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Electrochemical disinfection using boron-doped diamond electrode – The synergetic effects of *in situ* ozone and free chlorine generation

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HIGHLIGHTS

- BDD electrode is capable to achieve high disinfection level of *P. aeruginosa*.
- Synergetic effect of *in situ* generated O_3 and Cl_2 enhances the disinfection process.
- High current density boosts disinfection level; DBPs formation and energy demand.
- DBP formation and energy demand can be controlled over the applied current density.

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ABSTRACT

This work investigated the capability of using a boron-doped diamond (BDD) electrode for bacterial disinfection in different water matrices containing varying amounts of chloride. The feed water containing *Pseudomonas aeruginosa* was electrochemically treated while applying different electrode conditions. Depending on the applied current density and the exposure time, inactivation between 4- and 8-log of the targeted microorganisms could be achieved. The disinfection efficiency was driven by the generation of free chlorine as a function of chloride concentration in the water. A synergetic effect of generating both free chlorine and ozone *in situ* during the disinfection process resulted in an effective bactericidal impact. The formation of the undesired by-products chlorate and perchlorate depended on the water matrix, the applied current density and the desired target disinfection level. In case of synthetic water with a low chloride concentration (20 mg L^{-1}) and an applied current density of 167 mA cm^{-2}, a 6-log inactivation of *Pseudomonas aeruginosa* could be achieved after 5 min of exposure. The overall energy consumption ranged between 0.3 and 0.6 kW h m^{-3} depending on the applied current density and water chemistry. Electrochemical water disinfection represents a suitable and efficient process for producing pathogen-free water without the use of any chemicals.

1. Introduction

Due to the insufficient management of water resources in urban and rural areas in many parts of the world, millions of people are exposed every day to unsafe levels of microbiological and chemical pollutants in their drinking water. Poor water quality worldwide causes disease breakouts that endanger public health and especially children (World Health Organization, 2013). The need to disinfect both drinking water and effluents of wastewater treatment plants (WWTPs) has encouraged both scientists and engineers to develop new and cost-effective methods for effective water disinfection. Well-established chemical disinfection technologies such as chlorination or ozonation have different drawbacks that limit their application in some cases. The chemicals used in such technologies require high safety specifications to be considered, thus enhancing the operation costs. Furthermore, formation of disinfection by-products (DBPs) during chlorination or ozonation and the loss of disinfection efficiency through the presence of organic matter are crucial when considering those technologies (Sedlak and von Gunten, 2011; Li and Ni, 2012). The applicability of physical disinfection processes such as UV irradiation, membrane separation and thermal disinfection is associated with high cost and maintenance efforts and does not fulfil the requirements for primary and residual water disinfection (Martínez-Huitle and Brillas, 2008; Schmalz et al., 2009).

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In the last few decades, alternative systems to conventional disinfection methods were developed. The most promising ones are based on the *in situ* electrogeneration of disinfection agents (Kraft, 2008; Martínez-Huitle and Brillas, 2008; Ghernaout and Ghernaout, 2010). It offers an environmentally friendly, economically and operationally competitive technology, which is known to be applicable against a wide range of microbiological contaminations in water. A critical factor in these electrochemical processes is the role of the anode material. Among others, boron-doped diamond (BDD) has shown remarkable properties to be applied as anodic material (Kraft, 2007; May, 2008). Beside its inertness and the chemical stability, it has the highest known oxygen evolution overpotential due to its low adsorption capacity leading to the formation of other oxidants before oxygen evolves (Fujishima, 2005). Reactive oxygen species (ROS), such as hydroxyl radicals, ozone, singlet oxygen and hydrogen peroxide, are formed during the operation in water on the surface of the electrode and in the bulk solution leading to a high efficiency during the oxidation process. In the presence of ions, such as chloride, sulfate and bicarbonate, free chlorine, peroxodisulphate and other weak oxidants can be produced during the electrolysis, which are known to be powerful disinfectants (Polcaro et al., 2009; Pérez et al., 2010). A potential drawback of electrochemical disinfection using BDD electrodes is the formation of disinfection by-products (DBPs) (Bergmann and Rollin, 2007; Bergmann et al., 2011; Haaken et al., 2012). The highly reactive oxidant species formed during the electrolysis process – mainly hydroxyl radicals and ozone - are able to oxidize halogenated ions present in water (von Gunten and Pinkernell, 2000; Deborde and von Gunten, 2008). Among the generated inorganic by-products, bromate, chlorate and perchlorate are of great concern because of their negative impact and possible carcinogenic effect on human health (Bergmann et al., 2010, 2011). Moreover, the reaction of halogen species with organic molecules found in water will promote the formation of the harmful adsorbable organically bound halogens (AOX) and the trihalomethanes (THMs).

