Chemical Engineering Journal 260 (2015) 188–198

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Decomposition of 2-naphthol in water using a non-thermal plasma reactor

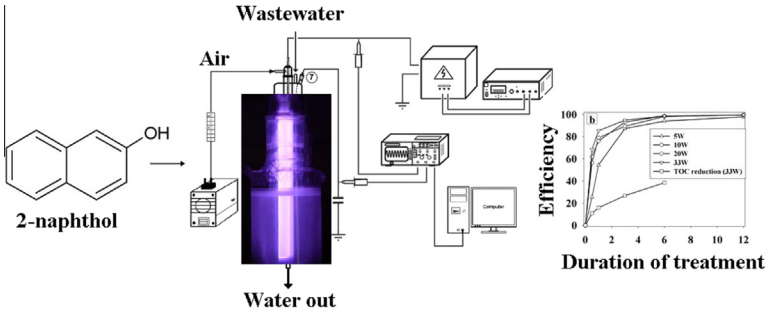
Edvinas Krugly [a,*], Dainius Martuzevicius [a], Martynas Tichonovas [a], Dalia Jankunaite [a], Inga Rumskaite [a], Jolanta Sedlina [b], Viktoras Racys [a], Jonas Baltrusaitis [c,*]

[a] Department of Environmental Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254 Kaunas, Lithuania
[b] Institute of Physical Energetics, Riga Technical University, Aizkraukles 21, LV-1006 Riga, Latvia
[c] Department of Chemical Engineering, Lehigh University, B336 Iacocca Hall, 111 Research Drive, Bethlehem, PA 18015, USA

HIGHLIGHTS

- DBD plasma reactor was used to decompose 2-naphthol in simulated wastewater.
- Important decomposition parameters were determined using screening experiment.
- Low 8.98 Wh/g power consumption for ozone generation was achieved.
- 95% Decomposition of 2-naphthol was achieved within 6 min.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 May 2014
Received in revised form 1 August 2014
Accepted 27 August 2014
Available online 6 September 2014

Keywords:
DBD plasma
2-Naphthol
Decomposition kinetics
Decomposition products
Toxicity

ABSTRACT

We examined the degradation of 2-naphthol in a pilot dielectric barrier discharge (DBD) semi-continuously operated non-thermal plasma reactor. Plasma was generated in a quartz tube with the ambient air used as a feed gas for the reactor. The performance of the reactor was evaluated according to the ozone amount produced both in the gas and liquid phase, as well as the overall decomposition efficiency of 2-naphthol. The decomposition kinetics, as well as the intermediary reactive products of 2-naphthol decomposition were determined using the combination of high performance liquid chromatography with ultraviolet detection (HPLC/UV), Fourier transform infrared spectroscopy (FTIR) and gas chromatography/mass spectroscopy (GC/MS) analyses. The overall effectiveness of the process was established according to the degree of total organic carbon (TOC) mineralization, while toxicity tests were performed using *Daphnia magna*. Ozone production (i.e., its concentration in the gas phase), ranged between 0.39 mg L^{-1} and 1.52 mg L^{-1} when varying the discharge power between 5 and 33 W. The decomposition efficiency of 2-napthtol reached 98.6% in 6 min at 33 W based on the HPLC measurements. The FTIR and GC/MS analyses revealed that degradation intermediates consisted mostly of oxygen functional group containing compounds, such as carboxylic acids. Based on the data reported here, we propose a novel dual stage organic wastewater decomposition reactor utilizing excess renewable electricity.

* Corresponding authors. Address: Department of Chemical Engineering, Lehigh University, B336 Iacocca Hall, 111 Research Drive, Bethlehem, PA 18015, USA. (J. Baltrusaitis).

E-mail addresses: edvinas.krugly@ktu.lt (E. Krugly), daimart@ktu.lt (D. Martuzevicius), martynas.tichonovas@ktu.lt (M. Tichonovas), dalia.jankunaite@ktu.lt (D. Jankunaite), inga.rumskaite@stud.ktu.lt (I. Rumskaite), sedlina.jolanta@inbox.lv (J. Sedlina), viktoras.racys@ktu.lt (V. Racys), job314@lehigh.edu (J. Baltrusaitis).

http://dx.doi.org/10.1016/j.cej.2014.08.098
1385-8947/

1. Introduction

Phenolic compounds comprise a large group of aromatic hydrocarbons found in the environment and result from both anthropogenic (e.g., wood extracts, additives in paper production, and agricultural activities) [1,2] and natural (e.g., bacterial degradation of polycyclic aromatic hydrocarbons or PAHs) [3,4] processes. Additionally, phenolic compounds, including naphthols, are present in oil [5] and, due to the emergent use of shale oil, represent an emerging threat to groundwater quality [1]. Due to their high toxicity and persistence in the environment, these phenolic compounds and their derivatives have been included on the priority pollutant list by the US Environmental Protection Agency (EPA) and the European Union [6].

In particular, 2-naphthol forms as a secondary product of many industrial activities including the chemical, paper, paint and pesticide industries [7], and it is a known hazardous substance to humans and the environment. Additionally, 2-naphthol is more toxic than 1-naphthol and biodegrades relatively slowly, posing challenges for its efficient removal [8]. For example, the in vivo and in vitro toxicity of 2-naphthol has been previously investigated, primarily motivated by its formation as a derivative of naphthalene biological processing [9–12]. Naphthalene is metabolized by Cytochrome P450 isoenzymes into a series of naphthols, including 2-naphthol and naphthoquinones, via naphthalene-1,2 oxide [9]. Mouse and lung cells were affected [9], as well as thyroid activity [12]. With established toxicity, efficient treatment methods for removing naphthols from industrial wastewater are needed.

