Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20778

77 (2017) 237–246
May

Degradation of nitroaromatic compounds in subcritical water: application of response surface methodology

Berkant Kayan[a,*], Sema Akay[a], Belgin Gözmen[b], A. Murat Gizir[b], Muhammet Demirel[b], Dimitrios Kalderis[c]

[a]*Department of Chemistry, Arts and Science Faculty, Aksaray University, Aksaray, Turkey, Tel. +903822882693; emails: berkantkayan@gmail.com (B. Kayan), sema.akay7@gmail.com (S. Akay)*
[b]*Department of Chemistry, Arts and Science Faculty, Mersin University, Mersin, Turkey, emails: bgozmen@yahoo.com (B. Gözmen), agizir@mersin.edu.tr (A. Murat Gizir), m.demirel84@hotmail.com (M. Demirel)*
[c]*Department of Environmental and Natural Resources Engineering, School of Applied Sciences, Technological and Educational Institute of Crete, Chania, Crete, Greece, email: dkalderis@chania.teicrete.gr*

Received 4 November 2016; Accepted 3 April 2017

ABSTRACT

In this study, subcritical water has been used as a medium for degradation of 2,4-dinitrotoluene (2,4-DNT), 4-nitrotoluene (4-NT) and 2-amino-4-nitrotoluene (2-A-4-NT). The effect of temperature, oxidant concentration and time were studied and the optimal combination of reaction parameters was established using response surface methodology in a Box-Behnken design. Of all the parameters examined, temperature showed the most positive effect on the degradation of the nitroaromatic compounds. Optimal reaction conditions were found to be a temperature of 240°C, 210°C and 236°C, time of 180, 178 and 172 min, oxidant concentration of 100, 99.64 and 99.61 mM for 2,4-DNT, 4-NT and 2-A-4-NT, respectively. Since high-temperature was applied, the possibility of formation of subcritical degradation products existed; therefore, total amounts of degraded nitroaromatic compounds and formed intermediate products were determined by gas chromatographic–mass spectrometric analysis.

Keywords: Subcritical water; Degradation; Nitroaromatic compounds; Response surface methodology; Box-Behnken

1. Introduction

Historically, 2,4,6-trinitroluene (TNT) has been the most widely used military explosive, due to the low manufacturing cost, safety of handling and high explosive power. However, in many cases of military conflict, residual TNT from artillery shells, bombs and other munitions has been found to contaminate soil and adjacent surface waters. Wastewater from equipment washing processes after munitions filling or demilitarization operations can also pose an environmental threat. Several processes – dissolution, microbial transformations, sorption and others – control the fate of TNT on soil and water. The interactions between TNT and these processes are complex and often produce different degradation routes, which may lead to by-products of higher toxicity. The environmental fate and toxicity of TNT and its metabolites have been thoroughly reviewed [1–4].

2,4-Dinitrotoluene (2,4-DNT) is a synthetic substance used primarily as a chemical intermediate for the production of toluene diisocyanate. It is also used in the production of TNT, dyes and polyurethane foams. 2,4-DNT has been found in the soil, surface water and groundwater, air around manufacturing facilities and contaminated waste sites. It slowly decomposes in water by microbial organisms and can be degraded by sunlight in surface water. 2,4-DNT does not adsorb strongly to the soil particles. Therefore, it can move

---

* Corresponding author.

1944-3994/1944-3986

from soil into groundwater, where it can contaminate drinking water [5].

4-Nitrotoluene (4-NT) and 2-amino-4-nitrotoluene (2-A-4-NT) are by-products produced during the aerobic microbial reduction of TNT. The microbial degradation of TNT starts with the reduction of two nitro groups to amines – the reduction of the third nitro group requires anaerobic conditions [3]. The enzymes that catalyze these reactions are called nitroreductases – each one of them leads to a different degradation pathway. Therefore, near-complete reduction of TNT can only be achieved by consortia of enzymes and rarely occurs in nature. Khan et al. [4] analyzed the toxicological profile of TNTs microbial intermediates and concluded that although aerobic TNT degradation pathways may be advantageous from a toxicological point of view, anaerobic degradation may be preferred over aerobic degradation because of its potential for complete TNT mineralization.

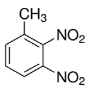
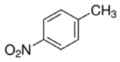
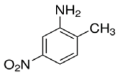
To date, research groups worldwide have mainly focused on the degradation of TNT itself both on soil and on wastewater, however, the published literature on the environmental fate and treatment methods of TNT by-products and metabolites is much more limited. Research on these substances has mostly focused on advanced oxidation processes and bacterial degradation. 2,4-DNT has been studied more compared with 4-NT and 2-A-4-NT. Chen and Su [6] combined persulfate anions with ultrasonic irradiation and determined that complete elimination of 2,4-DNT can be achieved under the optimal conditions of ultrasonic power intensity at 126 W cm^{-2}, temperature of 45°C and persulfate anion concentration of 2 wt%. The degradation pathway they proposed, included an oxidation step to form dinitrobenzoic acid, followed by a decarboxylation step to form 1,3-dinitrobenzene, before mineralization occurred. The same team combined an electro-Fenton process with ultrasonic radiation to achieve complete mineralization of 2,4-DNT [7]. Fenton treatment was also the choice of Jho et al. [8], who studied the effect of Pb and Cu (often present in explosives-contaminated sites) in 2,4-DNT degradation. Their results showed that the use of Fenton reagents to degrade 2,4-DNT resulted in significant mobilization of Pb and Cu in soil. Therefore, prior removal of Pb and Cu was recommended.

Liu et al. [9] prepared a series of mesoporous photocatalysts and tested their performance on a wastewater containing 2,4-DNT, 2,6-DNT and 2,3-DNT. After 240 min irradiation time and 1 wt% doping of yttrium and lanthanum, >80% degradation of each of the DNT isomers was achieved. Using solar simulation equipment, Luning Prak et al. [10] investigated the photocatalysis rates of 2,4-DNT and 2,6-DNT and their metabolites in marine waters. The rates of 2,4-DNT and 2,6-DNT photolysis were found slower than those of their more toxic by-products dinitrobenzyl alcohol and dinitrobenzaldehyde, respectively. However, other DNT by-products did not undergo photolysis significantly – therefore, they may accumulate in marine environments if not transformed by other processes such as microbial decay. Finally, they concluded that pH, temperature and nitrate concentration variations over a range of environmentally relevant values did not affect the DNTs photolysis rates [11].

