

Degradation of a cyanobacterial toxin by advanced non-thermal plasmas

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Introduction

Cyanobacteria can produce various toxic secondary metabolites, e.g. the hepatotoxic and potentially carcinogenic cylindrospermopsin (CYN). Due to increased eutrophication of surface waters, toxic cyanobacterial blooms occurred more frequently in recent years, consequently increasing the abundance of CYN and other cyanotoxins [1]. In order to mitigate the risk these toxins pose, appropriate treatment technologies are required to assure their removal and provide hazard-free drinking water. Recognizing the potential danger CYN poses to human health, the WHO currently evaluates the need of a guideline value for CYN in drinking water [2].

Recent research on CYN removal from drinking water includes different approaches such as biodegradation [3], activated carbon filtration [4] as well as degradation by chlorine [4, 5], ozone [5, 6] and different advanced oxidation processes (AOPs) [7-9]. AOPs promote the formation of hydroxyl radicals and other reactive species in situ. Amongst AOPs, non-thermal plasmas (NTPs) have increasingly received more attention for their potential application in water treatment due to their capability to produce a vast range of reactive species such as ozone, hydroxyl radicals, nitrogen oxides, photons and electrons in situ [10, 11]. NTPs are generated by electric discharges in water or gas under atmospheric or low pressure. They were shown to effectively degrade recalcitrant organic compounds, e.g. pharmaceuticals, that are not or somewhat less susceptible to conventional and other advanced treatment methods [10]. Despite their potential, the application of NTPs for cyanotoxin removal from drinking water has scarcely been investigated and is limited to very few cyanotoxins like the prototypical microcystin with a focus on gas-phase discharge systems [12].

This study is the first to provide a basic understanding of the interaction of different NTPs with CYN and to compare gas- and liquid-phase discharge systems in this context.

Results

In the first part of the presented study, CYN was treated by six different plasmas and its removal was quantified by HPLC-DAD. The different plasma sources can be distinguished by their physico-chemical plasma characteristics, i.e. type of discharge and associated plasma-chemistry. A pulsed corona-like discharge submerged in water,

pulsed dielectric barrier discharge (DBD) in a water mist, gliding arc discharge, plasma jet submerged in water, pulsed spark discharge submerged in water and pulsed surface discharge at the air-water interface were compared based on their efficacy to degrade CYN, i.e. toxin degradation per applied energy (E_{CYN} in mg/kWh). After 60 min of plasma treatment, the plasma sources could be ranked according to their degradation efficacy as follows: spark discharge > gliding arc discharge > DBD > corona-like discharge > surface discharge > plasma jet (Figure 1).

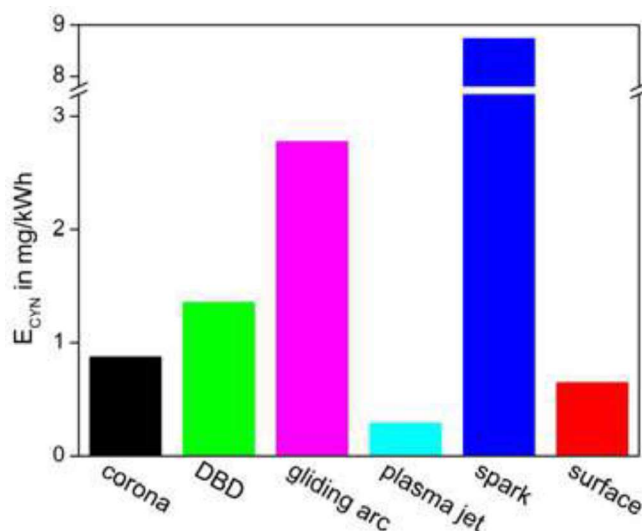


Figure 1 Comparison of CYN degradation efficacy (E_{CYN}) after 60 min of treatment by six different electric discharges ($n = 2$, except for gliding arc discharge).

