Water Research 140 (2018) 191–199

Contents lists available at ScienceDirect

Water Research

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

Improved blackwater disinfection using potentiodynamic methods with oxidized boron-doped diamond electrodes

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ARTICLE INFO

Article history:
Received 13 October 2017
Received in revised form
3 February 2018
Accepted 7 April 2018
Available online 18 April 2018

Keywords:
Boron-doped diamond
Reactive oxygen species
Electrochemical disinfection
Electrochemical advanced oxidation processes (EAOP)
Blackwater
Decentralized water treatment

ABSTRACT

Electrochemical disinfection (ECD) has become an important blackwater disinfection technology. ECD is a promising solution for the 2 billion people without access to conventional sanitation practices and in areas deficient in basic utilities (e.g., sewers, electricity, waste treatment). Here, we report on the disinfection of blackwater using potential cycling compared to potentiostatic treatment methods in chloride-containing and chloride-free solutions of blackwater (*i.e.*, untreated wastewater containing feces, urine, and flushwater from a toilet). Potentiodynamic treatment is demonstrated to improve disinfection energy efficiency of blackwater by 24% and 124% compared to static oxidation and reduction methods, respectively. The result is shown to be caused by electrochemical advanced oxidation processes (EAOP) and regeneration of sp^2-surface-bonded carbon functional groups that serve the dual purpose of catalysts and adsorption sites of oxidant intermediates. Following 24 h electrolysis in blackwater, electrode fouling is shown to be minimized by the potential cycling method when compared to equivalent potentiostatic methods. The potential cycling current density is 40% higher than both the static oxidative and reductive methods. This work enhances the understanding of oxygen reduction catalysts using functionalized carbon materials and electrochemical disinfection anodes, both of which have the potential to bring a cost-effective, energy efficient, and practical solution to the problem of disinfecting blackwater.

1. Introduction

Approximately 40% of the world population does not have access to appropriate sanitation (Water, Sanitation and Hygiene Strategy Overview, 2017). Limited infrastructure and poverty in developing areas has hindered use of suitable blackwater treatment practices. Microbial species such as *E. coli*, helminths, and other excreted pathogens are commonly present in untreated blackwater and lead to a range of illnesses including gastroenteritis. Over 1.4 million people die each year as a result of diarrheal illness caused by poor sanitation or insufficient treatment of wastewater, with 43% of the deaths being children 5 and under (Prüss-Üstün et al., 2008; Wastewater management: A UN-Water Analytical Brief, 2015). While methods such as membrane filtration, UV irradiation, pasteurization, chlorination, and ozonation have been studied for the treatment of wastewater, these treatment practices have seen limited adoption in developing countries due to high investment costs, high energy requirements, complex maintenance, dependence on supply and storage of chemicals, and generation of harmful by-products (Bourrouet et al., 2001; Jefferson et al., 2001; Jhansi et al., 2013; Lazarova, 1999; Rajala et al., 2003).

Electrochemical disinfection (ECD) provides a scalable, low cost, low maintenance, and energy efficient alternative to current disinfection methods (Stoner, 1973; Stoner et al., 1982). Strong oxidants, such as chlorine containing species (CCS) and reactive oxygen species (ROS), can be generated in blackwater without the addition of chemicals. CCS and ROS are effective at inactivating

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https://doi.org/10.1016/j.watres.2018.04.022

harmful microorganisms such as *E. coli* (Drogui et al., 2001; Gordon et al., 1998; Shimada and Shimahara, 1982; Stoner et al., 1982; Venczel et al., 1997; Venkitanarayanan and Ezeike, 1999). While CCS, such as HClO, Cl_2, and ClO^-, can be efficiently generated and can effectively treat wastewater (Raut et al., 2014, 2013), ROS have been reported to have greater pathogen inactivation efficiency, higher reactivity, and no hazardous long-term effects (Chen et al., 2017; Jeong et al., 2006; Jeong et al., 2009). For instance, H_2O_2, an ROS, will decompose into water upon exposure to sunlight. Similarly, $^{\bullet}OH$, O_2^-, and other ROSs will also decompose to water if not used for pathogen inactivation or other reactions. Conversely, CCSs will often linger in solution when unreacted, leading to potentially harmful environmental and physiological side-effects (Background on Drinking Water Standards in the Safe Drinking Water Act (SDWA), 1996; Brungs, 1973).

Several electrode materials have been reported to efficiently produce CCS and ROS. Chlorination of blackwater using CCS is a fundamental method of ECD. Mixed metal oxides (MMOs), BDD, and Pt electrodes have been shown to be effective chlorine generators for ECD at oxidative potentials (Martínez-Huitle et al., 2015; Martínez-Huitle and Ferro, 2006). MMOs have been a focus of ECD (Chen, 2004; Jeong et al., 2009). However, the electrochemical properties of these materials, such as electroactivity and low over-potentials for water electrolysis, lead to oxidant production with diminished coulombic efficiency (Chen, 2004; Jeong et al., 2009). Boron-doped diamond (BDD) is a potential electrode material that does not have these deficiencies. Previous papers have shown that BDD electrodes have low electroactivity, a wide solvent window, mechanical robustness, resistance to corrosion in challenging chemical environments, and ability for polarity reversal without degrading the performance of the electrode (Einaga, 2010; Einaga et al., 2014; Fujishima et al., 2005; Luong et al., 2009; Macpherson, 2015; Marselli et al., 2003; Swain et al., 1998). Application of BDD as electrochemical electrodes to generate CCS and ROS in aqueous environments has also been studied (Jeong et al., 2007, 2006; Jeong et al., 2009). Particularly important is the ability of BDD to generate ROS with improved efficiency over other electrode materials due to the large over-potential needed for water splitting (Cañizares et al., 2002). Less expensive and non-sp^3 carbon-based materials, such as activated carbon or carbon nanotubes, have also been explored as ECD electrodes (Radjenovic and Sedlak, 2015). While these materials are easy to synthesize and hold promise as oxygen reduction catalysts (Chen et al., 2017) to form H_2O_2, they are often unsuitable for use as anodes in ECD systems as they have low oxygen evolution over-potentials leading to diminished CCS and $^{\bullet}OH$ generation efficiencies compared to BDD.