Bioremediation of contaminated soils is often based on the activity of microorganisms to slowly decrease the contaminant levels. In the case of DNTs, several bacteria strains have been reported to be effective in reducing the nitro groups to amines. *Shewanella marisflavi* EP1 [10], *Pseudomonas putida* NDT1, *Pseudomonas fluorescens* NDT2, *Bacillus cereus* NDT4, *Achromobacter* sp. NDT3 [12,13], *Bacillus subtilis*, *Burkholderia phytofirmans*, *Pseudomonas mandelii* [14] and *Rhodococcus pyridinivorans* NT2 [15] have been successfully used in laboratory-scale tests. It is safe to conclude that mixtures of microbial strains are able to treat more effectively and degrade DNTs faster, compared with individual strains. However, more work is required to understand the molecular basis of microbial catabolic sequences toward designing a full-scale bioremediation strategy that will be applied in the field [16]. Phytoremediation methods are commonly used for the removal of explosives in soil and wastewater. Podlipná et al. [17] studied the ability of hemp, flax, sunflower and mustard plants to grow on soils contaminated with 2,4-DNT. At concentrations up to 1 mg L^{-1}, the crop plants showed adequate tolerance to the explosive substance, indicating their potential for treating soils contaminated with low concentrations of 2,4-DNT. Other methods for the degradation of TNT by-products and metabolites include electrochemical reduction [18], biochar-based reduction using dithiothreitol [19] and hydrothermal carbonization at 200°C [20].

In this study, a static experimental setup using subcritical water (hot water under enough pressure to maintain the liquid state) was used to degrade model solutions of 2,4-DNT, 4-NT and 2-A-4-NT (Table 1). Subcritical water has been successfully used in the past to remove and degrade various contaminants on soil and wastewater, such as polyaromatic hydrocarbons, dioxins, dyes and explosives [21–23]. With respect to TNT by-products and metabolites, only Oh et al. [24] have studied the subcritical water degradation of 2,4-DNT on synthesized contaminated soil. The authors prepared a 50 mg kg^{-1} DNT contaminated soil and processed it at temperatures ranging from 100°C to 300°C. At 300°C, no DNT was detected after 40 min treatment. However, it is important to note that the behavior of naturally contaminated soil is different from artificially contaminated soil, where the mass transfer limitation (from the inner pores of soil to solution) is practically non-existent [22]. In this work, the experimental parameters were optimized using response surface methodology (RSM). RSM is a combination of mathematical and statistical techniques used to study the effect of several variables influencing the responses by varying them simultaneously and carrying out limited number of experiments.

Table 1
Chemical structures and properties of nitroaromatic compounds

Compound	Structure	Chemical formula	Molar mass (g mol^{-1})
2,4-Dinitrotoluene		$C_7H_6N_2O_4$	182.134
4-Nitrotoluene		$C_7H_7NO_2$	137.14
2-Amino-4-nitrotoluene		$C_7H_8N_2O_2$	152.12

The validity of the method has been well established in various experimental setups and conditions, including subcritical water processes [25–28]. Finally, degradation pathways were determined and proposed for all compounds.

2. Materials and methods

2.1. Materials

2,4-DNT, 4-NT and 2-A-4-NT were purchased from Sigma-Aldrich (Steinheim, Germany). HPLC grade methanol and acetic acid were obtained by Merck Chemical (Istanbul, Turkey). Ultrapure water (18.2 MΩ cm^{-1}) was obtained from MilliPore Milli-Q Gradient water purification system and purged using nitrogen. The sample solutions were prepared at the required concentrations by serial dilution of the stock solution with 18 µS cm^{-1} ultrapure water. Hydrogen peroxide 35% (Merck, Turkey) was used as the oxidant.

2.2. Methods

Subcritical water experiments were described in detail in Yang et al. [29], Yang and Hildebrand [30] and Kayan and Gözmen [31]. A brief overview of the process is as follows: stainless steel vessels (7.07 mL capacity with 9 cm × 1 cm internal diameter) were used for the degradation process. Nitroaromatics were prepared at concentrations of 18.2, 13.7 and 15.2 mg L^{-1} for 2,4-DNT, 4-NT and 2-nitrotoluidine, respectively. Both ends of the vessels were wrapped with two layers of Teflon tape and one end was tightly sealed with an end cap. Each vessel was loaded with 5 mL nitroaromatic solution, H_2O_2 was added to the vessel (according to the required oxidant concentration, 50–75 and 100 mM) and capped. The experiments were performed in triplicate for all reaction conditions. Vessels were placed in a Shimadzu GC-9A oven for heating. All experiments were performed at a temperature range of 100°C–250°C for 30, 105 and 180 min. Subsequent to the desired reaction time, the vessels were removed from the oven and allowed to cool at room temperature.

All measurements were performed on an Agilent 1200 Infinity Series HPLC system (Santa Clara, CA, USA) equipped with 1200 series binary pump (G1310A), microvacuum degasser (G1322A), standard auto sampler (G13229A), thermostated column compartment (G1316A) and multi-wavelength detector (G1365D). Separation was achieved on a Kinetex C_{18} RP column (100 Å, 50 mm × 4.6 mm, 5 µm, Phenomenex, Torrance, CA, USA) maintained at 25°C. The mobile phase used was 60/39 v/v methanol/water to which 1% acetic acid was added. The flow rate was set at 1.20 mL min^{-1} and injection volume was 10 µL. UV detection was set at 280 nm. The mineralization of nitroaromatic solution was monitored by the reduction of the total organic carbon (TOC), which was measured on a Shimadzu TOC-VCPN model TOC analyzer.

The gas chromatographic–mass spectrometric (GC–MS) analysis was performed using the 5890A Agilent model gas chromatograph, interfaced with an electron capture and 5975C mass selective detector. The aqueous solutions were extracted three times with 15 mL dichloromethane. A 3 µL sample was used for the GC–MS analysis. An HP5-MS capillary column (30 m × 0.25 mm × 0.25 µm) was used as the analytical column. Helium was used as the carrier gas with a flow rate of 2 mL min^{-1}. The GC injection port temperature was set at 250°C (split mode = 1/5), and the column temperature was fixed at 70°C for 5 min. Subsequently, the column was sequentially heated at a rate of 5°C min^{-1} to 120°C and held for 1 min, at a rate of 8°C min^{-1} to 200°C and held for 5 min and at a rate of 10°C min^{-1} to 280°C and held for 10 min. The MS detector was operated in the electron impact mode (70 eV).

3. Results and discussion

3.1. Experimental design

RSM was used to determine the optimal experimental condition for target response. This is accomplished by changing one parameter when others are kept at a constant value. The advantage of RSM allows for a low number of required experiments which is advantageous in terms of time and cost. It is important to determine which parameters will be effective on an experimental response. In this study, temperature (T), oxidant concentration (C_{ox}) and time (t) were chosen as the process parameters (independent variables) to develop predictive models for simulation and optimization of the oxidation of nitro compounds. Box-Behnken design was used to identify the relationship between the response (decomposition %) and process variables. Table 2 presents the parameters and coded/actual operating ranges covered in RSM.