Methods commonly used in 2-naphthol removal include photocatalysis [13] and chemical oxidation [14], advanced oxidation procedures (AOPs) [15] and biodegradation [16], although there have been very recent developments of 2-naphthol removal via absorption/immobilization on composite bentonite clays [17]. Other approaches that have been applied to treatment of biomass gasification wash water containing phenols, PAH and ammonium include trickling filters [18] and ultrasonic destruction [19]. The consensus from these earlier studies is that 2-naphthol remains a difficult to degrade chemical contaminant, implying that innovative, more efficient treatment technologies must continue to be explored and developed.

Non-thermal plasma (NTP) based wastewater treatment methods are growing in popularity and viewed as more advantageous than commonly used AOPs with respect to formation of reactive oxygen species (or ROS) [20]. AOPs typically require external chemicals (e.g., H_2O_2, O_3 or UV light), whereas NTP generates them *in situ* via electrical discharge at the surface of an electrode in contact with H_2O or air [21,22]. Non-thermal plasma has recently been investigated for the oxidation of various organic compounds in water, including phenolic compounds, organic dyes, and pharmaceuticals (Jiang et al. 2014). As recently reported for 4-chlorophenol [23], 2,4-dibromophenol [24] and other phenolic compounds, very high decomposition rates can be achieved using NTP. This enhancement, when compared to the oxidative technologies, is due to *in situ* production of ozone and other transient oxidizing species ($O_2^{+\cdot}$, H_3O^+, $O_2^{-\cdot}$, and $O_3^{-\cdot}$), along with the UV radiation.

Recently, we have developed a dielectric barrier discharge (DBD) reactor for non-thermal plasma generation that can be cooled by wastewater and air (feed gas) [25]. In comparison to traditional reactors, these improvements allow for lower operational temperature and greater ozone generation intensity. At the same time, since the reactor is immersed into the wastewater, the distance between the DBD zone and the target organic compounds is minimized. For this reason, ozone formed in the air is almost instantaneously dispersed into the wastewater, minimizing its decomposition in the gas phase. Additionally, simultaneous UV light generation provides another possibility of process intensification due to its use in combination with the oxidizing agents produced *in situ* (or via integration with photocatalytic, such as TiO_2, thin films into reactor design) It should be noted that the reactor works as a capacitive electric circuit element in the resonant high voltage converter circuit. Therefore, a high efficiency for electric power conversion can be achieved, leading to low electricity consumption. This type of wastewater treatment can serve as a sink of the surplus renewable electricity during the peak hours or windy days.

In this work, we demonstrate 2-naphthol decomposition using a dielectric barrier discharge non-thermal plasma reactor. As discussed, the DBD reactor provides all of the benefits of non-thermal plasma technologies, namely its ability to generate UV light, ozone and active radicals, such as hydroxyl, *in situ*, without any chemical addition or use of the UV lamps [26,27]. 2-naphthol was chosen as a representative pollutant from the group of polycyclic organic compounds. For the experiment, 2-naphthol was dissolved in tap water with concentrations ranging from 5 to 30 mg L^{-1}, thus forming a simulated wastewater. Notably, these concentrations are representative of chemical industry wastewater, where relatively low flow rates and high strength waste are common. Such high concentrations, therefore, enable simulating the operation of the DBD reactor while also adapting it to real industrial wastewater treatment. Modeling of our experimental parameters thereby allows for the identification of the most significant design parameters necessary for efficient treatment process.

2. Materials and methods

2.1. Experimental setup

Our experimental setup has been previously reported elsewhere [25], with the principal layout shown in Fig. 1. This setup utilizes an indirect plasma method for wastewater treatment. Conceptually, it involves ozone generation in the plasma zone with subsequent wastewater treatment via the UV radiation, ozone and the reactive radicals it generates in air and solution. We note that the effect of UV on the decomposition of the contaminants in this reactor is difficult to decouple from that of the ozone, thus the complete performance was evaluated. Unlike the experimental setup used in our previous study, new diffusers were installed to operate the reactor exclusively in a semi-continuous mode. The working resonant frequency was also altered to 8.19 kHz due to transformer construction changes. In the reactor, dielectric barrier discharge plasma was generated within the quartz cylinder. A central glass cylinder was used as a high voltage electrode with the current supplied by the working copper electrode, transferring plasma via the air gap to the UV-transparent quartz tube, surrounded by the model wastewater. A grounded copper rod served as a counter electrode and was immersed into wastewater, which also acted as a cooling medium for the DBD reactor. The reaction was performed within the outer glass tube, with specifications including an 80 mm inner diameter, 600 mm height and a wall thickness of 2 mm. High voltage was generated using an AC high voltage power supply, which was constructed in the laboratory of the Department of Environmental Technology, Kaunas University of Technology, Lithuania. It consisted of a driver, operating on full-bridge principle, and a high voltage transformer. In the current reactor, the voltage averaged to 20 kV (40 kV V_{pp}) at the lowest power of 5 W and about 22 kV (44 kV V_{pp}) at the highest power of 33 W. The air pump was used to supply air into the reactor for plasma generation the DBD discharge zone. Generated ozone and other highly reactive oxidizing species were dispersed into the model wastewater water using four fritted glass diffusers (1.5×3.5 mm).