An investigation on a novel ballast water treatment method and system based on ion-exchange membrane electrolysis

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Discharge of marine species into foreign environments through the ballast water of ships brought large quantities of environmental and economic losses to the world’s coastal regions. Based on ion-exchange membrane electrolysis, a new method coupled system design consisting of ion-exchange membrane electrolyzer, electrolytic anode and electrolytic cathode is proposed. Products of the electrolytic anode are used for the ballast water treatment. Optimal parameters including current density, cell voltage and current efficiency were theoretically obtained. Experimental validation also was carried out. Six algae species including Chlorella vulgaris, Nitzschia closterium f.minutissima, Platymonas subcordiformis, Dunaliella salina, Isochrysis galbana and Prorocentrum micans were performed by this system under the optimal conditions. The proposed approach had the more efficient kill ability for the algae life.

[Keywords: Ballast water, Ion-exchange membrane electrolysis, Available chlorine concentration, Algal]

Introduction

Ballast water is always used to ensure balance and stability of ship and plays a very important role in navigation safety, it is also the main way of alien marine biological invasion. Some of these invaders affect native living organisms and others may take greatly impact economic activities, such as fishing and hydro-power generation1. Most (80%) of the ballast water tanks are identified that they contained identifiable organisms and living aquatic organisms2,3. This kind of invasion will lead to the great losses for water supply, electric power industry and even death to human health4,5. Invasive species has been recognized as one of the four key environmental threats to the ocean by The Global Environment Facility6.

In February 2004, the International Maritime Organization (IMO) in London passed the <International Convention For The Control And Management Of Ships’ Ballast Water And Sediments>, which contains standards for ballast water treatment and provides the first global unified statutory basis for the global maritime sector management and control of ships' ballast water7. Treatment options for ballast water currently under consideration by the scientific communities include ballast water exchange8,9, primary separation devices such as cyclonic separation and filtration10,11, heat treatment12, UV13, a range of chemical biocides and active substances14,15. The purpose of chlorine as a disinfectant and electro chlorination to prevent marine growth in seawater systems has been well-known.

Seawater or other source of water with NaCl can be used to generate a disinfecting solution containing chlorine by passing an electrical current through the solution. Outer anode and cathode are usually made in seamless titanium pipe and the anode surface is coated with proprietary precious metal oxides, mainly ruthenium and iridium. Recently, a new kind of electrode has been developed. This experiment anode was the metal anode (DSA). DSA®-type electrodes show good technological performance, and this success is due to desirable feature such as high stability of the active coating, good overall performance under mild conditions, high conductivity, low cost and commercial availability16. Diamond electrode is made in the coating conventional electrode materials (thin film conductive diamond deposited on highly doped polycrystalline or monocrystalline silicon substrates)17. Engracia Lacasa et al.18 treated simulated ballast water by using diamond electrodes. Many international organizations
and research institutions are trying to study an effective treatment of ballast water invasive marine organisms\textsuperscript{19,20}.

Present study consists a new method coupled system design for ballast water treatment, based on ion exchange membrane electrolysis. Anode chamber and cathode chamber are isolated by ion-exchange membrane, which makes the electrolysis products separated. Products of the electrolytic anode are used for the ballast water treatment and those of the electrolytic cathode are used for the flue gas desulfurization treatment.