A total of 17 runs were performed by Design Expert software in duplicate due to the Box-Behnken Design (BBD) matrix in Table 3 and average values were used in data analysis. The number of runs was calculated by using the following formula:

$$N = k^2 + k + \mathrm{cp} \tag{1}$$

where k is the factor number and cp is the replicate number of the central point [32]. The RSM model that includes linear and quadratic variables as well as interaction terms is given in Eq. (2):

$$\begin{aligned}\text{Response}\left(\text{Decomposition }\%\right) = \beta_0 + \sum_{0=1}^{k}\beta_i x_i + \sum_{0=1}^{k}\beta_{ii}x_i^2 \\ + \sum_{i=1}\sum_{j=1}\beta_{ij}x_i x_j + \varepsilon\end{aligned} \tag{2}$$

The obtained data were evaluated by analysis of variance (ANOVA) and the results are shown in Table 4. It can be seen that the proposed models for all three compounds were highly significant depending on a very low p values (<0.0001). On the contrary, very high F values (87.42, 126.75 and 110.51 for 2-A-4-NT, 4-NT and 2,4-DNT, respectively) indicate that the proposed models adequately explain the variation in the data and the estimated factors are real. Furthermore, the F

Table 2
Coded and actual levels of independent variables in the BBD

Coded variables	Temperature, °C	Oxidant concentration, mM	Time, min
–1	100	50	30
0	175	75	105
+1	250	100	180

value for temperature was at least tenfold those of time and oxidant concentration, indicating that temperature is by far the process-controlling variable. The *F* values for time and oxidant concentration are of the same order, indicating that both a similar effect to the decomposition process.

The coefficient and adjusted coefficient of determination (R^2 and R^2_{adj}) illustrate the adequacy of a model if they are close to 1. In systems involving three variables, the predictive equation for the decomposition is obtained from the following second-order polynomial equations given below for 2-A-4-NT, 4-NT and 2,4-DNT, respectively:

$$\begin{aligned}\text{Decomposition }\% = {} & +74.60 + 33.63T + 5.38C_{ox} + 7.75t + 1.75TC_{ox} \\ & + 1.00Tt + 0.50C_{ox}t - 17.68T^2 - 3.67C_{ox}^2 - 2.42t^2\end{aligned} \tag{3}$$

$$\begin{aligned}\text{Decomposition }\% = {} & +64.80 + 29.25T + 5.75C_{ox} + 4.75t + 3.75TC_{ox} \\ & + 1.25Tt - 0.25C_{ox}t - 20.28T^2 + 1.23C_{ox}^2 + 3.72t^2\end{aligned} \tag{4}$$

$$\begin{aligned}\text{Decomposition }\% = {} & +57.20 + 30.63T + 4.63C_{ox} + 4.50t + 1.00TC_{ox} \\ & + 2.25Tt + 0.75C_{ox}t - 19.10T^2 + 3.40C_{ox}^2 + 3.65\end{aligned} \tag{5}$$

The negative and positive signs of the regression coefficients indicate the dissident and synergistic effects of each variable. Pareto chart could be used to see these effects more clearly [33,34]. This chart indicated that temperature is the

Table 3
Box-Behnken design for subcritical water oxidation of 2-NT, 4-NT and 2,4-DNT and observed responses

Run	Temperature (T) °C	Oxidant (C_{ox}) mM	Time (t) min	Decomposition %		
				2-A-4-NT	4-NT	2,4-DNT
1	100	50	105	17	12	10
2	250	50	105	77	63	65
3	100	100	105	26	21	16
4	250	100	105	93	87	75
5	100	75	30	15	15	5
6	250	75	30	84	71	66
7	100	75	180	23	23	13
8	250	75	180	96	84	83
9	175	50	30	54	62	57
10	175	100	30	62	69	66
11	175	50	180	74	71	61
12	175	100	180	84	77	73
13	175	75	105	75	66	58
14	175	75	105	76	65	57
15	175	75	105	75	64	58
16	175	75	105	74	65	56
17	175	75	105	73	64	57

Table 4
ANOVA for the response surface quadratic models for wet peroxide oxidation of 4-NT, 2-A-4-NT and 2,4-DNT

Compound	Source	Degrees of freedom	Sum of squares	Mean square	*F* value	*p* Value
2-A-4-NT	Model	11,234.17	9	1,248.24	87.42	<0.0001
	Temperature	9,045.13	1	9,045.13	633.48	<0.0001
	Oxidant concentration	231.12	1	231.12	16.19	0.0050
	Time	480.50	1	480.50	33.65	0.0007
	Residual	99.95	7	14.28		
	Lack of fit	94.75	3	31.58	24.29	0.0050
	Pure error	5.20	4	1.30		
	Total	11,334.12	16			
4-NT	Model	9,113.32	9	1,012.59	126.75	<0.0001
	Temperature	6,844.50	1	6,844.50	856.79	<0.0001
	Oxidant concentration	264.50	1	264.50	33.11	0.0007
	Time	180.50	1	180.50	22.59	0.0021
	Residual	55.92	7	7.99		
	Lack of fit	52.00	3	17.33	17.69	0.0090
	Pure error	3.92	4	0.98		
	Total	9,169.24	16			
2,4-DNT	Model	9,455.69	9	1,050.63	110.51	<0.0001
	Temperature	7,503.13	1	7,503.13	789.21	<0.0001
	Oxidant concentration	171.13	1	171.13	18.00	0.0038
	Time	162.00	1	162.00	17.05	0.0044
	Residual	66.55	7	9.51		
	Lack of fit	63.75	3	21.25	30.36	0.0033
	Pure error	2.80	4	0.70		
	Total	9,522.24	16			

4-NT: $R^2 = 0.9912$, $R^2_{\text{adj}} = 0.9798$, CV% = 5.96, adequate precision = 28.55.
2-A-4-NT: $R^2 = 0.9939$, $R^2_{\text{adj}} = 0.9861$, CV% = 4.91, adequate precision = 32.29.
2,4-DNT: $R^2 = 0.9930$, $R^2_{\text{adj}} = 0.9840$, CV% = 5.98, adequate precision = 30.39.

most important parameter for all three compounds (Fig. 1). The impacts of the remaining two parameters (C_{ox} and *t*) were considered as equal.

The normalized decomposition of 2-A-4-NT, 4-NT and 2,4-DNT by subcritical water oxidation was predicted by use of Eqs. (3)–(5). The experimental results and predicted decomposition % values were in good agreement (Fig. 2).

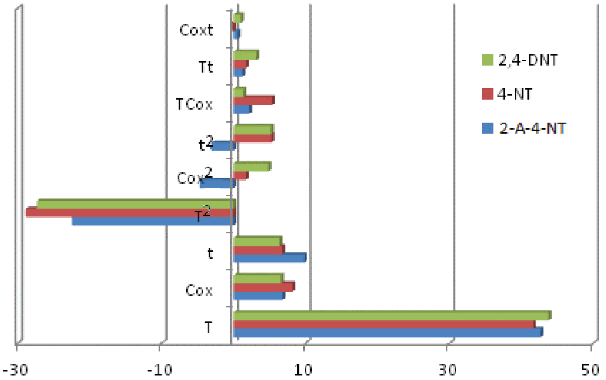


Fig. 1. Pareto chart.

According to R^2 values, 99% of the variations of decomposition % for the three compounds were explained by the model obtained and only 0.60%–0.90% of the variation was not explained by these equations.

