Degradation of Cylindrospermopsin using Advanced Non-Thermal Plasma Technologies

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Abstract

The application of non-thermal plasmas in wastewater and air purification received a lot of attention, but their potential application in drinking water treatment has scarcely been investigated. Classified as Advanced Oxidation Processes, plasmas ignited in water or at the air-water interface generate a vast range of reactive species capable of removing water contaminants.

The efficiency to degrade cylindrospermopsin (CYN, cyanobacterial toxin) was compared for six different plasma sources. A spark discharge showed the most energy-efficient degradation, followed by the other investigated systems, which showed similar trends.

Two approaches were selected for further in-depth study of the degradation efficiency and underlying mechanisms. For a follow-up detailed study, a corona-like and a dielectric barrier discharge were selected based on the CYN degradation efficiency, usability of the reactors and plasma-chemistry. For the corona-like plasma, the degradation efficiency increased with increasing voltage and solution pH. After 15 min of plasma treatment at pH ≥ 7.5, degradation of CYN even progressed without further plasma application. The pH-dependency was not observed for the dielectric barrier discharge (DBD), whose degradation efficiency increased with decreasing operating voltage. The corona-like plasma promotes degradation primarily via •OH, whereas the DBD produces mainly O_3 and NO_x.

The application of non-thermal plasmas (NTPs) appears to be an innovative and promising approach for effective removal of cyanotoxins such as cylindrospermopsin from drinking water.

Keywords: non-thermal plasma, advanced oxidation process, cylindrospermopsin, cyanotoxin

1. Introduction

Cyanobacteria can produce a range of toxic metabolites, including the hepatotoxic alkaloid cylindrospermopsin. The WHO currently evaluates the need of a guideline value for CYN for drinking water. CYN can be degraded using various technologies e.g. ozonation (Onstad et al., (2007)) and Advanced Oxidation Processes (AOPs), e.g. UV/H_2O_2 (He et al., (2013)).

Amongst AOPs, NTPs increasingly receive more attention for their potential application in water treatment due to their capability to produce a vast range of reactive chemical species including O_3, •OH and NO• (Scholtz et al., (2015)). Furthermore, recalcitrant organic compounds, e.g. pharmaceuticals, that are not or less susceptible to conventional and other advanced treatment methods were shown to be effectively degraded by NTPs (Banaschik et al., (2015)). The available information for the use of NTPs for the degradation of cyanotoxins is limited to microcystins and anatoxin-a. This study is the first to report the use of NTPs to degrade CYN.

2. Degradation of CYN using NTPs

Aqueous CYN was subjected to six different plasmas and its reduction was quantified by HPLC-DAD. The plasma sources can be distinguished by their physico-chemical plasma characteristics, e.g. type of discharge and associated plasma-chemistry. After 60 min of treatment, the spark discharge showed the highest energy efficiency with 13% CYN degradation after applying 3.6 kJ. Following, corona-like, surface, DBD and gliding arc plasmas showed similar trends. The plasma jet was the least efficient plasma source, resulting in 20% degradation after 60 min of treatment and applying 216 kJ (**Figure 1**A).

Based on these results, usability of the reactors and plasma-chemistry, the corona-like plasma and DBD sources were selected for in-depth studies. Selected parameters were optimized with regard to the degradation efficiency. Increase of applied voltage resulted in higher CYN degradation for the corona-like discharge. For an electrical discharge in water, •OH and H_2O_2 are the predominantly formed oxidative species. The degradation efficiency also increased at elevated pH. After 15 min of treatment, ongoing CYN degradation was still observed without further plasma application at pH ≥ 7.5. Oxidation by produced H_2O_2 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 could be the reason. Correspondingly, persistent microbicidal effects of plasma treated water were previously reported in other studies (see Scholtz et al., (2015) for a brief compilation regarding this topic). Wire diameter and

pulse duration appeared to not have a significant effect on the degradation of CYN.

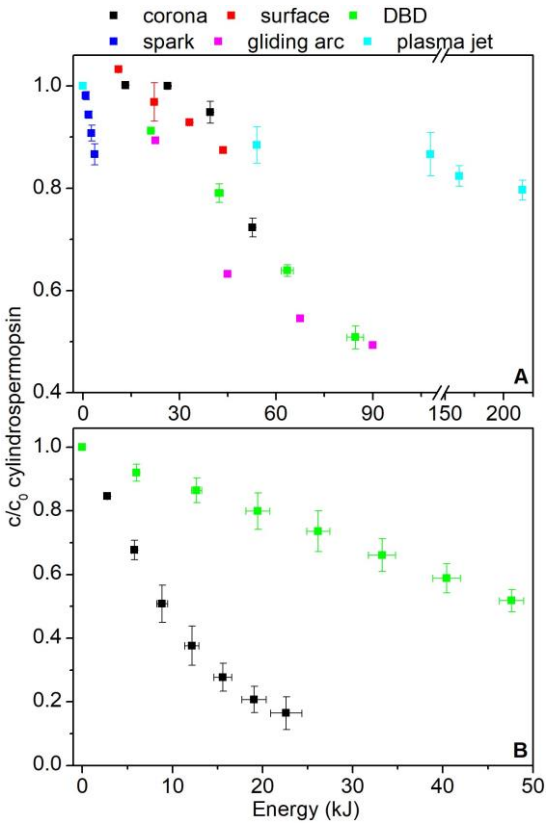

Figure 1. Degradation of CYN with six different NTPs applied for 60 min (**A**, n = 2, except for gliding arc discharge) and with corona-like and DBD plasma after optimization for 140 min (**B**, n = 3). Error bars represent standard deviation.

For a DBD in air, O_3 and NO_x are the dominant species. Although ozonation of CYN was shown to be pH-dependent (Onstad et al., (2007)), the degradation using the DBD was observed to be pH-independent. However, due to the production of NO_x, the pH decreased substantially from an initial pH 9 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. Increasing the applied operating voltage decreased the degradation efficiency in the DBD which can be associated with a reduced O_3 yield. For a DBD in air at atmospheric pressure, consumption of oxygen in NO_x reactions is more efficient than O_3 production at elevated voltages. Furthermore, produced O_3 can be depleted by reactions with N and NO (Kogelschatz et al., (1988); Pekárek, (2012)). Again, pulse duration did not significantly affect the degradation efficiency.

The corona-like discharge was more efficient than the DBD (**Figure 1**B). H_2O_2 was determined colorimetrically using titanyl sulfate and served as an indicator for the presence of •OH. After 60 min of plasma application, approximately 30 mg/L H_2O_2 were produced by the corona-like discharge, whereas only about 2.9 mg/L were produced by the DBD, suggesting a difference in 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 •OH and O_3 in the corona-like and the DBD plasma, respectively.

3. Conclusions

This is one of the first reports demonstrating that CYN was effectively degraded by different NTPs, suggesting the high potential of these innovative technologies for their application in drinking water treatment.

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