The applicability of BDD electrodes for electrochemical disinfection has been tested at laboratory and pilot scale. Different operational parameters, microorganism species and water matrices were investigated. For instance, the applied current density shows a significant role in the bactericidal kinetics (Furuta et al., 2004; Schmalz et al., 2009; Griessler et al., 2011; Yao et al., 2011). The applied current density and the chloride content in the feed water have been identified as the most influential factors (Polcaro et al., 2009; Schmalz et al., 2009; Pérez et al., 2010; Yao et al., 2011). The role of hydroxyl radicals in the disinfection process also depends on the water content. In case of the presence of chloride and bicarbonate, its role is almost negligible. The direct disinfection effect of hydroxyl radicals in absence of radical scavengers is obvious (Diao et al., 2004; Jeong et al., 2006; Schmalz et al., 2009). However, past studies have not considered the relationship between the studied parameters, the formatted DBPs and the energy demand of the process.

The scope of this study was to investigate the influence of chloride ion concentration on the disinfection performance of a BDD electrode on the ubiquitous model organism *Pseudomonas aeruginosa (P. aeroginosa)* and the formation of disinfection by-products. *P. aeruginosa* was chosen because of its important role in public health, particularly with regards to nosocomial infection and diseases in immunodeficient patients (Panis et al., 2009). Bacterial inactivation was tested under variation of the applied current density and different chloride ion concentrations. The major objective of this study was to link the bacterial inactivation capacity of BDD diamond with the energy demand and the formation of inorganic DBPs in order to define optimal process conditions.

2. Experimental section

2.1. Experimental setup

Experiments were performed using a conductive diamond electrode system (CONDIAPURE®- CONDIAS GmbH, Germany). The batch reactor system consisted of a flow through cell with a volume of 45 cm^3 equipped with a BDD electrode stack, pump, a 20 L tank, power supply, and two sensors placed on the hoses connecting the different parts (Fig. 1).

The electrode stack consisted of two BDD cathodes and two BDD anodes on a niobium substrate (CONDIAS GmbH, Germany) with an overall effective anode area of 24 cm^2. A nafion cation exchange membrane was placed in direct contact to each cathode and anode in order to receive a gap-free sandwich structure. This enhanced the current density locally and therefore promoted ozone formation and enabled to operate the electrode at low conductivities (Kraft et al., 2006a, 2006b). The system was operated in a recirculation that flow rate could be adjusted between 0.5 and 10 L min^{-1}. The applied current could be regulated between 0 and 10.0 A. All experiments were conducted at room temperature (25 ± 2 °C) and slightly alkaline pH value (8.5 ± 0.5). Two current densities, 42 and 167 mA cm^{-2}, were applied during this study. Kraft et al. (2006b) has shown that the best current efficiency (20–24%) for ozone generation to be located in the range of 50–175 mA cm^{-2}, after this range the efficiency decreased owing to an increase in ozone decay in the water. Prior studies (Heim et al., 2011; Ureña de Vivanco et al., 2013) have shown that efficient ozone production applying the same BDD electrode at lower current densities than 42 mA cm^{-2} is not sufficient. This could be due to the confined of generated hydroxyl radicals to the electrode surface. In this context, the lowest applied current density in this study (42 mA cm^{-2}) was chosen with respect to the possibility of efficient ozone production as well as a minimum energy consumption during the process. The other applied current density (167 mA cm^{-2}) was selected to assure a sufficient ozone generation and simultaneously a worst-case scenario for DBPs formation. All experiments were carried out in duplicate and showed a good reproducibility within a 95% confidence interval within the microbiological method. The mean values of the results of the replicated experiments are presented.

2.2. Chemicals

Phosphoric acid (85%), 5,5-indigodisulphonic acid sodium salt (indigo carmine), sodium hydroxide (NaOH), sodium thiosulfate ($Na_2S_2O_3$), calcium chloride ($CaCl_2$), potassium bromide (KBr), potassium iodide (KI), magnesium sulphate heptahydrate ($MgSO_4$ $8H_2O$), sodium hydrogen carbonate ($NaHCO_3$) and sodium nitrate

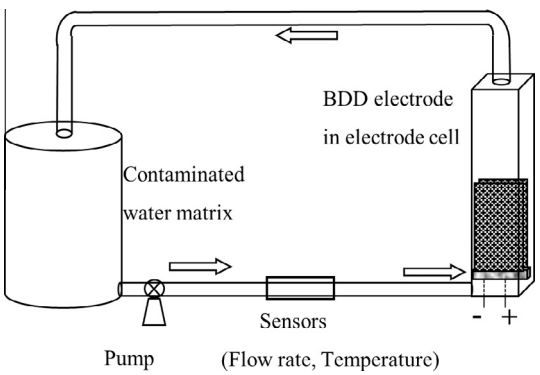

Fig. 1. Experimental setup of the BDD electrode and the reactor unit.