Check for updates

Water Practice & Technology

IWA PUBLISHING

© 2022 The Authors

Water Practice & Technology Vol 17 No 1, 84 doi: 10.2166/wpt.2021.088

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

H. Ates [a,*], M. E. Argun [a] and N. Kurt [b]

[a] Faculty of Engineering and Natural Science, Department of Environmental Engineering, Konya Technical University, Konya, Turkey
[b] Institution of Graduate Education, Department of Environmental Engineering, Konya Technical University, Konya, Turkey
*Corresponding author. E-mail: hates@ktun.edu.tr

HA, 0000-0001-7506-6811; MEA, 0000-0001-7203-1971; NK, 0000-0003-4515-644X

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),

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (http://creativecommons.org/licenses/by/4.0/).

Downloaded from http://iwaponline.com/wpt/article-pdf/17/1/84/989082/wpt0170084.pdf
by guest

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). H_2O_2 (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 R^2 values were detected as 5 ng/L, 15 ng/L, 116% and 0.999.

Downloaded from http://iwaponline.com/wpt/article-pdf/17/1/84/989082/wpt0170084.pdf
by guest

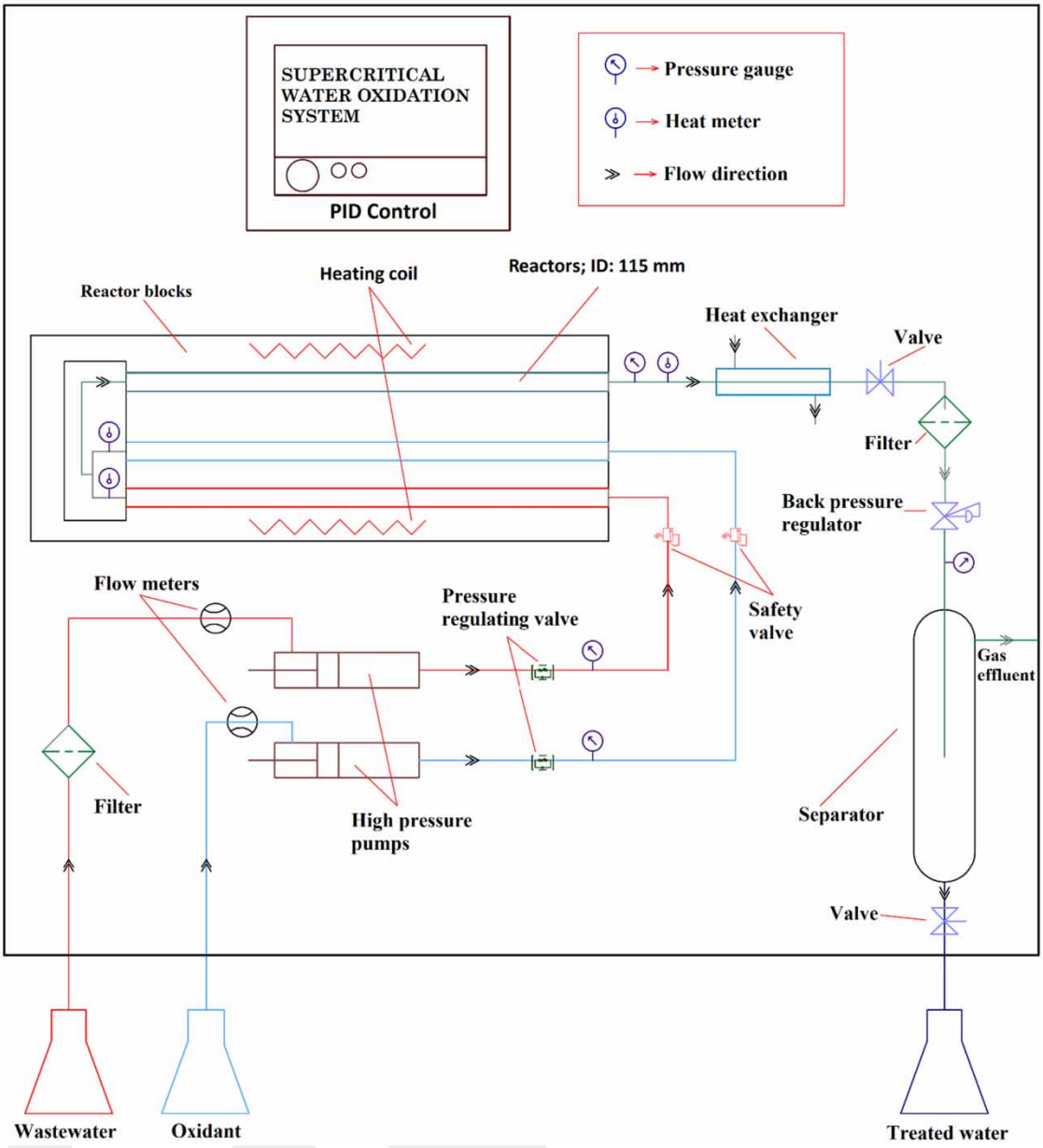


Figure 1 | Designed view of the instrument.

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).

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

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

Downloaded from http://iwaponline.com/wpt/article-pdf/17/1/84/989082/wpt0170084.pdf
by guest

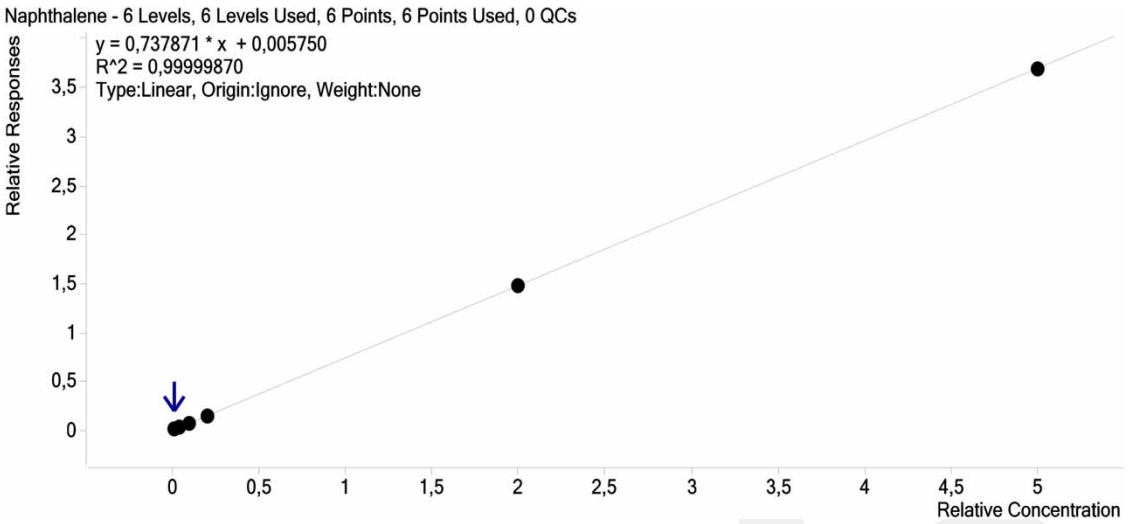


Figure 2 | Calibration curve of naphthalene for quantitative analyses.

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

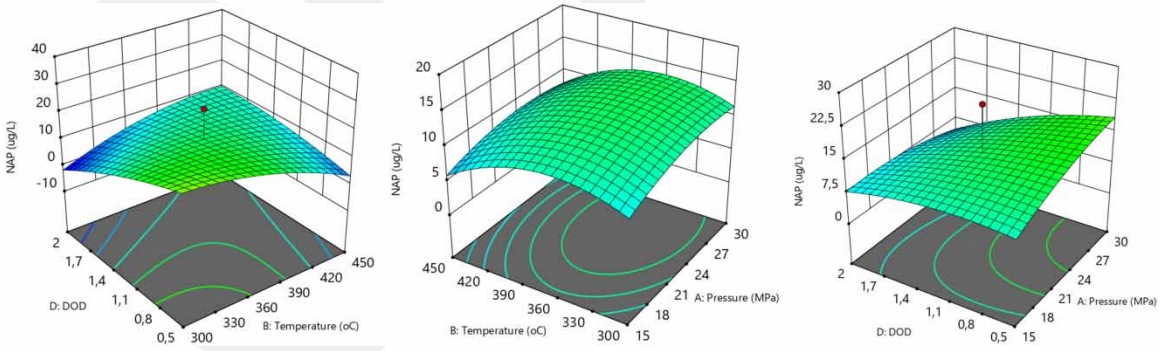


Figure 3 | Effects of independent variables on the remained naphthalene concentration.

