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Electrochemical disinfection of simulated ballast water on conductive diamond electrodes

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HIGHLIGHTS

- Ballast water treatment deals with invasive species elimination.
- Electrochemical disinfection is an easy to apply process on-board.
- Modeling of chlorine generation during electrochemical disinfection was performed.
- Both bacteria (*E. coli*) and higher organisms (*A. salina*) were tested as model microorganisms.

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ABSTRACT

In this work, the electrochemical disinfection with conductive diamond electrodes was studied to treat simulated ballast water. *Artemia salina* was used as indicator organism and *Escherichia coli* as indicator bacterium. The influence of salinity (3 and 30 g/L NaCl simulating brackish and ballast water, respectively), current density (up to 1273 A/m^2) and operation mode (batch and single-pass) on inactivation and total residual chlorine production rates was investigated. An increase in salinity and current density generally had a beneficial effect on both rates. *A. salina* in ballast water was completely inactivated after 45 min of batch treatment at 255 A/m^2 (corresponding to about 200 mg/L of produced chlorine) and this increased to 60 min in brackish water. *A. salina*, whose inactivation follows first order kinetics, was found to be more resistant to electrochemical disinfection than *E. coli*. The complete inactivation of *E. coli* was achieved in less than 5 min of batch operation at 127 A/m^2, whereas the concentration of produced chlorine was less than 20 mg/L. Operation in single-pass mode was less effective for *A. salina* because it did not suffer mechanical stress, whereas *E. coli* inactivation occurred at low current densities and irrespective of the salinity due to both direct oxidation on the surface of conductive diamond anode and chemical reactions with chlorine species and/or reactive oxygen species.

1. Introduction

Ballast water is defined as the water carried by ships to ensure stability, trim and structural integrity. If a ship is empty of cargo, it will fill with ballast water whereas if it loads cargo, the ballast water will be discharged. The International Maritime Organization (IMO) estimates that at least 7000 different species are being carried in ships' ballast tanks around the world [1]. These marine species are microorganisms, phytoplankton, zooplankton, etc. and most of them do not survive the journey or the new environmental conditions where they are discharged. However, some species survive in the host environment under favorable circumstances. At this point, the environmental impact of these last species often results in unpredictable ecological, economic and social impacts [2–4].

The methodology recommended by the IMO guidelines for ballast water treatment involves its exchange to reduce the risk of transfer of harmful aquatic organisms. Nevertheless, this method has ship-safety limitations because it is not completely effective in removing organisms from ballast water. Then, effective ballast water management and/or treatment methods should be developed in order to replace the ballast water exchange at sea. So far, several technologies have been suggested for ballast water treatment, including filtration [5], irradiation with ultraviolet light [6,7], sterilisation with ozone [8,9], disinfection with chlorine species [10] or hydrogen peroxide [11], addition of biocides to ballast water to kill organisms [12,13] and sonication [14].

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In recent years, electrochemical processes have been tested for water disinfection [15–18]. Electrochemical disinfection can be defined as the eradication of microorganisms using an electric current passed through the water by means of suitable electrodes. The advantages of electrochemical water disinfection in comparison to other chemical methods include (i) simplicity of the equipment, (ii) easy automation of the process, (iii) the fact that additional chemicals are not required since the disinfectant dose can be easily controlled varying the current density applied, and (iv) the relatively low current requirement that may allow the use of green energy sources such as solar cells or fuel cells [19–21]. Furthermore and in the specific case of saline water treatment, electrochemical disinfection takes advantage of the electrolytic production of chlorine species such as hypochlorite and hypochlorous acid (i.e., electrochlorination) [22–25].

The selection of a proper anodic material is a key point in electrolytic processes. In this way, dimensionally stable anodes (DSAs) present good efficiencies in the production of hypochlorite, which is critical for the wide use of electrochemical technology in many environmental applications [22,26]. Nevertheless, a new anode material, namely boron-doped diamond (BDD), has been developed in recent years and it exhibits good properties for electrochemical applications. The BDD anode allows operation at harsh oxidation conditions and, consequently, promotes the generation of several oxidants such as peroxosalts, ozone or hydrogen peroxide, which would be difficult or even impossible to be produced with other anodic materials [27–32].

The efficacy of electrochemical disinfection in killing a wide spectrum of microorganisms has been reported in the literature [33–35]. The high bactericidal capacity is attributed to several functions such as the generation of toxic oxidants like persulphate [36] or chlorine species [37], direct oxidation on the electrode surface [34,38], inactivation by reactive intermediate products such hydroxyl radicals, ozone, and hydrogen peroxide. [39–41], and/or the electric field effect [33,38,41]. To the best of our knowledge, the electrochemical disinfection of ballast water has only recently been reported in the literature; seawater spiked with *E. coli* [42,43] or *Enterococcus faecalis* (*E. faecalis*) [42] was treated on a titanium anode and process performance was assessed in terms of energy consumption to achieve IMO discharge standards and post-treatment environmental implications (e.g. corrosion of materials, ecotoxicity to seawater species).