3.2. Influence of temperature and oxidant concentration on the degradation efficiency

To show the type and size of influence of the independent variables and their interactions on the decomposition process, 3D response surfaces were drawn. Fig. 3 represents the effect of temperature and H_2O_2 concentration on the decomposition of the nitro compounds, at constant time (175 min). Temperature has a significant influence on the decomposition for all three compounds and played a critical role, earlier observed in Fig. 1. According to Figs. 3(a)–(c), as the temperature is raised, so does the decomposition efficiency. At the lowest oxidant concentration of 50 mM, raising the temperature from 100°C to 250°C resulted in a decomposition % increase of 60%, 50%, 55% for 2-A-4-NT, 4-NT and 2,4-DNT, respectively. A similar trend was observed at the highest oxidant concentration of 100 mM. On the other hand, at the lower end of the temperature range (100°C–160°C), increasing the oxidant concentration had no effect on the decomposition. Above 160°C, the increase in oxidant concentration had a minor effect, in all cases. This clearly shows that in the experimental temperature

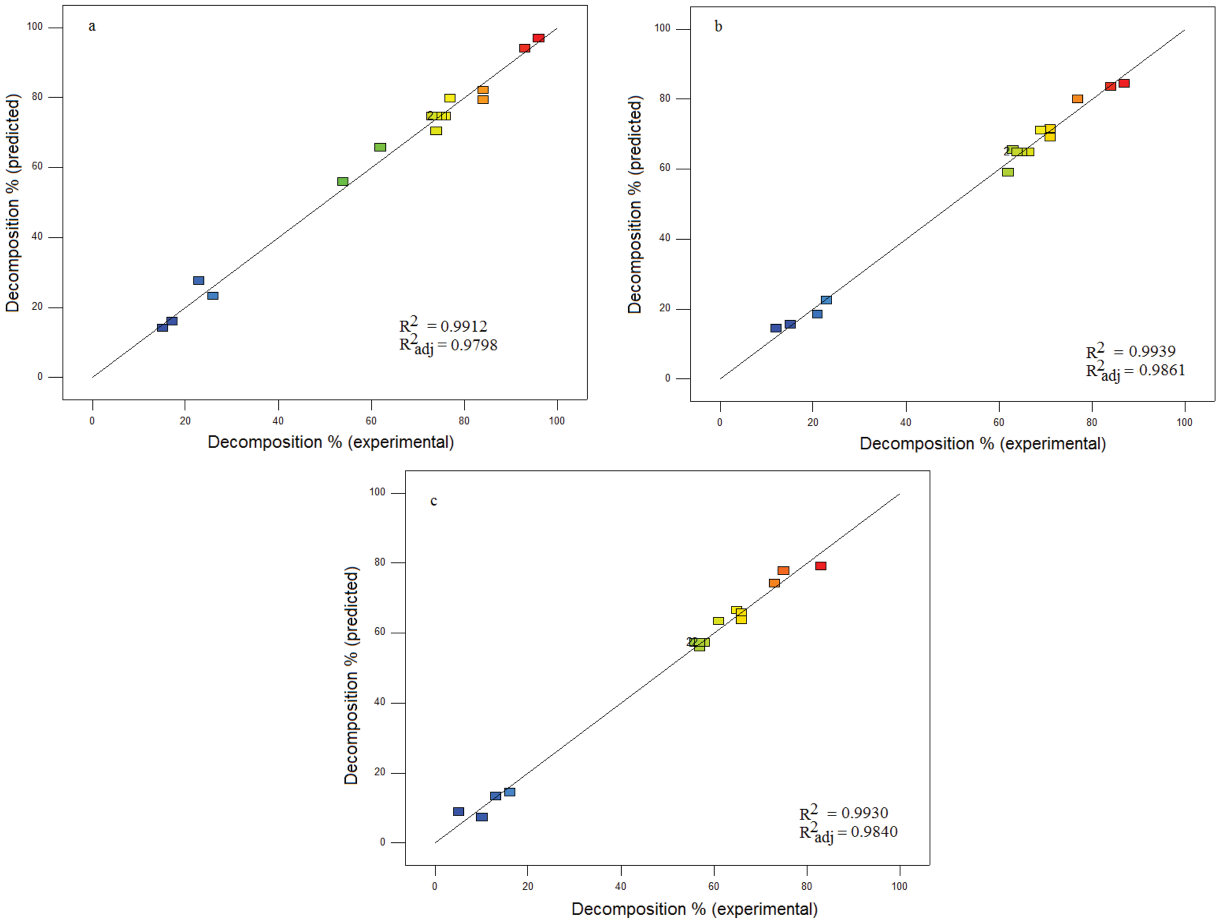


Fig. 2. Comparison of the experimental data with those predicted for (a) 2-A-4-NT, (b) 4-NT and (c) 2,4-DNT by the BBD.

range used for our experiments, there is a consistent conversion of H_2O_2 to •OH radicals, which depends on the initial oxidant concentration and not temperature. However, it is impossible to know the exact effect of temperature on •OH production without measuring the residual H_2O_2 in real time or at the end of the experiment. Therefore, adding the necessary amounts of H_2O_2 in the vessel, does not necessarily mean that the production of hydroxyl radicals will be adequate to sustain the decomposition of the nitroaromatics until mineralization (Eqs. (6) and (7)). Additionally, during the design of such experiments, one has to take into account the potential consumption of hydroxyl radicals from the various by-products produced during treatment (Eq. (8)).