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

Downloaded from http://iwaponline.com/wpt/article-pdf/17/1/84/989082/wpt0170084.pdf
by guest

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	94.4
	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

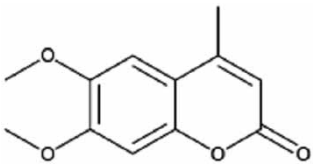
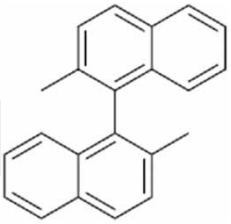
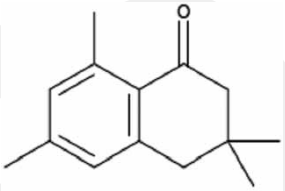
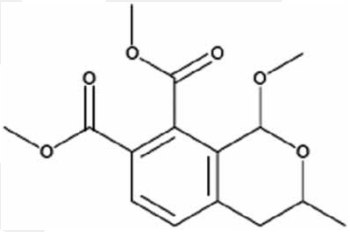
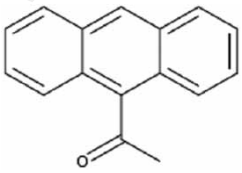
RE, Removal efficiency.
*Three times repeated experimental condition.

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 CO_2 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 CO_2 and H_2O. 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 CO_2 after two months (Langenhoff 1997).

Downloaded from http://iwaponline.com/wpt/article-pdf/17/1/84/989082/wpt0170084.pdf
by guest

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

Comound name	Molacular 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.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support of Konya Technical University scientific research fund (Grant No. 211001011). Also, this manuscript was presented in the 12th IWA young professionals conference and selected for publication in Water Practice and Technology.

DATA AVAILABILITY STATEMENT

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

Downloaded from http://iwaponline.com/wpt/article-pdf/17/1/84/989082/wpt0170084.pdf
by guest

REFERENCES

Abdel-Shafy, H. I. & Mansour, M. S. M. 2016 A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum* **25**(1), 107–123.

Argun, M. E., Akkus, M. & Ates, H. 2020 Investigation of micropollutants removal from landfill leachate in a full-scale advanced treatment plant in Istanbul city, Turkey. *Science of the Total Environment* **748**, 141423.

Ates, H. & Argun, M. E. 2018 Removal of PAHs from leachate using a combination of chemical precipitation and Fenton and ozone oxidation. *Water Science & Technology* **78**(5), 1064–1070.

Ates, H. & Argun, M. E. 2021 Fate of PAHs under subcritical and supercritical conditions in landfill leachate: removal or formation? *Chemical Engineering Journal* **414**, 128762.

ATSDR (Agency for Toxic Substances and Disease Registry) 1995 *Toxicological Profile for Naphthalene (Update)*. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.

Bermejo, M. D., Cantero, F. & Cocero, M. J. 2008 Supercritical water oxidation of feeds with high ammonia concentrations: pilot plant experimental results and modeling. *Chemical Engineering Journal* **137**(3), 542–549.

Bhargava, S. K., Tardio, J., Prasad, J., Föger, K., Akolekar, D. B. & Grocott, S. C. 2006 Wet oxidation and catalytic wet oxidation. *Industrial & Engineering Chemistry Research* **45**, 1221–1258.

Dolinova, J., Ruzicka, R., Kurkova, R., Klanova, J. & Klan, P. 2006 Oxidation of aromatic and aliphatic hydrocarbons by OH radicals photochemically generated from H_2O_2 in ice. *Environmental Science Technology* **40**, 7668–7674.

Funke, J., Prasse, C., Lütke Eversloh, C. & Ternes, T. A. 2015 Oxypurinol – a novel marker for wastewater contamination of the aquatic environment. *Water Research* **74**, 257–265.

Hug, C., Ulrich, N., Schulze, T., Brack, W. & Krauss, M. 2014 Identification of novel micropollutants in wastewater by a combination of suspect and nontarget screening. *Environmental Pollution* **184**, 25–32.

Irwin, R. J. 1997 Environmental Contaminants Encyclopedia, PAHs Entry. National Park Service, Washington, DC.