In this context, the main objective of this study was to examine the potential of electrochemical disinfection over BDD to treat simulated ballast water. *Artemia salina* (*A. salina*) was chosen as an indicator organism, while *Escherichia coli* (*E. coli*) was selected as indicator bacterium. The influence of salinity, current density and operation mode on *A. salina* and *E. coli* mortality rates, as well as on chlorine production was investigated.

2. Materials and methods

2.1. Test organism

The artificial water was prepared diluting sodium chloride into osmosis water to obtain a final concentration of 30 g/L NaCl (seawater) or 3 g/L NaCl (brackish water).

A. salina in the form of dehydrated cysts was provided by the Hellenic Center of Marine Research (Greece). *A. salina* cysts were kept refrigerated (4–5 °C) in the absence of light. Prior to use, they were hatched into nauplii larvae for 24 h. To initiate the growth procedure a volume of 25 mL of the cysts was placed in 1 L of artificial seawater [17]. A water bath was used to keep the temperature at 28 °C [44]. Continuous aeration was provided through constant airflow. The hatching of *A. salina* was complete after a period of 24 h. Then, the *A. salina* suspension was diluted to 10 L of artificial sea or brackish water (feed water).

The bacterial strain used in the present study was *E. coli* (DSMZ 498) (DSMZ, German Collection of Microorganisms and Cell Cultures). One hundred microliters of the bacterial strain of *E. coli* were spread over the surface of the appropriate solid agar medium (HiCrome™ Coliform Agar, HiMedia Laboratories) in 90 mm Petri dishes and then incubated for 24 h at 37 °C. Finally, the bacterial pellet was suspended in sterile 0.8% (w/v) NaCl aqueous solution and diluted to the required cell density corresponding to a cell concentration of approximately 10^6–10^7 CFU/mL [35,45]. The concentration of the suspensions was adjusted measuring the optical density according to the McFarland standards [46].

2.2. Electrochemical experiments

Experiments were carried out in a DiaCell (type 100) single compartment electrolytic flow-cell manufactured by Adamant Technologies (Switzerland). BDD on silicon was used as anodic and cathodic material. Both electrodes were circular with a diameter of 10 cm each and an electrode gap of 10 mm.

Experiments were carried out in both batch and single pass modes and under galvanostatic conditions (Fig. 1). Polarity was automatically inverted every 10 min to avoid operational problems such as the formation of films of carbonates on the surface of the cathode or the passivation of the anode. In batch mode, 10 L of simulated ballast or brackish water were loaded in a vessel and continuously recirculated in the cell by means of a peristaltic pump at a constant flowrate of 20 L/min, whereas in single pass mode, 30 L of simulated ballast or brackish water were loaded in the vessel. A spiral coil immersed in the effluent vessel and connected to tap water supply was used to remove the heat released from the electrolytic process. Thus, all experiments were conducted at uncontrolled temperature which never exceeded 30 °C.

2.3. Experimental procedure

The current density ranged between 0 and 1273 A/m^2, which corresponds to current values from 0 to 10 A. The mechanical stress control was performed with the run at 0 A/m^2. The gradient velocity was calculated and it ranged from 700 to 1300 s^{-1}, which is between or slightly higher than that typically used in a coagulation process [47]. Two samples of 0.1 L each were collected in beakers: the first beaker contained 2 mL sodium thiosulphate ($Na_2S_2O_3{\cdot}5H_2O$ purchased from Merck, Germany) stock solution (1 N) in order to instantly destroy free chlorine produced during electrolysis and avoid microorganisms death during sample handling due to residual chlorine. The second beaker did not contain any sodium thiosulphate and it was used to measure total residual chlorine. Here, it is important to point out that 2 mL of 1 N sodium thiosulphate solution were sufficient to reduce up to 200 mg/L of residual chlorine in seawater [17]. Samples were collected from the outlet of the electrochemical cell. In batch experiments, samples were taken at 5, 10, 15, 30, 45, 60, 75 and 90 min and analyzed with regard to the population of *A. salina* or at 2, 5, 10, 15, 30, 60 and 90 min and analyzed with regard to the CFU/mL concentration of *E. coli*. In single-pass experiments, just a sample was taken at each current density studied after 5 s. The influence of total residual chlorine was also studied adding the appropriate amounts of 2 g/L sodium hypochlorite stock solution (without water pumping or electricity) to the effluent vessel in order to achieve levels of 50, 100 and 200 mg/L free residual chlorine [17].