

Naphthalene mineralization by supercritical water oxidation and determination of by-products using non-target analysis

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ABSTRACT

In this study, the fate of naphthalene was investigated with a supercritical water oxidation process (SCWO). Also, the effectiveness of different operating conditions including pressure, temperature, residence time and oxidant dose on the formation of by-products was determined. The experimental sets were determined by the experimental design program and the effect of the selected variables on the removal of the naphthalene was associated statistically. According to obtained results, naphthalene by SCWO process was mineralized up to 98.5%. Removal efficiencies in sub- and supercritical conditions were between 94 and 100%. Derivatives of aldehyde, propanoic acid, benzene acetic acid and benzofuran were detected as by-products at many experimental conditions and also, some intermediates with a molecular weight higher than naphthalene were determined.

Key words: by-products, mineralization, naphthalene, supercritical water oxidation

HIGHLIGHTS

- High mineralization in both sub- and supercritical conditions.
- By-products of the binding reaction in low levels were detected.
- The individual effect of oxidant dose, the dual effect of temperature and oxidant dose and second-order effect of time were found significant on the removal of naphthalene.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) widely found in nature can be of natural and synthetic origin. Natural and anthropogenic sources of PAHs in the environment are poorly degradable polymers, oil combustion, the use of mothballs, fumigants and deodorizers, metal industries and many others (Abdel-Shafy & Mansour 2016). Increased industrial activity has resulted in the release of a wide variety of PAHs to the environment. Naphthalene and anthracene have been reported as the most common detected PAH compounds in wastewaters (Argun *et al.* 2020; Nas *et al.* 2020). Naphthalene, used as an intermediate in the manufacture of azo dyes, phthalic anhydride, surfactants, and pesticides, has caused an increase in naphthalene concentration in nature (Mangal 2020). Other routes of movement to the aquatic medium of naphthalene are known as rain and runoff waters (Irwin 1997) because the naphthalene can transfer between air and water depending on its solubility and environmental conditions. Also, anaerobic degradation of some organic matters can lead to the PAH formation (Argun *et al.* 2020; Nas *et al.* 2020). Therefore, naphthalene was detected in high levels (0.01–15 µg/L) in many aquatic environments (Staples *et al.* 1985; Kalmykova *et al.* 2014; Oturan *et al.* 2015; Ates & Argun 2018; Argun *et al.* 2020). All living creatures are exposed to naphthalene directly (inhalation, ingestion, and dermal contact) or indirectly (food chain). It was reported that these exposures could cause many acute and chronic health problems (ATSDR 1995).

Supercritical water oxidation (SCWO) is defined as one of the most effective and green treatment methods. The SCWO process can be used as an alternative treatment method, especially in industrial waters containing refractory compounds. Studies have shown that SCWO can mineralize organics in a very short time by turning water into an excellent solvent at critical pressure (22.1 MPa) and temperature (374 °C). The researchers have investigated the degradation of ammonia (Bermejo *et al.* 2008), phenolic compounds (Zhang *et al.* 2019),

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pharmaceuticals (Ma *et al.* 2018; Mylapilli & Reddy 2019), organophosphate flame retardants (Yang *et al.* 2019) and pesticides (Xu *et al.* 2015) by the SCWO process. However, although PAHs are characterized as mutagenic or carcinogenic pollutants, a few studies (Onwudili & Williams 2007; Xu *et al.* 2013; Ates & Argun 2021) on the SCWO of PAHs are found in the literature. These studies presented degradation products for a limited number of operating conditions and there is still a need for comprehensive studies on this subject. It was reported that some PAHs could increase by SCWO in the complex matrix of the leachate under some conditions (Ates & Argun 2021). However, there is still a gap whether PAH formation is due to the degradation of complex organics or transformation of PAHs to each other. Therefore, our research focused on the qualitative identification of the final and intermediate products formed during SCWO of naphthalene in sub- and supercritical conditions. Also, the effectiveness of independent variables including temperature, pressure, oxidant dose, and residence time on naphthalene removal was determined.

