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Electrochemical disinfection of simulated ballast water on PbO_2/graphite felt electrode

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ABSTRACT

A novel PbO_2/graphite felt electrode was constructed by electrochemical deposition of PbO_2 on graphite felt and characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) analysis. The prepared electrode is a viable technology for inactivation of *Escherichia coli*, *Enterococcus faecalis*, and *Artemia salina* as indicator organisms in simulated ballast water treatment, which meets the International Maritime Organization (IMO) Regulation D-2. The effects of contact time and current density on inactivation were investigated. An increase in current density generally had a beneficial effect on the inactivation of the three species. *E.faecalis* and *A.salina* were more resistant to electrochemical disinfection than *E. coli*. The complete disinfection of *E.coli* was achieved in <8 min at an applied current density of 253 A/m^2. Complete inactivation of *E. faecalis* and *A.salina* was achieved at the same current density after 60 and 40 min of contact time, respectively. *A. salina* inactivation follows first-order kinetics.

1. Introduction

The unladen ships must be filled with ballast water to maintain balance, stability, trim, and structural integrity of ships during voyage. A wide variety of marine species including bacteria and other microbes, eggs, cysts, and larvae of various species are found in ballast water (Ruiz et al., 2000). The International Maritime Organization (IMO) estimates that >7000 different species in ballast tanks are carried across the world's oceans everyday (Oemcke and van Leeuwen, 2003). Invasive aquatic species constitute >80% of the world's marine ecoregions (Battle, 2009). Marine invasive species is regarded as a serious threat to global marine environmental safety. The ballasting and deballasting processes have been identified as major factors promoting the growth of marine invasive species (Martinez et al., 2013; Hess-Erga et al., 2010; Miller et al., 2011). The IMO adopted the International Convention for the Control and Management of Ships' Ballast Water and Sediments in 2004 (IMO, 2004) to avoid the impacts of the marine invasive species on health, environment, and economy. Furthermore, Regulation D-2 of the IMO for living organisms in discharged ballast water is expected to be implemented by 2016 for all existing ships (Nanayakkara et al., 2011). Several ballast water management systems have been proposed in the last decade including filtration, electrolysis, ultraviolet (UV) radiation, sonication, and chemical methods. Each of these ballast water management systems has some advantages and disadvantages. Several efforts have been taken with regard to electrochemical disinfection due to its high treatment efficiency, low cost, wide spectrum disinfection, convenience, and environmental compatibility (Patermarakis and Fountoukidis, 1990; W.Y. Liang et al., 2005; Sarkka et al., 2008). Furthermore, the electrochemical disinfection can be achieved by the electrolytic production of chlorine species during ballast water treatment (Kraft, 2008; Khelifa et al., 2004; Rychen et al., 2003). The electrochemical disinfection is mainly attributed to the electric field effect (Grahl and Markl, 1996) and the presence of active chemical oxidants such as chlorine species (HOCl, OCl^-) (Schmalz et al., 2009), hydrogen peroxide, and reactive oxygen species (ROS) (hydroxyl radicals, ozone, and hydrogen peroxide) (Diao et al., 2003; Feng et al., 2004; W. Liang et al., 2005). However, the ROS, especially •OH, could attack or cause the breakdown of the cell membrane and cell wall, or electrolyze the molecules on the cell surface, leading to considerable cell death and lyses.

Anodic materials with high efficiency play an important role in electrochemical disinfection. Dimensionally stable anodes (DSAs) and boron-doped diamond (BDB) possess properties suitable for various environmental electrochemical applications (Bergmann et al., 2008; Schmalz et al., 2009). However, compared with DSAs and BDB, PbO_2 is not only easy to prepare and of lower cost, but also one of the best electrode materials with good electrical conductivity, high oxygen

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overpotential, chemical inertness, and good resistance to corrosion (Velichenko et al., 2000; Quiroz et al., 2005). The high electrocatalytic activity of PbO_2 as an anode is mainly based on the oxidation of •OH (Cao et al., 2009; Chen et al., 2009).

In this study, a PbO_2/graphite felt anode was prepared and its effectiveness for electrochemical disinfection with regard to simulated ballast water treatment was evaluated.

2. Materials and methods

2.1. Simulated ballast water

The artificial seawater was prepared by diluting unrefined sea salt with deionized water to obtain a final concentration of 30 g/L NaCl.

Escherichia coli cells (ATCC 10798) and *Enterococcus faecalis* (ATCC 47077) cells were cultured in Luria–Bertani (LB) nutrient broth and tryptic soy broth medium at 37 °C for 20 h, respectively. The bacterial cells were then collected by centrifugation at 4000 rpm for 15 min and were washed thrice using 0.9% (*w*/*w*) saline water. The bacterial pellet was resuspended in the abovementioned artificial seawater to obtain a cell concentration of approximately 10^6–10^7 CFU/100 mL for preparing the simulated ballast water.

Artemia salina cysts were kept refrigerated (4–5 °C) in the absence of light. A volume of 25 mL of the cysts was placed in 1 L of the abovementioned artificial seawater. The cysts hatched to nauplii larvae for 24 h. A water bath was used to maintain the temperature at 28 °C. Continuous aeration was provided through constant airflow. Then, 100 mL of the *A. salina* suspension was diluted to 1 L of artificial seawater for preparing the simulated ballast water.

