Marine Pollution Bulletin xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Enhancing the efficacy of electrolytic chlorination for ballast water treatment by adding carbon dioxide

Hyung-Gon Cha [a,b], Min-Ho Seo [a], Heon-Young Lee [c], Ji-Hyun Lee [d], Dong-Sup Lee [b], Kyoungsoon Shin [a], Keun-Hyung Choi [e,*]

[a] South Sea Research Institute, Korea Institute of Ocean Science and Technology, 41 Jangmok-1gil, Jangmok-myun, Geoje-si 656-834, Republic of Korea
[b] Department of Oceanography, Busan National University, 2 Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 609-735, Republic of Korea
[c] New Water Tech Co. Ltd., Unit 204 Sanhak-Kwan, Dongkuk St. 32, Ilsan-donggu, Goyang-si 410-820, Republic of Korea
[d] Korea Testing & Research Institute, 411 Daun-dong Jung-gu, Ulsan 681-802, Republic of Korea
[e] Department of Oceanography and Ocean Environmental Sciences, Chungnam National University, 99 Daehak-ro, Yusung-gu, Daejeon 305-764, Republic of Korea

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Electrochlorination
Carbon dioxide
Synergistic effects
Ballast water

ABSTRACT

We examined the synergistic effects of CO_2 injection on electro-chlorination in disinfection of plankton and bacteria in simulated ballast water. Chlorination was performed at dosages of 4 and 6 ppm with and without CO_2 injection on electro-chlorination. Testing was performed in both seawater and brackish water quality as defined by IMO G8 guidelines. CO_2 injection notably decreased from the control the number of *Artemia franciscana*, a brine shrimp, surviving during a 5-day post-treatment incubation (1.8 and 2.3 $\log_{10}$ reduction in seawater and brackish water, respectively at 6 ppm TRO + CO_2) compared with water electro-chlorinated only (1.2 and 1.3 $\log_{10}$ reduction in seawater and brackish water, respectively at 6 ppm TRO). The phytoplankton *Tetraselmis suecica*, was completely disinfected with no live cell found at >4 ppm TRO with and without CO_2 addition. The effects of CO_2 addition on heterotrophic bacterial growth was not different from electro-chlorination only. Total residual oxidant concentration (TRO) more rapidly declined in electro-chlorination of both marine and brackish waters compared to chlorine + CO_2 treated waters, with significantly higher amount of TRO being left in waters treated with the CO_2 addition. Total concentration of trihalomethanes (THMs) and haloacetic acids (HAAs) measured at day 0 in brackish water test were found to be 2- to 3-fold higher in 6 ppm TRO + CO_2-treated water than in 6 ppm TRO treated water. The addition of CO_2 to electro-chlorination may improve the efficiency of this sterilizing treatment of ballast water, yet the increased production of some disinfection byproducts needs further study.

1. Introduction

Electro-chlorination is one of the most cost-effective and widely adopted approaches for disinfection and purification of water. It produces hypochlorite by passing direct current through electrodes within an electrolytic cell, using salts as electrolytes, and generating oxidized chlorine. It also has many other applications such as treatment of swimming pool water (Gomà et al., 2010), cooling water towers (Jenner et al., 1998), prevention of biofouling in desalination (Thangappan and Sampathkumaran, 2008), and ship ballast water (Lloyd's Register, 2012; Tsolaki et al., 2010).

One of the fast-growing areas of its application is for treatment of ship ballast water. Ballast water management systems (BWMS) based on electro-chlorination now account for more than a third of all BWMS installed on ships (Lloyd's Register, 2012). Electro-chlorination of ballast water is not only highly effective, but it is also safer. It eliminates the need for storing concentrated chlorine on ships and handling of chlorine gas, which is highly toxic and corrosive.