MATERIALS AND METHODS

Experimental conditions were created with the Design Expert program (version 11.0.5.0). The effects of four independent variables were examined with 27 runs by using central composite design (Table 1). Levels of significance were considered as ‘not significant’ for $p > 0.05$ and ‘significant’ for $p < 0.05$.

Table 1 | Independent variables and experimental ranges using for naphthalene oxidation

	A: Pressure (MPa)	B: Temperature (°C)	C: Time (min)	D: DOD
Minimum	10.0	250	3	0.10
-1	15.0	300	5	0.50
Mean	22.5	375	10	1.25
+1	30.0	450	15	2.00
Maximum	35.0	500	18	2.50

A horizontally placed tube reactor (290 cm × 1.15 cm ID), which has 25 ml/min flow capacity, was used as an SCWO reactor under sub- and supercritical water conditions (Biosan Inc., Turkey). The schematic diagram of the reactor is given in Figure 1. The maximum operating pressure and temperature of the reactor are 35 MPa and 600 °C, respectively. Change of both temperature and pressure was controlled by PID. The temperature was measured by three heat sensors inside the reactor. Wastewater and oxidant were fed into the reactor with the high-pressure pumps when the working temperature was reached. The treated wastewater was left from the reactor after the residence time was completed. The high temperature of treated wastewater was cooled down quickly by a heat exchanger and then high pressure was decreased by a back-pressure regulator.

Naphthalene (Supelco) solution was prepared at a concentration of 0.5 mg/L. Treatment conditions of naphthalene aqueous solution by SCWO process were performed in the range of 250–500 °C, 3–20 min, 10–35 MPa and 0.1–2.5 DOD (dimensionless oxygen dose). H₂O₂ (Merck, Germany) was used as oxidant and the desired oxidant dose was calculated according to Equation (1). Treated samples were extracted according to EPA 3510C method by using GC grade solvents. Then, both quantitative analysis of naphthalene and qualitative analyses of final products were carried out with the method of EPA 8270 D by gas chromatography-mass spectrometry (Agilent 7890B GC & 5977A MSD) coupled with HP-5MS column (30 m × 0.25 mm × 0.25 μm, Agilent). The working conditions of column and GC-MS instrument were reported in previous study (Argun *et al.* 2020). Linearity of the method was determined by using the calibration curve of naphthalene, which was prepared at the six different concentrations in the range of 0.05–50 μg/L (Figure 2). The recovery value of the method was validated by using a surrogate standard (AccuStandard) and internal standard was also used to calculate naphthalene concentration and to minimize instrumental errors. The impurities and water content of the extracts were cleaned up by the column including silica gel (Fisher Scientific, USA), glass fiber (Merck) and sodium sulfate (Merck). Quality assurance parameters of the method including limit of detection (LOD), limit of quantification (LOQ), recovery and R² values were detected as 5 ng/L, 15 ng/L, 116% and 0.999.