Based on these results, but also on the usability of the reactors and their plasma-chemistry, the corona-like discharge and DBD sources were selected for in-depth studies. For the corona-like discharge submerged in water, the effects of operating voltage, electrode wire diameter and solution pH on CYN degradation efficacy were investigated. An electric discharge in water primarily produces hydroxyl radicals and hydrogen peroxide which is formed as a product of hydroxyl radicals. An increase in the supplied voltage resulted in higher CYN degradation due to increased formation of hydroxyl radicals. The degradation efficacy also increased at elevated pH. After 15 min of plasma treatment at $\text{pH} \geq 7.5$, ongoing CYN degradation was observed even without further plasma application. Oxidation by produced hydrogen peroxide was neglected because of its ineffectiveness to degrade CYN. Hence, a residual oxidative effect of the plasma treated water by other long-lived reactive species or degradation mechanisms could be the reason. Correspondingly, persistent microbicidal and oxidative effects of plasma treated water were previously reported in other studies, which could have interesting implications for drinking water treatment, e.g. as an alternative to chlorine disinfection [11, 13]. Changing the wire diameter did not appear to have a significant effect on the degradation of CYN.

For the DBD in air with water droplets, the effects of operating voltage and solution pH on CYN degradation efficacy were examined. An electric discharge in air mainly produces ozone and nitrogen oxides. Increasing the applied operating voltage decreased the degradation efficacy which can be associated with a lower ozone yield. For a DBD in air at atmospheric pressure, consumption of oxygen in reactions with nitrogen oxides is more efficient than ozone production at elevated voltages. Furthermore, produced ozone can be depleted by reactions with nitrogen and nitric oxide [14]. Although ozonation of CYN was reported to be pH-dependent, the degradation by the DBD was observed to be pH-independent [6]. However, due to the production of nitrogen oxides, the solution pH decreased substantially, e.g. from an initial pH 9.0 to an approximate pH of 3.5 after 60 min of plasma treatment. A pH-buffer could not be used, because it increased the conductivity of the solution and consequently, altered discharge characteristics which would have complicated the comparison of experiments at different pH values.

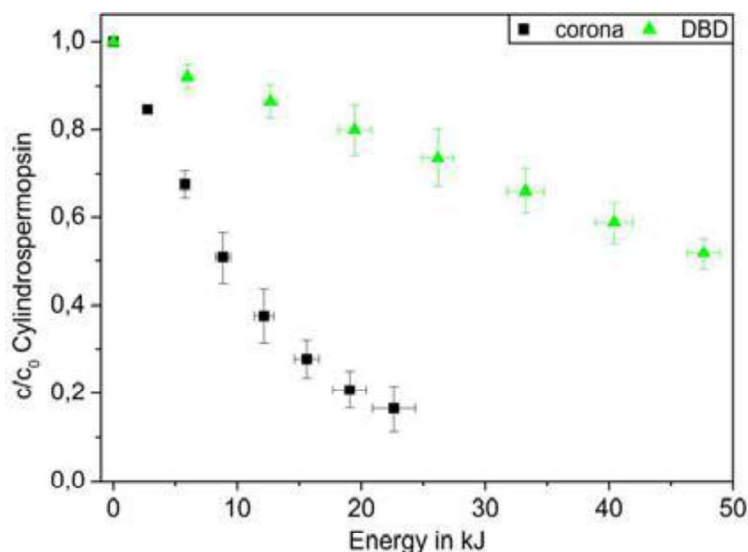


Figure 2 Comparison of CYN degradation by a corona-like discharge in water and a DBD in a water mist after optimization of studied parameters for a treatment time of 140 min (n = 3, error bars represent standard deviation).

After optimization of both plasma processes in the studied parameter range, their degradation kinetics and mechanisms were compared. CYN degradation by the corona-like discharge submerged in water followed pseudo first order reaction with an efficacy of 60.0 ± 5.3 mg/kWh, while the DBD in air with water droplets was less effective with 7.1 ± 0.8 mg/kWh and pseudo zeroth order kinetics (Figure 2). Hydrogen peroxide was determined colorimetrically using titanium sulfate and served as an indicator for the presence of hydroxyl radicals. After 60 min of plasma application in the absence of CYN, approximately 30 mg/L hydrogen peroxide were produced by the corona-like discharge, while only about 2.9 mg/L were produced by the DBD, suggesting a difference in the degradation mechanism. Using HPLC-MS, distinctive product peaks for the corona-like discharge and DBD were observed. Additionally, three other product peaks were substantially elevated for the DBD. This indicates that the degradation is based on

different mechanisms, i.e. by hydroxyl radicals and ozone in the corona-like and the DBD plasma, respectively.

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