Approximately 3.5 gigatons of ballast water are being used globally each year for stability and maneuverability of ships during voyages (Endresen et al., 2004). Ballast water carries a variety of organisms, some of which may be non-native and nuisances in receiving bodies of water, causing extensive ecological and

* Corresponding author at: Department of Oceanography and Ocean Environmental Sciences, Chungnam National University, 99 Daehak-ro, Yusung-gu, Daejeon 305-764, Republic of Korea. Tel.: 82428216432.
E-mail address: keunhchoi@cnu.ac.kr (K.-H. Choi).

http://dx.doi.org/10.1016/j.marpolbul.2015.03.025
0025-326X/

economic damage. Over two-thirds of recent non-native species introductions in marine and coastal areas are likely due to transfer by ships, and ballast water transport and discharge are the most common mode of that transfer (Endresen et al. 2004).

Ballast water treatment via physical exchange of ballast water with oceanic water has been practiced for some time (Locke et al., 1993), and BWMS can also be installed on board to treat water during ballasting to prevent the transfer of harmful aquatic organisms and pathogens. BWMS will be required to be installed for most ocean-going vessels in accordance with the International Convention for the Control and Management of Ships Ballast Water & Sediments adopted in 2004, when it enters into force (IMO, 2004).

Despite its merits, electro-chlorination of ballast water has two major issues that need to be addressed. (1) Power consumption to generate high total residual oxidants (TRO) concentration increases disproportionally at lower salinities (Lacasa et al., 2013). (2) Many BWMS employ high TRO concentrations, >10 ppm, during ballasting to kill or suppress the growth of organisms inside ballast tanks (MEPC, 2014 and references therein). However, high levels of TRO, although effective, may produce high concentrations of disinfection byproducts (DBPs) that could be harmful for the environment receiving discharged waters (Tsolaki et al., 2010; Werschkun et al., 2014). It would be better, therefore, to find an inexpensive means to achieve high mortality rate of organisms in ballast water with relatively low TRO, while producing readily degraded disinfection byproducts. Enhancing the efficiency of the electro-chlorination process could lead to better and more environment-friendly treatment of ballast water.

Efficiency of electro-chlorination may vary according to conditions in ballast water, such as salinity, pH and temperature. Especially, the relative concentrations of reactive halogenated compounds at aqueous equilibrium depend on pH. The standard reduction potential for the formation of hypobromous acid from bromide is 1.33 V as compared to 1.49 V for the equivalent chloride reaction (WHO, 2000). This results in oxidation nearly all of the chlorine present (to a limit of 65 ppm) from hypochlorous acid (HOCl) to hypobromous acid (HOBr). At low pH, TRO will cause formation of more HOCl and/or HOBr than the less powerfully oxidative hypochlorite (OCl^-) and hypobromite (OBr^-). A pH reduction down to 6 will increase the proportion of HOCl or HOBr by 7%. HOCl is 80–200 times stronger than OCl^- in terms of pathogen disinfection (White, 1999). A way to decrease pH in water is to dissolve CO_2 by injecting it as gas or aqueous solution. Increased CO_2, and thus lowered pH will increase the proportion of HOCl and HOBr, which could increase toxicity to organisms (Kim et al., 2013).

In this study, we examined the combined effects of increased levels of CO_2 and TRO on the survival of plankton and heterotrophic bacteria in simulated ballast water. The study was designed to test whether injection of CO_2 increases the death of plankton in ballast water and thus could be used for BWMS employing electro-chlorination.

2. Materials and methods

2.1. Electro-chlorination and CO_2 injection system

The electro-chlorination system was set up on a pier at South Sea Research Institute (SSRI) of Korea in Jangmok Bay. Prior to initiating the electrolysis assays, the parameters were selected as follows: tank volume 1 m^3, operational voltage for generating TRO concentrations up to 6 ppm with CO_2 injection rate at 100 ml min^{-1} to reduce pH 6 for both seawater (salinity > 32) and brackish water (salinity = 15).