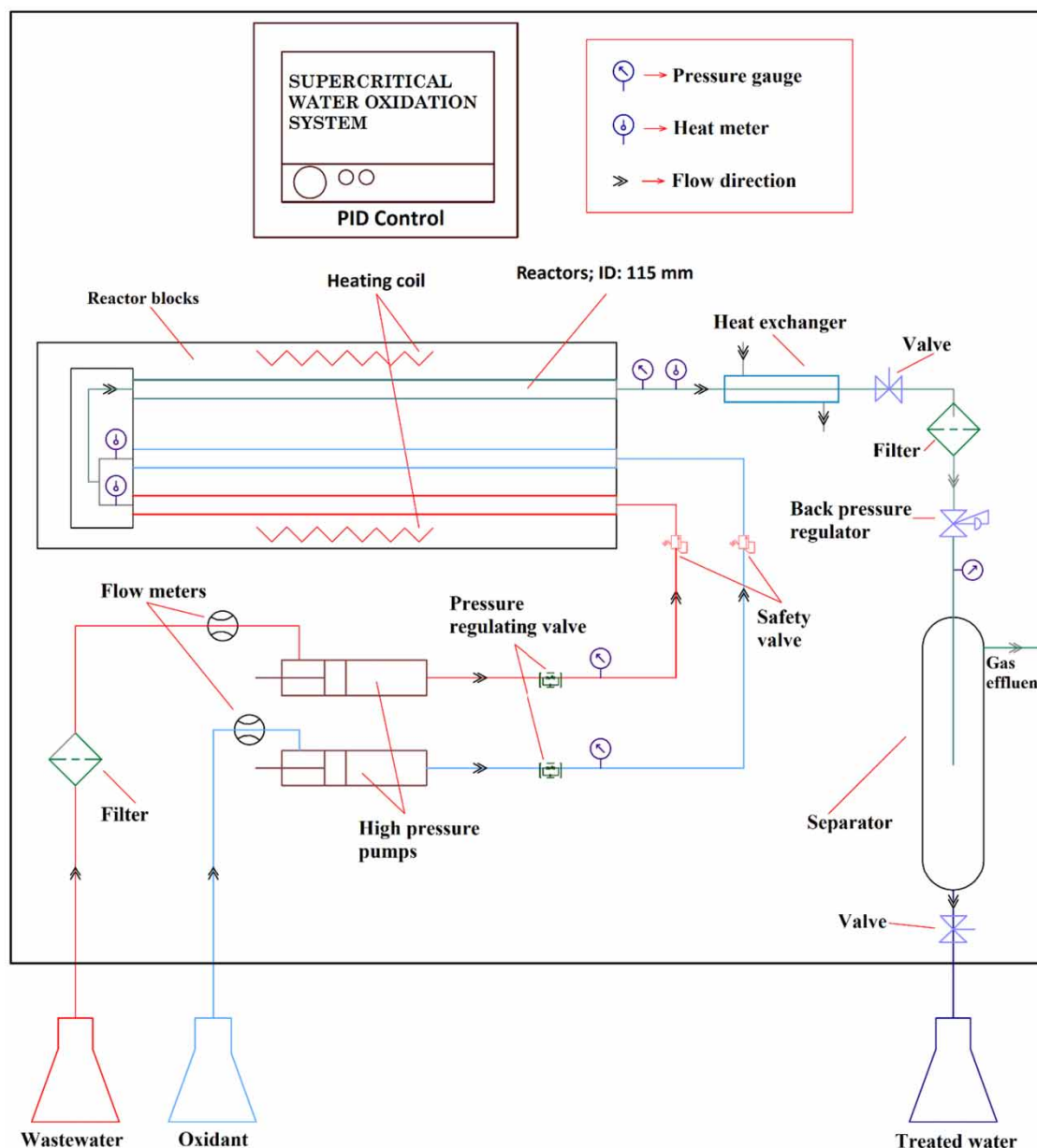


Figure 1 | Designed view of the instrument.

GC-MS non-target analysis were carried out to determine the degradation products of naphthalene via matching of compounds in the database (NIST library) with all peaks detected in the mass spectrum of the sample (Figure S1). Components such as target ion, qualifier ions, and retention time are used for accurate peak identification in Mass Hunter Workstation Unknown Analysis software (Version B.07.01).

$$\text{Dimensionless oxidant dose (DOD)} = \frac{\text{Chemical equivalent of oxidant}}{\text{Chemical equivalent of analyte COD}} \quad (1)$$

RESULTS AND DISCUSSION

The relationships between naphthalene removal and the four important variables including temperature, pressure, time and oxidant dose were analysed for the SCWO process using response surface methodology (RSM). The model was found significant at the 95% confidence level since the *p*-value was less than 0.05. Also, the individual effect of oxidant dose, the dual effect of temperature and oxidant dose and second-order effect of time were found significant on the removal of naphthalene by ANOVA test. The results of the model