Kalmykova, Y., Moona, N., Strömvall, A.-M. & Björklund, K. 2014 Sorption and degradation of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachate using sand, activated carbon and peat filters. *Water Research* **56**, 246–257.

Langenhoff, A. 1997 *Biotransformation of Toluene, Benzene and Naphthalene Under Anaerobic Conditions*. Agricultural University of Wageningen, Wageningen, the Netherlands. ISBN 90-5485-660-2.

Ma, T. Z., Hu, T. T., Jiang, D. D., Zhang, J. L., Li, W., Han, Y. & Ormeci, B. 2018 Treatment of penicillin with supercritical water oxidation: experimental study of combined ReaxFF molecular dynamics. *Korean Journal of Chemical Engineering* **35**(4), 900–908.

Mangal, Z. 2020 Naphthalene. *International Journal of Creative Research Thoughts* **8**(6), 3260–3268.

Mylapilli, S. V. P. & Reddy, S. N. 2019 Sub and supercritical water oxidation of pharmaceutical wastewater. *Journal of Environmental Chemical Engineering* **7**(3), 9.

Nas, B., Argun, M. E., Dolu, T., Ates, H., Yel, E., Koyuncu, S., Dinç, S. & Kara, M. 2020 Occurrence, loadings and removal of EU-priority polycyclic aromatic hydrocarbons (PAHs) in wastewater and sludge by advanced biological treatment, stabilization pond and constructed wetland. *Journal of Environmental Management* **268**, 110580.

Onwudili, J. A. & Williams, P. T. 2007 Reaction mechanisms for the decomposition of phenanthrene and naphthalene under hydrothermal conditions. *Journal of Supercritical Fluids* **39**, 399–408.

Oturan, N., van Hullebusch, E. D., Zhang, H., Mazeas, L., Budzinski, H., Le Menach, K. & Oturan, M. A. 2015 Occurrence and removal of organic micropollutants in landfill leachates treated by electrochemical advanced oxidation processes. *Environmental Science Technology* **49**(20), 12187–12196.

Prasse, C., Schlüsener, M. P., Schulz, R. & Ternes, T. A. 2010 Antiviral drugs in wastewater and surface waters: a new pharmaceutical class of environmental relevance? *Environmental Science Technology* **44**(5), 1728–1735.

Savage, P. E. 1999 Organic chemical reactions in supercritical water. *Chemical Reviews*, **99**, 603–622.

Staples, C. A., Werner, A. F. & Hoogheem, T. J. 1985 Assessment of priority pollutant concentrations in the United States using storet database. *Environmental Toxicology and Chemistry* **4**, 131–142.

Xu, S., Fang, Z. & Koziński, J. A. 2003 Oxidation of naphthalene in supercritical water up to 420 °C and 30 MPA. *Combustion Science and Technology* **175**(2), 291–318.

Xu, Z. R., Zhu, W., Li, M., Zhang, H. W. & Gong, M. 2013 Quantitative analysis of polycyclic aromatic hydrocarbons in solid residues from supercritical water gasification of wet sewage sludge. *Applied Energy* **102**, 476–483.

Xu, D. H., Wang, S. Z., Zhang, J., Tang, X. Y., Guo, Y. & Huang, C. B. 2015 Supercritical water oxidation of a pesticide wastewater. *Chemical Engineering Research & Design* **94**, 396–406.

Yang, B. W., Cheng, Z. W. & Shen, Z. M. 2019 Decomposition of 14 organophosphate flame retardants during supercritical water oxidation. *Journal of the Taiwan Institute of Chemical Engineers* **95**, 40–47.

Zhang, H. W., Zhang, X. M., Ding, L., Gong, M., Su, Y. & Wang, S. W. 2019 Polymerization and oxidation of phenols in supercritical water. *Water Science and Technology* **80**(4), 620–633.

Zhou, Z., Yu, Y., Qin, J., Zhang, J., Cheng, F. & Wu, W. 2017 Liquid-phase oxidation of naphthalene with H_2O_2 in the presence of ordered mesoporous V-m-Al_2O_3 catalysts. *Journal of Chemical Sciences* **129**(9), 1373–1380.

First received 16 July 2021; accepted in revised form 31 August 2021. Available online 13 September 2021

Downloaded from http://iwaponline.com/wpt/article-pdf/17/1/84/989082/wpt0170084.pdf
by guest