2.2. Electrode preparation and characterization

The PbO_2/graphite felt electrode was prepared by electrochemical deposition on graphite felt ($10 \times 4 \times 0.5$ cm). Firstly, the graphite felt was sonicated with 40% NaOH solution and 1:1 (*V*/*V*) HNO_3/H_2SO_4 for 30 min. Finally, the graphite felt was washed with deionized water and transferred to an electrochemical deposition cell containing 0.5 M $Pb(NO_3)_2$ in 0.1 M HNO_3 solution. The electrochemical deposition of PbO_2 on graphite felt was carried out under an applied current of 50 mA/cm^2 for 30 min. The X-ray diffraction (XRD) pattern of the PbO_2/graphite felt electrode was recorded using a D8 Advance X-ray diffractometer (Bruker). Scanning electron microscopy (SEM) observations were recorded using the JEOL JSM-5610LV (Japan). All of the experiments were carried out at room temperature.

2.3. Electrochemical disinfection experiments

All electrochemical disinfection experiments were carried out in a 1000-mL open mezzanine beaker. The PbO_2/graphite felt was considered the anode and a Ti sheet with the same area the cathode. The two electrodes were installed parallel to each other, and an electrode gap of 10 mm was maintained. Constant current was applied with a workstation CHI 660 D (China). During inactivation, the suspension was magnetically stirred to ensure the efficiency of mass transfer. Electrochemical disinfection experiments were performed at 25 ± 2 °C, which was maintained by a thermostat device.

2.4. Analytical methods

During the experiments, sampling and measurement of the microorganisms before and after electrochemical disinfection were done in triplicate. About 2 mL of the reaction solution was withdrawn at specific time intervals. For the analysis of microorganisms, the sample was immediately quenched with excess $Na_2S_2O_3$ (20 mM) to eliminate free chlorine produced during electrolysis and avoid death of microorganisms during sample handling due to residual chlorine.

The viability of *E.coli* or *E.faecalis* in the reaction solution was determined by a colony-counting technique. A series of 10-fold dilutions were conducted, 0.1 mL of each dilution was plated on LB agar or Zobell 2216E agar, and these plates were incubated at 37 °C for 24 h. All materials used were autoclaved at 121 °C for 20 min before testing.

The samples were then transferred into Petri dishes (90 mm in diameter), and *A.salina* was counted with a colony counter apparatus. The organisms were declared alive or dead based on their movement.

Residual chlorine was measured according to the standard 4500 Cl-B method I (APHA, AWWA, WEF, 1998).

3. Results and discussion

3.1. Characterization of PbO_2 electrode

The XRD pattern of PbO_2 on graphite felt prepared by electrochemical deposition in Fig. 1 showed the characteristic reflections of β-PbO_2 with a tetragonal structure (Yu et al., 2009). The graphite felt diffraction peaks almost cannot be observed in the XRD pattern of PbO_2/graphite felt. The SEM image showed that the average crystal size of β-PbO_2 on graphite felt was about 0.5 μm (Fig. 2). The fibers of graphite felt were compactly covered by the electrochemically deposited β-PbO_2 microcrystals; the latter caused the disappearance of graphite felt diffraction peaks in the XRD pattern of PbO_2/graphite felt. The result was in accordance with the XRD patterns.

3.2. Production of total chlorine

Regarding the production of chlorine during electrolysis of artificial seawater, Fig. 3 presents the changes in residual chlorine concentration with respect to electrolysis time and current density. The higher the applied current density and the longer the electrolysis time, the higher the residual chlorine concentration achieved. In addition, a linear relationship between the residual chlorine concentration in the reactor and electrolysis time is observed. Thus, current density is considered an important parameter with regard to total residual chlorine production.

3.3. Disinfection performances

The electrochemical disinfection performance of PbO_2/graphite felt as the anode in simulated ballast water was evaluated by the inactivation of *E.coli*, *E. faecalis*, and *A. salina*, the three of the IMO-regulated microorganisms.

3.3.1. Disinfection of E. coli

Fig. 4 shows the inactivation of *E.coli* as a function of electrolysis time and applied current densities. *E.coli* inactivation occurred readily in a short electrolysis time. The microbial inactivation levels of almost 3.4

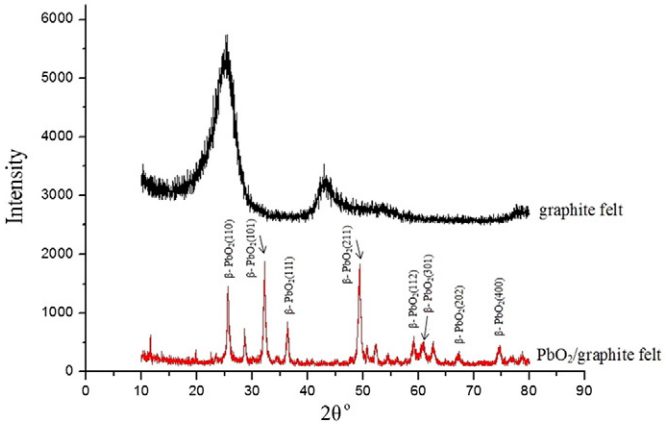

Fig. 1. XRD patterns of PbO_2 electrodeposited on graphite felt.