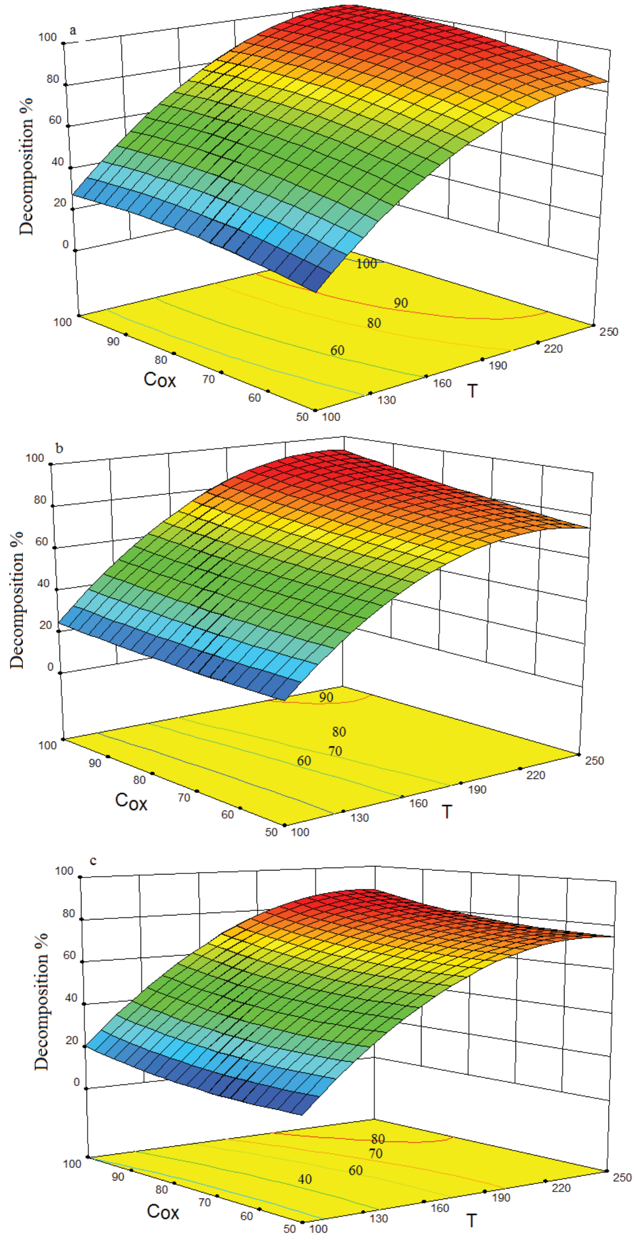


Fig. 3. Effect of temperature and oxidant concentration on decomposition of (a) 2-A-4-NT, (b) 4-NT and (c) 2,4-DNT (t = 175 min).

$$H_2O_2 \rightarrow 2^{\bullet}OH \tag{6}$$

$$^{\bullet}OH + \text{nitroaromatics} \rightarrow \text{secondary products} \tag{7}$$

$$^{\bullet}OH + \text{secondary products} \rightarrow \text{tertiary product} \tag{8}$$

The main initial reaction is the electrophilic addition of hydroxyl radical on the aromatic ring [35]. According to the electron-withdraving/meta-directing effect of $-NO_2$ group and the electron-donating/ortho–para directing effect of the $-CH_3$ group, the rank of 2-A-4-NT > 4-NT > 2,4-DNT is expected for the decomposition efficiency. At the same time, an increase in temperature facilitates the breaking of bonds and therefore degradation efficiency is enhanced.

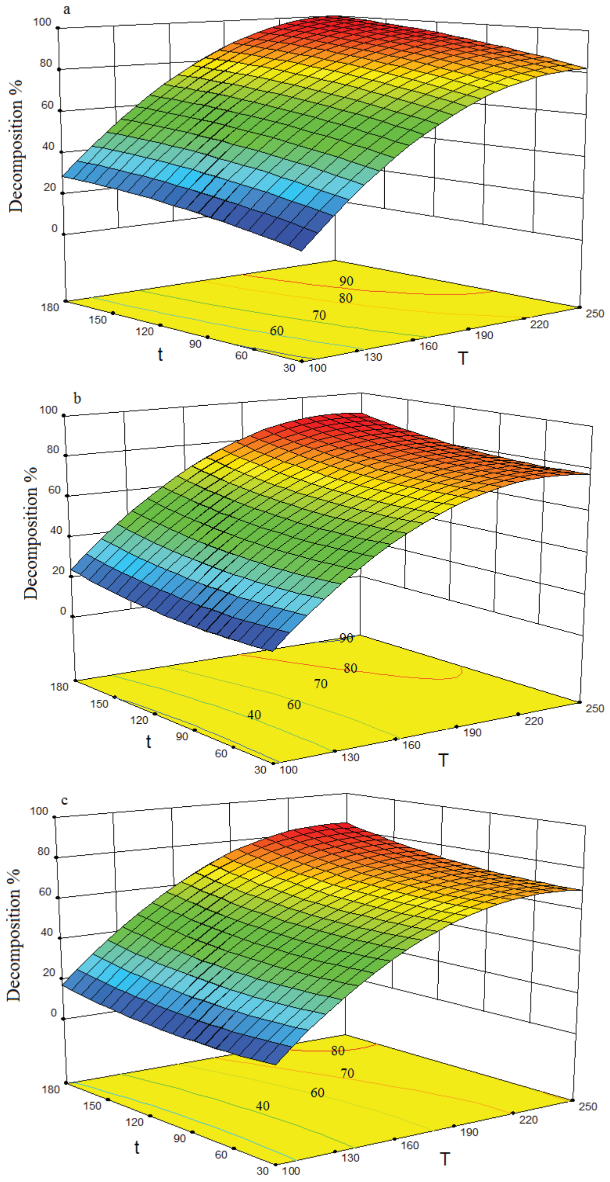


Fig. 4. Effect of temperature and time on decomposition of (a) 2-A-4-NT, (b) 4-NT and (c) 2,4-DNT (C_{ox} = 90 mM).

3.3. Influence of temperature and time on the degradation efficiency

Figs. 4(a)–(c) show the effect of time and temperature on decomposition persent at a constant hydrogen peroxide concentration of 90 mM. The critical role of temperature was again observed here. For all nitroaromatics, increasing the temperature resulted in significantly higher decomposition efficiency. However, at a given temperature, increasing the treatment time did not have a significant effect on decomposition. This shows that as soon as the production of •OH is stabilized, then decomposition proceeds without fluctuations until all H_2O_2 is converted or the nitroaromatic substance is completely decomposed. Time had practically no effect at lower temperatures (<160°C) where •OH production is slower. Increasing the treatment time from 30 to 180 min, did not increase the decomposition %. At temperatures