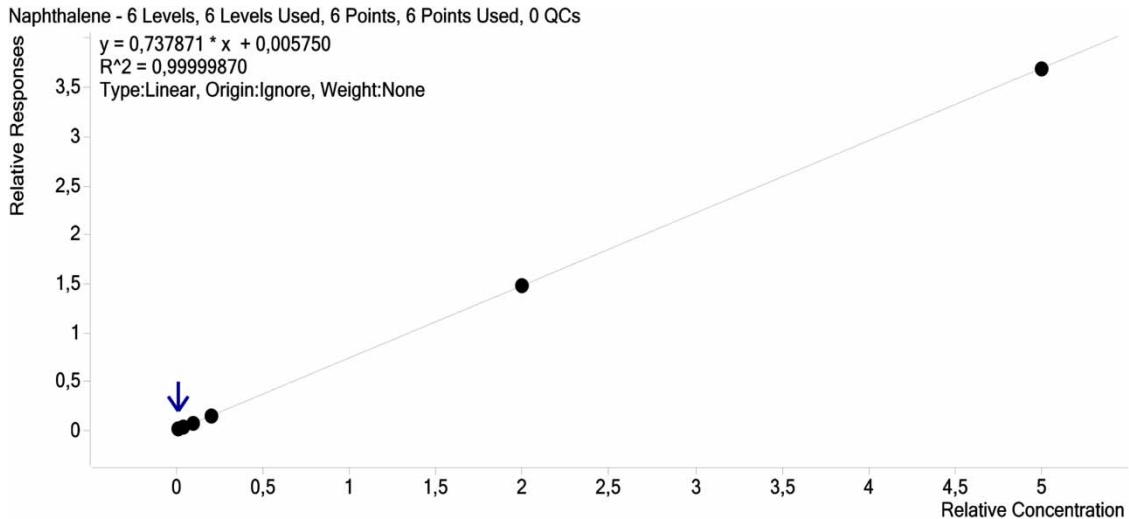


Figure 2 | Calibration curve of naphthalene for quantitative analyses.

calculated by RSM and the obtained model data are given in [Table 2](#) and [Figure 3](#), respectively. According to the obtained results, naphthalene was removed at between 93 and 100%. The minimum naphthalene removal (93%) was performed at 5 min, 0.5 DOD, 300 °C and 30 MPa. Naphthalene was removed entirely in the operating conditions of 2.0 DOD and 15 min for the same temperature and pressure values. Also, the degradation of naphthalene increased as the oxidant concentration increased.

Table 2 | ANOVA analysis of parameters and model

Source	Model	A-Pressure	B-Temperature	C-Time	D-DOD	BD	C ²	Lack of Fit
	Significant							Not significant
F-value	3.12	0.611	0.6656	0	6.3	15.91	6.52	0.2774
p-value	0.0457	0.4545	0.4356	0.9949	0.0333	0.0032	0.031	0.9161

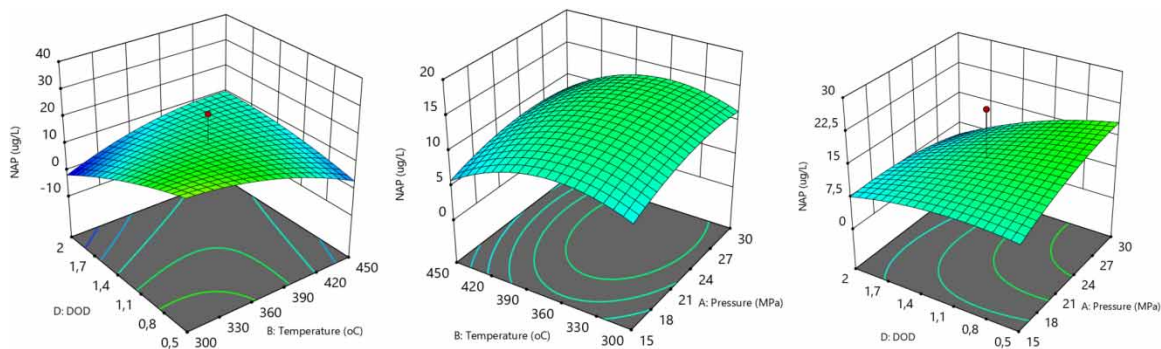


Figure 3 | Effects of independent variables on the remained naphthalene concentration.

