3^- practically coincided with

the theoretical maximum value (see Fig. 5). The degree of nitrogen mineralization also varied in a large range. Complete mineralization (97–100%) was achieved in O_3/H_2O_2 (pH 2.5), O_3 (pH 2.5), and O_3/UV (pH 9.5) treatments. In most other processes mineralization was 70–90%, except the Fenton, O_3/UV (pH 2.5), and UV/H_2O_2 processes where it was only 50–60%.

The acute toxicity of the initial and treated 2,4-DNP was studied with the *Daphnia magna* test. The median effective concentration of the initial solution of 2,4-DNP was 0.0459±0.0023 mM. All treatment processes, namely the Fenton, hydrogen peroxide photolysis, and ozonation, enabled to remove the toxicity. It was found that the detoxification of 2,4-DNP solution takes place along with its degradation. Figure 6 shows that the reduction of the toxicity took place with the progress of the ozonation of 2,4-DNP and no formation of toxic by-products was observed. Thus, advanced oxidation can be used not only for the destruction of 2,4-DNP but also, which is extremely important, for the detoxification of its aqueous solutions.

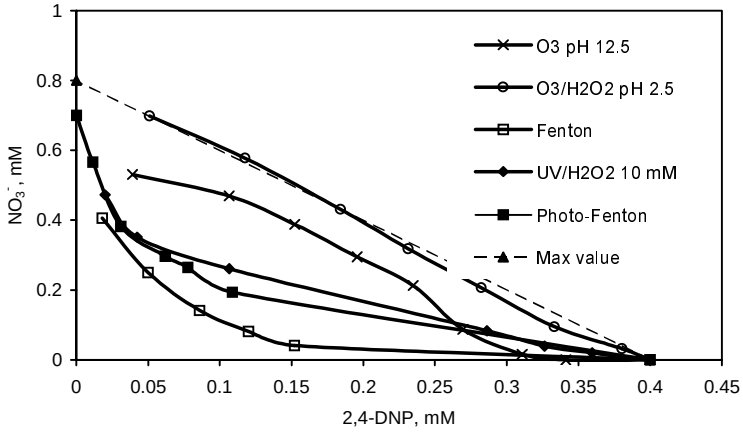

Fig. 5. Formation of nitrate ion versus destruction of 2,4-DNP with different AOP.

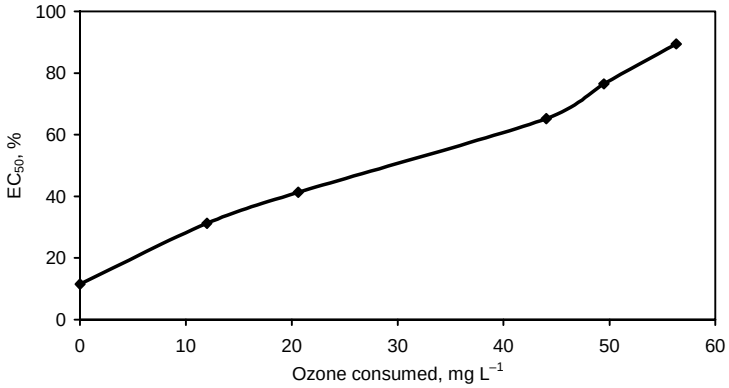

Fig. 6. Changes in the toxicity of 2,4-DNP during the ozonation at pH 2.5.

CONCLUSIONS

The destruction of 2,4-DNP with AOP such as hydrogen peroxide photolysis, the Fenton treatment, and ozonation combined with hydrogen peroxide and UV-radiation was studied. The results demonstrated that 2,4-DNP can be destructed within a few minutes with the Fenton treatment. The degradation of 2,4-DNP with hydrogen peroxide photolysis involved a very long reaction time compared with the Fenton reaction. Ozonation and ozonation combined with UV-radiation and hydrogen peroxide can be successfully applied for the degradation of 2,4-DNP. The degradation rate of 2,4-DNP with non-accompanied ozonation was slightly dependent on the pH. The degradation rates of 2,4-DNP in O_3/UV treatment were quite similar to those observed in ozonation at pH 9.5 and somewhat higher at pH 2.5. No significant differences were observed in the ozone consumption in the O_3/UV treatment and non-accompanied ozonation at both pH values. 2,4-DNP degradation can be accelerated by application of a combination of O_3/H_2O_2/UV. The degradation rate of 2,4-DNP with O_3/H_2O_2/UV is definitely dependent on the concentration of H_2O_2. Moreover, the 2,4-DNP degradation rate in the O_3/H_2O_2/UV treatment was the highest among all combinations that included ozonation. Ozone specific consumption can be also reduced in the O_3/H_2O_2/UV treatment compared with non-accompanied ozonation and other combinations.

AOP treatment enabled to improve the biodegradability of 2,4-DNP. The degree of nitrogen mineralization was from 50 to 100% in different AOP during the destruction of 2,4-DNP. AOP enabled to remove the toxicity, as the degradation by-products of advanced oxidation of 2,4-DNP were found to be nontoxic according to the *Daphnia magna* acute toxicity test.

Although all these processes led to the degradation of 2,4-DNP, the Fenton treatment was found to be the most promising way for the destruction of 2,4-DNP.

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2,4-DINITROFENOOLI EEMALDAMISEKS KASUTATAVATE TÄIUSTATUD OKSÜDATSIOONIPROTSESSIDE VÕRDLUS

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On uuritud 2,4-dinitrofenooli (2,4-DNP) eemaldamist täiustatud oksüdatsiooniprotsessidega, nagu vesinikperoksiidfotolüüs ja osoonimine vesinikperoksiidiga. Selgus, et Fentoni reagendiga töötlemisel võib 2,4-DNP eemaldada mõne minuti jooksul, 2,4-DNP lagundamine vesinikperoksiidfotolüüsil nõuab palju pikemat reaktsiooniaega.

2,4-DNP lagundamisvõimaluste võrdlemiseks kasutati osoonimisel UV-kiirgust ja vesinikperoksiidi. Ilmnes, et 2,4-DNP võib edukalt lagundada kõigi uuritud täiustatud oksüdatsiooniprotsessidega. 2,4-DNP lagunemise kiirus oli O_3/UV töötlusel ligikaudu sama, mis osoonimisel pH 9,5 korral, kuid mõnevõrra suurem kui pH 2,5 puhul. 2,4-DNP lagunemist võib kiirendada, rakendades kombinatsiooni O_3/H_2O_2/UV (kiirus sõltus täielikult H_2O_2 kontsentratsioonist). Seejuures oli 2,4-DNP lagunemiskiirus O_3/H_2O_2/UV töötlusel kõrgeim ja osooni erikulu madalaim võrreldes kõigi teiste uuritud osoonikombinatsioonidega.

Täiustatud oksüdatsiooniprotsesside rakendamine võimaldas tõsta 2,4-DNP biodegradatsiooni. Lämmastiku mineralisatsiooni aste 2,4-DNP lagundamisel oli erinevate oksüdatsiooniprotsesside puhul 50%-st kuni 100%-ni. Täiustatud oksüdatsiooniprotsessid kõrvaldasid ka toksilisust: lagundamise kõrvalproduktid osutusid *Daphnia magna* akuutse toksilisuse testi järgi mittemürgisteks.

Kuigi kõik uuritud protsessid viisid 2,4-DNP lagundamisele, osutus Fentoni reaktiivi kasutamine 2,4-DNP eemaldamisel kõige perspektiivsemaks.