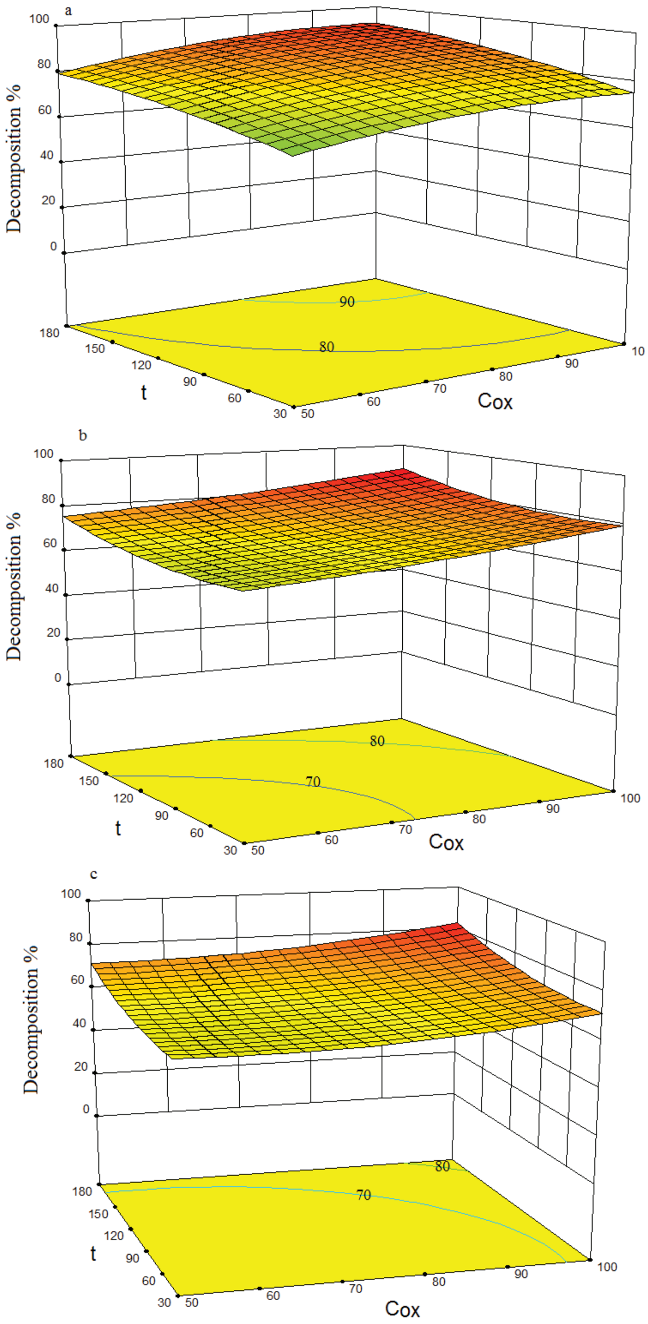


Fig. 5. Effect of time and oxidant concentration on decomposition of (a) 2-A-4-NT, (b) 4-NT and (c) 2,4-DNT (*T* = 200°C).

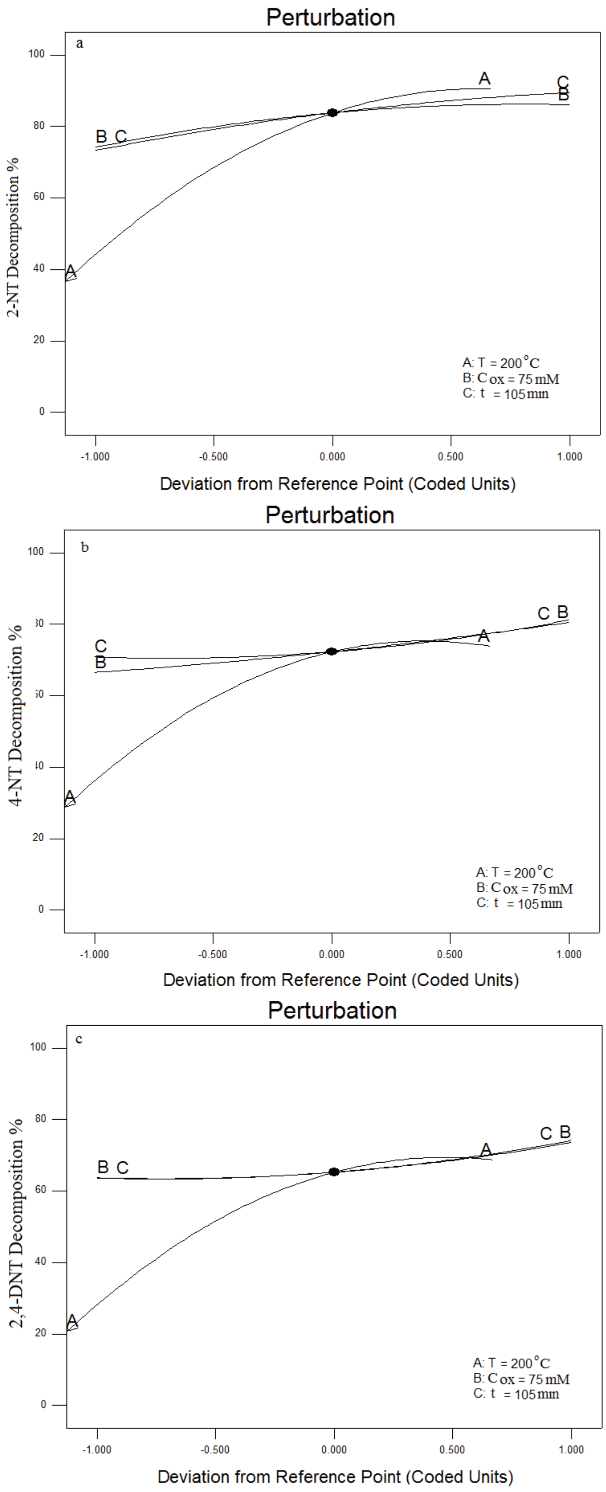


Fig. 6. Overlay plot of perturbation of all variables.