2.2. Preparation of test water

Test waters (1 m^3) for saline (salinity > 32) and brackish (salinity at 15) water condition were prepared in accordance with the IMO G8 guidelines (IMO, 2008). Seawater for the tests was drawn by pumping from the surface of Jangmok Bay into a 1 m^3 polyethylene non-toxic water tank on the pier. For brackish water tests (salinity of 15), the bay water was diluted with tap water that had been aerated overnight to remove its residual TRO. Water temperature, if lower than 15 °C, was raised to 15 °C with a submersible, thermostatic regulator (LifeTech Inc., China).

2.3. Augmentation of chemical compounds and test organisms

A total of 10 cycles with 5 test cycles for seawater and brackish water, respectively, with each test cycle lasting 5 days. The whole experiments could not be finished within a short period and the experiments spanned over 4 months during which environmental characteristics of the bay water were regularly monitored (Table 1). The bay water contained low concentration of dissolved organic carbon (DOC, <2 ppm, Table 1) and particulate organic carbon (POC, 1–2 ppm, Dr. PG Jang, personal comm.). To meet the required test condition as stipulated in the IMO G8 guidelines (IMO, 2008) for DOC, POC and total suspended solids (TSS), glucose (Sigma–Aldrich Co., 3.3 and 13.3 g m^{-3} for seawater and brackish water condition, respectively) and starch (Sigma–Aldrich Co., 5.3 and 66.7 g m^{-3}, respectively) were added to the test water. These chemical additions satisfied the test soup conditions as required in the IMO G8 guideline for brackish water with >50 mg l^{-1} TSS and >5 mg l^{-1} DOC against seawater with only >1 mg l^{-1} TSS and >1 mg l^{-1} DOC, and are routinely applied for land-based tests at the test facility located at the SSRI where these CO_2 experiments were conducted.

The guidelines also set the desired level of abundance for plankton: 10^5 individuals m^{-3} for organisms >50 μm and 10^3 individuals m^{-3} for plankton of 10–50 μm in minimum dimension. Both pre-cultured *Artemia franciscana*, a brine shrimp, representing zooplankton (>50 μm in minimum dimension) and *Tetraselmis suecica*, a marine green alga, representing phytoplankton (10–50 μm in minimum dimension) were added to the test water at the IMO G8 guideline concentrations (Table 1). *A. franciscana* (INVE aquaculture, http://www.inveaquaculture.com/) were hatched from dehydrated cysts. A water bath kept the temperature at 18–20 °C for 2 days with continuous aeration through constant air flow during development of the cysts (Madhu, 2009). The freshly hatched ones were then carefully separated from the remaining cysts. The green (Chlorophyta) microalga, *T. suecica* (Kylin) Butcher, supplied from Chlorland Inc. (Geoje, Korea), was grown on f/2 Guillard medium at 20 °C under LD 12:12 cycles for several days until they reach exponential growth phase. Natural seawater (pH of 8.3) was filtered through a membrane filter with a nominal pore size of 0.7 μm and was autoclaved at 121 °C for 20 min and stored at 4 °C until use for culture of the phytoplankton. Both zooplankton and phytoplankton culture were added to the 1 m^3 seawater or brackish test water immediately before the water was treated with the electro-chlorination system. The test water was aerated from the bottom with an aerator installed at the bottom to mix the whole water column and provide oxygen during the experiments.

2.4. Controls and treatment of organisms using CO_2 injection and electro-chlorination system

The experiments were carried out sequentially. The first test water (200 l) containing the phytoplankton and zooplankton were pumped through the electro-chlorination system without the system activated to serve as a control. Another water of 400 l

Please cite this article in press as: Cha, H.-G., et al. Enhancing the efficacy of electrolytic chlorination for ballast water treatment by adding carbon dioxide. Mar. Pollut. Bull. (2015), http://dx.doi.org/10.1016/j.marpolbul.2015.03.025