Mechanisms of sub- and supercritical oxidation include many oxidative and non-oxidative reactions and are therefore quite complex ([Savage 1999](#); [Bhargava et al. 2006](#)). On the other hand, some researchers specified that non-target analysis is a useful method for the determination of a broad variety of environmentally relevant substances and their unknown transformation products ([Prasse et al. 2010](#); [Hug et al. 2014](#); [Funke et al. 2015](#)). Naphthalene mineralization by SCWO was observed to be very high for all experiments and the ratio of transformation products of naphthalene was determined as <10% ([Table 3](#)). [Ates & Argun \(2021\)](#) have reported that naphthalene could be formed and increase at a low DOD value and especially in subcritical conditions. However, in their study, it was unclear whether the naphthalene formed was due to the complex organic

structure of the landfill leachate or due to the inability to remove naphthalene. The results of this study indicated that naphthalene could be mineralized even in the subcritical conditions and therefore PAH formation in real wastewater might be due to transformation of complex organic matters under insufficient conditions such as lower oxidant dose, pressure or temperature.

Table 3 | Mineralization and partial mineralization rates of naphthalene under experimental conditions

	Operation conditions				Partial degradation (%)	Completely mineralization (%)	Unreacted naphthalene (%)	RE
	Pressure (MPa)	Temperature (°C)	Time (min)	DOD				
Subcritical conditions	10	375	10	1.25	0.04	96.86	3.10	96.9
	15	300	5	0.50	0.71	95.26	4.00	96.0
	15	300	15	0.50	5.17	89.93	4.85	95.1
	15	300	5	2.00	1.46	98.14	0.40	99.6
	15	450	5	0.50	2.35	97.55	0.30	99.9
	15	450	5	2.00	0.00	98.00	2.00	98.0
	15	450	15	0.50	1.88	97.22	0.80	99.1
	23	250	10	1.25	10.46	87.94	1.60	98.4
	30	300	5	0.50	0.07	92.83	7.11	92.9
	30	300	15	0.50	0.45	93.35	6.17	93.8
	30	300	5	2.00	5.48	93.92	0.60	99.4
	30	300	15	2.00	1.44	98.56	0.00	100
	Supercritical conditions	23	375	3	1.25	0.13	94.27	5.64
23		375	10	0.09	1.14	96.46	2.40	97.6
23*		375	10	1.25	0.41	96.69	2.90	97.1
23		375	10	2.41	5.50	92.90	1.60	98.4
23		375	18	1.25	0.59	94.01	5.40	94.6
30		450	5	0.50	2.93	93.67	3.40	96.6
30		450	15	2.00	2.09	95.41	2.50	97.5
30		450	15	0.50	0.93	96.67	2.40	97.6
34		375	10	1.25	2.88	95.92	1.20	98.8

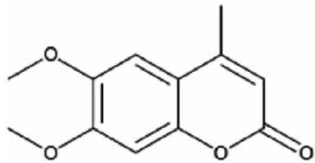
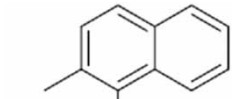
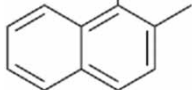
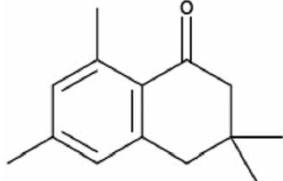
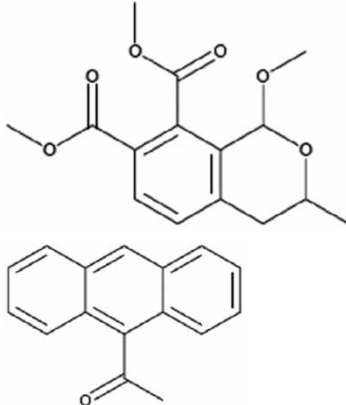
RE, Removal efficiency.