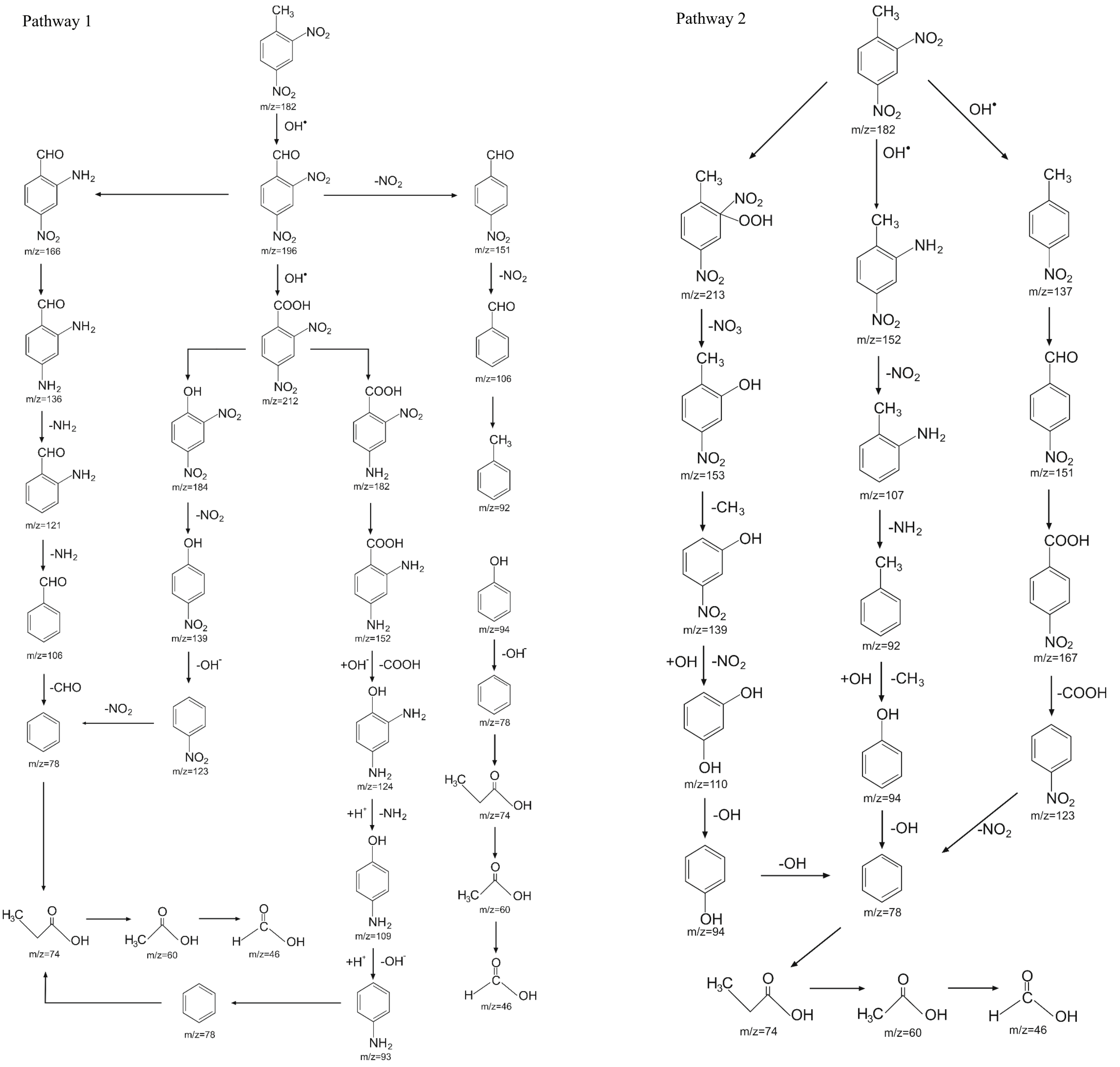


Fig. 7. Proposed degradation pathway for 4-NT, 2-A-4-NT and 2,4-DNT.

above 160°C, increasing treatment time resulted in ~10% increase in the decomposition efficiency. This can probably be explained by the heat transfer limitation between the oven and the stainless steel vessels. For the reactor, reaching 250°C requires considerably more time than reaching 100°C. In such experiments, time 0 is usually taken as the time the vessel is entered at the preheated oven. Therefore, Figs. 4(a)–(c) indicate that it took <30 min for the reactor to reach 100°C, however, considerably >30 min to reach 250°C and this was shown in the increased decomposition %. Measuring of rate constants for the reactions between the •OH radical and the nitroaromatics would help to determine the impact of heat transfer, however, this would require a dynamic (flow) setup where frequent sampling could occur.

For 2-A-4-NT, near-complete decomposition was achieved at 250°C and 180 min treatment time, whereas at the same conditions, decomposition efficiency was 90% and 85%, for 4-NT and 2,4-DNT, respectively. This shows that 2-A-4-NT decomposition is more feasible compared with the other two nitroaromatics.

3.4. Influence of time and oxidant concentration on the degradation efficiency

Fig. 5 presents the interactive effect of time and oxidant concentration at a constant temperature (200°C). For all nitroaromatics, raising the treatment time and/or oxidant concentration, had practically no effect on decomposition. This confirms the conclusions drawn earlier about the dominating role of temperature.

The perturbation plot enabled us to see clearly the effect of the three factors simultaneously. As can be seen in Fig. 6, temperature (*A*) is the controlling parameter for achieving maximum decomposition. The sharp curvature of temperature (*A*) and the nearly flat curvatures that correspond to the oxidant concentration (*B*) and time (*C*), confirm the conclusions drawn earlier from the 3D response surfaces.

3.5. Proposed degradation pathway for 4-NT, 2-A-4-NT and 2,4-DNT

Based on the GC–MS results (described below), the early stage degradation pathways for each of the nitroaromatics under examination, can be seen in Fig. 7. Two potential routes are proposed for 2,4-DNT. The compounds rapidly decreased, while at the same time there was an increase of intermediate by-products.

HO· radical attacks to the aromatic ring in ortho-, meta- and para-position strongly depend on the kind of substituent present on the ring. The oxidation of this parent compound can produce 2,4-nitrobenzaldehyde and 2,4-nitrobenzoic acid at *m*/*z* = 196 and 212, respectively. Further oxidation and decarboxylation of this 4-nitrobenzoic acid can give nitrophenol (*m*/*z* = 139), nitrobenzene (*m*/*z* = 123) and benzene (*m*/*z* = 78).

The second route is the reduction of nitro groups into amino groups giving the *m*/*z* value 166 and 136. 2,4-Nitrobenzaldehyde further can be converted to 2-A-4-NT and 2,4-aminotoluene, respectively. Further deamination of 2,4-aminotoluene can give benzaldehyde (*m*/*z* = 106) and benzene (*m*/*z* = 78). The last step involves opening of the aromatic ring, leading to small organic acids.

4. Conclusions

The novel static subcritical water setup used for the degradation of the nitroaromatic compounds proved to be effective. The effect of temperature, treatment time and amount of oxidant were studied with single factor experiments, in order to determine the preliminary ranges of the parameters before further optimization. Experiments have shown that in all cases, the chosen parameters influenced the reaction greatly, whereas temperature proved to be the most influential. The influence sequence for experiment factors was temperature > oxidant concentration > treatment time. Using Box-Behnken experimental design, the optimal reaction conditions were found to be: temperature of 240°C, 210°C and 236°C; time of 180, 178 and 172 min; oxidant concentration of 100, 99.64 and 99.61 mM for 2,4-DNT, 4-NT and 2-A-4-NT, respectively. Total amounts of degraded compounds were also observed and results have shown that high temperatures, long treatment times and increasing oxidant concentrations contribute to a higher amount of degraded nitroaromatics. The main intermediates were separated and identified by GC–MS, and a plausible degradation pathway for 2,4-DNT, 4-NT and 2-A-4-NT was proposed.

References

[1] J.L. Clausen, C. Scott, I. Osgerby, Fate of nitroglycerin and dinitrotoluene in soil at small arms training ranges, Soil Sediment Contam., 20 (2011) 649–671.

[2] P. Leffler, E. Brännäs, D. Ragnvaldsson, H. Wingfors, R. Berglind, Toxicity and accumulation of trinitrotoluene (TNT) and its metabolites in atlantic salmon alevins exposed to an industrially polluted water, J. Toxicol. Environ. Health A, 77 (2014) 1183–1191.

[3] D. Kalderis, A.L. Juhasz, R. Boopathy, S. Comfort, Soils contaminated with explosives: environmental fate and evaluation of state-of-the-art remediation processes (IUPAC Technical Report), Pure Appl. Chem., 83 (2011) 1407–1484.

[4] M.I. Khan, J. Lee, J. Park, A toxicological review on potential microbial degradation intermediates of 2,4,6-trinitrotoluene, and its implications in bioremediation, KSCE J. Civ. Eng., 17 (2013) 1223–1231.

[5] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Dinitrotoluenes, US Department of Health and Human Services, Public Health Service, Atlanta, GA, 2013. Available at: http://www.atsdr.cdc.gov/toxfaqs//tfacts109.pdf

[6] W.S. Chen, Y.C. Su, Removal of dinitrotoluenes in wastewater by sono-activated persulfate, Ultrason. Sonochem., 19 (2012) 921–927.

[7] W.S. Chen, C.P. Huang, Decomposition of nitrotoluenes in wastewater by sonoelectrochemical and sonoelectro-Fenton oxidation, Ultrason. Sonochem., 21 (2014) 840–845.