Despite the promise of BDD, there is limited literature investigating its use as an energy efficient electrode for microbial inactivation. Jeong et al. compared BDD to other anodes and found that it was the most efficient in generating ROS to inactivate *E. coli* and investigated bacterial inactivation using specific ROS (Jeong et al., 2007, 2006; Jeong et al., 2009). It was shown that $^{\bullet}OH$ generated at a constant oxidative current density could disinfect *E. coli* with greater efficiency than CCS and other ROS. However, the mechanism of ECD of blackwater using BDD anodes is unclear. It may be from chlorination, or from production of $^{\bullet}OH$, H_2O_2, $^{\bullet}O_2^-$, and O_3. Jeong et al. (Jeong et al., 2006; Jeong et al., 2009) attempted to determine the mechanism using multiple disinfection studies by varying the electrolyte and using scavengers. They determined that while chlorination can often be the cause for disinfection when using a BDD anode, the most kinetically favorable electrochemical pathway to producing CCS is likely indirect oxidation of Cl^- mediated by $^{\bullet}OH$. It should be mentioned that these studies did not include reductive generation of H_2O_2, which is possible from BDD with surface non-diamond content, such as boron-doped ultra-nanocrystalline diamond (BD-UNCD) (Thostenson et al., 2017).

ECD of microorganisms has commonly been studied through constant current oxidative methods, although potentiometric methods promise greater coulombic efficiency due to targeted ROS generation (Martínez-Huitle et al., 2015). In constant current methods, the potential of the cell increases with time to maintain the applied current-density, often moving the cell potential well beyond the onset of ROS generation and into the oxygen evolution reaction (OER) and/or hydrogen evolution reaction, sacrificing efficiency for time savings (Martínez-Huitle et al., 2015; Martínez-Huitle and Ferro, 2006). Unlike constant current and potentiostatic methods, potentiodynamic methods provide potentially increased efficiency by keeping the electrode from fouling through reverse polarization and controlling the potential (Macpherson, 2015).

In contrast to other BBD electrodes, BD-UNCD electrodes have a unique ability to generate ROS in aqueous environments at both anodic and cathodic potentials. Recently, our group reported on generation of oxidants and energy efficient disinfection of *E. coli* using BD-UNCD electrodes (Raut et al., 2014, 2013; Thostenson et al., 2017). We previously demonstrated that oxidative functionalization of sp^2-bonded carbon present on the BD-UNCD surface can catalyze the reductive generation of H_2O_2 from dissolved oxygen following the oxygen reduction reaction (ORR) (Thostenson et al., 2017). Subsequent potential cycling was shown to create and stabilize these ORR catalysts through a potentiodynamic-controlled process. Similar correlations of sp^2 and defective carbon structures have been cited to catalyze the ORR for H_2O_2 production (Chen et al., 2017; Macpherson, 2015).

Here we report on the benefits of potential cycling, a potentiodynamic method, for sanitizing blackwater and compare it to potentiostatic methods. We focus on potentiometric operation rather than constant current operation to ensure preservation of catalytic functional groups on the surface of BD-UNCD electrodes by not over-oxidizing or over-reducing them (Thostenson et al., 2017). Moreover, we demonstrate that potential cycling between targeted potentials using functionalized BD-UNCD electrodes in diluted blackwater can decrease the energy needed for disinfection of microbial species. Functionalized BD-UNCD electrodes are shown to provide binding sites for improved electrochemical processes. Subsequent potential cycling of the functionalized BD-UNCD electrodes serves the dual purposes of maintaining the binding sites and keeping the ORR catalysts active. Through a 24 h study in undiluted blackwater, the potential cycling of BD-UNCD is demonstrated to yield an electrode surface with less fouling and with higher current efficiency compared to potentiostatic methods. This work adds to the continuing investigations of ORR catalysts using functionalized carbon materials that have the potential to bring a cost-effective, energy efficient, and practical solution to the problem of disinfecting blackwater.

2. Methods

2.1. Electrode fabrication

BD-UNCD films (thickness 2 μm) on SiO_x/Si (1 μm/500 μm) with geometric areas between 0.5 and 1.5 cm^2 were cleaved from a 4 in (10.16 cm) UL25 wafer purchased from Advanced Diamond Technologies (Romeoville, IL). The wafer has a reported surface roughness of <10 nm rms, with grain sizes on the order of 3–5 nm and electrical resistivity of 0.1 Ω-cm. Cleaved pieces from this wafer were electrically connected to a thin copper wire using silver paste (Ted Pella, PN#16031) and front contact made to the BD-UNCD surface. The contact was left to dry on a hot plate at 80 °C for