*Three times repeated experimental condition.

Although very high naphthalene removal was observed in this study, various reaction intermediates were also obtained. Not only oxidation products but also thermal cracking by-products were identified throughout the treatment with non-target analysis. Some detected by-products in treated samples were benzene (with thermal cracking), p-benzoquinone, benzene acetic acid, 2,4,6-trihydroxybenzaldehyde and so on (with oxidation). Additionally, binding reaction products such as 3-hydroxy-7-methoxy-2-naphthoic acid, 1-naphthalenemethanol and so on were also detected as intermediate products. Some other reaction intermediates were given in Table 4. Table 3 shows both partial and complete mineralization rates of naphthalene in experimental conditions. Although the interaction between experimental conditions and naphthalene removal was found to be statistically significant, the result was not the same for partial degradation of naphthalene. The highest partial degradation rate was determined as 10.5% at the lowest temperature. The partial mineralization rate at high oxidant doses is higher than the lower ones. This may be due to the formation of polyols as by-products in high oxidant doses. Xu *et al.* (2003) stated that CO₂ was always importantly higher than the other detected by-products during SCWO of naphthalene and also several detected by-products were salicylaldehyde, phthalic anhydride, 1,4-naphthoquinone, chromone, dibenzofuran and fluorenone.

In the past decades, many treatment methods such as biodegradation, photocatalysis, aerobic catalytic oxidation and ozonation have been used for naphthalene degradation. However, low conversion ratios with these processes are obtained in terms of the end products such as CO₂ and H₂O. Zhou *et al.* (2017) reported that, with the catalytic oxidation, only half of the naphthalene transformed to phthalic anhydride, 1,4 naphthoquinone and others. In another study, transformation products of naphthalene were determined as naphthol, naphthoquinone and hydroxynaphthalene with photo-oxidation (Dolinova *et al.* 2006). In the presence of sulphate in an anaerobic system, it was stated that 60% of naphthalene was transformed to CO₂ after two months (Langenhoff 1997).

Table 4 | Some by-products formed during SCWO of naphthalene (the ratios of these are <1%)

Compound name	Molecular formula	Molecular structure
2H-1-Benzopyran-2-one, 6,7-dimethoxy-4-methyl	$C_{12}H_{12}O_4$	
1,1'-Binaphthalene, 2,2'-dimethyl-	$C_{22}H_{18}$	
1(2H)-Naphthalenone, 3,4-dihydro-3,3,6,8-tetramethyl-	$C_{14}H_{18}O$	
Dimethyl 1-methoxy-3-methyl-isochroman-7,8-dicarboxylate	$C_{15}H_{18}O_6$	
Ethanone, 1-(9-anthracenyl)-	$C_{16}H_{12}O$	

CONCLUSION

Both the highest removal (100%) and the highest mineralization (98.6%) were obtained at the temperature of 300 °C, pressure of 30 MPa, oxidant dose of 2.0 and residence time 15 min. Naphthalene was mineralized to more than 90% in almost all the determined treatment conditions. Although 98% removal was achieved at 250 °C (the lowest temperature), the highest partial mineralization (10.5%) was obtained under this condition. The key parameters for naphthalene removal were determined as the individual effect of oxidant dose, the interaction effect of temperature and oxidant dose and the second-order effect of the time. This study clearly indicated that naphthalene alone could be mineralized even in the subcritical conditions. However, transformation of complex organic matters may be responsible for the naphthalene increase in real wastewater.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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