[8] E.H. Jho, J.W. Jung, K. Nam, Different fate of Pb and Cu at varied peroxide concentrations during the modified Fenton reaction in soil and its effect on the degradation of 2,4-dinitrotoluene, J. Chem. Technol. Biotechnol., 88 (2013) 1481–1487.

[9] X. Liu, H. Shang, C. Feng, Preparation of Y-$H_3PW_{12}O_{40}/TiO_2$ and La-$H_3PW_{12}O_{40}/TiO_2$ by hydrothermal method and its photocatalytic activity for dinitrotoluene decomposition, J. Rare Earths, 32 (2014) 17–22.

[10] D.J. Luning Prak, K.C. Gordon, J.M. Peterson, D.W. O'Sullivan, Photolysis of dinitrobenzyl alcohols, dinitrobenzaldehydes, and nitrobenzoic acids in seawater, estuary water, and pure water, Mar. Chem., 145–147 (2012) 29–36.

[11] D.J. Luning Prak, E.A. Milewski, E.E. Jedlicka, A.J. Kersey, D.W. O'Sullivan, Influence of pH, temperature, salinity, and dissolved organic matter on the photolysis of 2,4-dinitrotoluene and 2,6-dinitrotoluene in seawater, Mar. Chem., 157 (2013) 233–241.

[12] J. Huang, G. Ning, F. Li, G.D. Sheng, Biotransformation of 2,4-dinitrotoluene by obligate marine *Shewanella marisflavi* EP1 under anaerobic conditions, Bioresour. Technol., 180 (2015) 200–206.

[13] T. Hudcova, M. Halecky, E. Kozliak, M. Stiborova, J. Paca, Aerobic degradation of 2,4-dinitrotoluene by individual bacterial strains and defined mixed population in submerged cultures, J. Hazard. Mater., 192 (2011) 605–613.

[14] S. Thijs, N. Weyens, W. Sillen, P. Gkorezis, R. Carleer, J. Vangronsveld, Potential for plant growth promotion by a consortium of stress-tolerant 2,4-dinitrotoluene-degrading bacteria: isolation and characterization of a military soil, Microb. Biotechnol., 7 (2014) 294–306.

[15] D. Kundu, C. Hazra, N. Dandi, A. Chaudhari, Biodegradation of 4-nitrotoluene with biosurfactant production by *Rhodococcus pyridinivorans* NT2: metabolic pathway, cell surface properties and toxicological characterization, Biodegradation, 24 (2013) 775–793.

[16] B. Singh, J. Kaur, K. Singh, Microbial remediation of explosive waste, Crit. Rev. Microbiol., 38 (2012) 152–167.

[17] R. Podlipná, B. Pospíšilová, T. Vaněk, Biodegradation of 2,4-dinitrotoluene by different plant species, Ecotoxicol. Environ. Saf., 112 (2015) 54–59.

[18] X. Ni, Y. Zhao, Q. Song, Electrochemical reduction and in-situ electrochemiluminescence detection of nitroaromatic compounds, Electrochim. Acta, 164 (2015) 31–37.

[19] S.Y. Oh, J.G. Son, P.C. Chiu, Biochar-mediated reductive transformation of nitro herbicides and explosives, Environ. Toxicol. Chem., 32 (2013) 501–508.

[20] B. Weiner, I. Baskyr, J. Poerschmann, F.D. Kopinke, Potential of the hydrothermal carbonization process for the degradation of organic pollutants, Chemosphere, 92 (2013) 674–680.

[21] M.N. Islam, M.-S. Shin, Y.-T. Jo, J.-H. Park, TNT and RDX degradation and extraction from contaminated soil using subcritical water, Chemosphere, 119 (2015) 1148–1152.

[22] D. Kalderis, S.B. Hawthorne, A.A. Clifford, E. Gidarakos, Interaction of soil, water and TNT during degradation of TNT on contaminated soil using subcritical water, J. Hazard. Mater., 159 (2008) 329–334.

[23] V.M. Daskalaki, E.S. Timotheatou, A. Katsaounis, D. Kalderis, Degradation of Reactive Red 120 using hydrogen peroxide in subcritical water, Desalination, 274 (2011) 200–205.

[24] S.-Y. Oh, D.-S. Shin, Remediation of explosive-contaminated soils: alkaline hydrolysis and subcritical water degradation, Soil Sediment Contam., 24 (2015) 157–171.

[25] Y. Gong, X. Zhang, L. He, Q. Yan, F. Yuan, Y. Gao, Optimization of subcritical water extraction parameters of antioxidant polyphenols from sea buckthorn (*Hippophaë rhamnoides* L.) seed residue, J Food Sci. Technol., 52 (2015) 1534–1542.

[26] J. Ryu, H. Shin, Optimization of fatty acids production from lard via subcritical water-mediated hydrolysis, Korean Chem. Eng. Res., 53 (2015) 199–204.

[27] H.K. Reddy, T. Muppaneni, Y. Sun, Y. Li, S. Ponnusamy, P.D. Patil, P. Dailey, T. Schaub, F.O. Holguin, B. Dungan, P. Cooke, P. Lammers, W. Voorhies, X. Lu, S. Deng, Subcritical water extraction of lipids from wet algae for biodiesel production, Fuel, 133 (2014) 73–81.

[28] P. Kirmizakis, C. Tsamoutsoglou, B. Kayan, D. Kalderis, Subcritical water treatment of landfill leachate: application of response surface methodology, J. Environ. Manage., 146 (2014) 9–15.

[29] Y. Yang, B. Kayan, N. Bozer, B. Pate, C. Baker, A.M. Gizir, Terpene degradation and extraction from basil and oregano leaves using subcritical water, J. Chromatogr., A, 1152 (2007) 262–267.

[30] Y. Yang, F. Hildebrand, Phenanthrene degradation in subcritical water, Anal. Chim. Acta, 555 (2006) 364–369.

[31] B. Kayan, B. Gözmen, Degradation of Acid Red 274 using H_2O_2 in subcritical water: application of response surface methodology, J. Hazard. Mater., 201–202 (2012) 100–106.

[32] M. Edrissi, N.R. Asl, B. Madjidi, Interaction of mefenamic acid with cobalt(II) ions in aqueous media: evaluation via classic and response surface methods, Turk. J. Chem., 32 (2008) 505–519.

[33] B. Gözmen, Ö. Sönmez, M. Turabik, Response surface methodology for oxidative degradation of the Basic Yellow 28 dye by temperature and ferrous ion activated persulfate, Asian J. Chem., 25 (2013) 6831–6839.

[34] S. Hammami, N. Oturan, N. Bellakhal, M. Dachraoui, M.A. Oturan, Oxidative degradation of Direct Orange 61 by electro-Fenton process using a carbon felt electrode: application of the experimental design methodology, J. Electroanal. Chem., 610 (2007) 75–84.

[35] M. Pimentel, N. Oturan, M. Dezotti, M.A. Oturan, Phenol degradation by advanced electrochemical oxidation process electro-Fenton using a carbon felt cathode, Appl. Catal., B, 83 (2008) 140–149.