Materials and Methods

Principle of ion exchange membrane electrolysis

Ion exchange membrane is a perfluorinated cation exchange membrane which is a special kind of cation permselective membrane. Membrane allows cation and water molecules go through the membrane, anion and gas molecules cannot be allowed to pass through the membrane. Ion membrane contains sulfonic group (-SO$_3$H or -COOH). Hydrophilicity of the sulfonic groups make the membrane swells in solution and the film body becomes loose and generates many microporous. So the sulfonic group of hydrogen ion is exchanged with the solution of the cationic and the solution of chloride ion and hydroxide ion is rejected. After electrolysis, anode and cathode respectively produces Cl$_2$ and NaOH. Large amounts of available chlorine solution are generated as anode product for killing algae. Available chlorine can attack the algae causing cells to death due to its strong oxidation. The principle based on the partial electrolysis of NaCl is presented in seawater. NaCl is dissociated into Na$^+$ and Cl$^-$ that reacts at the anode to produce free chlorine (Cl$_2$). Successive reactions take place in the seawater including the formation of OH$^-$ that migrates to the cathode and reacts with Na$^+$ and Cl$_2$, producing NaOCl and H$_2$. The H$_2$ will be vented. Anode reaction that occurs in the electrolytic chlorine generator can be depicted as: $2\text{H}_2\text{O} \rightarrow \text{O}_2+4\text{H}^++4\text{e}\text{, } 2\text{Cl}^- \rightarrow \text{Cl}_2\uparrow+2\text{e}$, $\text{Cl}_2+\text{H}_2\text{O} \rightarrow \text{HCl}+\text{HClO}$. Cathode reaction that occurs in the electrolytic chlorine generator can be depicted as: $2\text{H}_2\text{O}+2\text{e}^- \rightarrow \text{H}_2\uparrow+2\text{OH}^-$. Theoretically calculation on electrolyte voltage

This experiment ion-exchange membrane electrolyzer used unit structure, it was rectangular groove plate. The effective area of electrolyzer was 0.2m$^2$, and the size was 400mm x 500mm. Anode was the metal anode (DSA). Cathode was active nickel electrode and was made of a diamond mesh. Ion-exchange membrane was produced by DuPont perfluorinated carboxylic acids compound membrane. Experimental conditions were configured as same as which in ship. Anolyte was seawater discharged by the fresh water generator. Mass fraction of NaCl was 4.5%. Because the seawater discharged by the fresh water generator was heated by main engine cylinder liner jacket water or steam, so the experimental temperature was at 75°C. The cell voltage was one of the most important factors which affect efficiencies of the ion-exchange membrane electrolyzer in the performance evaluation experiment. So the theoretical calculation of cell voltage was conducted before the experiment, and the cell voltage included the theoretical decomposition potential, anodic overvoltage, cathodic overpotential, the ion-exchange membrane voltage drop, the metal conductor voltage drop and the electrolyte ohmic voltage drop.

Theoretical decomposition potential value was equal to the difference between the anode equilibrium potential and the cathode equilibrium potential, that is:

$E^0 = \Phi^+ - \Phi^-$. By Nernst formula, the cathode equilibrium potential:

$\Phi^- = \Phi^0 + \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}}^2}{a_{\text{OH}^-}^2 \cdot P_{\text{H}_2}}$ (V)

Here, $\Phi^0$—Standard electrode potential. It was the electrode equilibrium potential (V) when the reactant and resultant were 1mol/L.

R — Gas constant, it was 8.31.

T — The absolute temperature of the cathode chamber, K.

F — The coulomb's constant, it was 96500.

$a_{\text{OH}^-}$ — The molar concentration of NaOH.

$P_{\text{H}_2}$ — The partial pressure of H$_2$. The value was equal to the difference between the total pressure and the partial pressure of saturated vapour under that temperature.

The experiment operating temperature was 75°C. The catholyte mass fraction of NaOH was 15%. This experiment partial pressure of saturated vapour was 0.3804 atm (0.038548MPa). Reference to the chlor-alkali industry, we combined with the actual
situation of this device, it was \( P_t=1.15 \) atm, \( P_{H_2}=0.7696 \) atm. Bringing all the values into formula, \( \Phi^- = -0.8360 \) V. By Nernst formula, anode equilibrium potential:

\[
\Phi^+ = \Phi^0 + \frac{RT}{2F} \ln \frac{P_{cl}}{P_{H_2}} \quad (V)
\]

\( \alpha_{cr} \) — Molar concentration of NaCl.

Reference to the chlor-alkali industry, it took \( P_t=1.1 \) atm, \( T=75^\circ \)C, the partial pressure of saturated vapour was 0.3804 atm (0.038548 MPa). By the equilibrium potential data table of the reaction of chlorine evolution\(^{21} \), \( \Phi^0=1.289 \) V. Bringing all the values into formula, \( \Phi^+ = 1.294 \) V. So the theoretical decomposition potential value was 2.1284 V.

The values of anodic overvoltage and cathodic overpotential were referencing to the overpotential data table of the DSA anodic overvoltage of chlorine evolution and low carbon steel cathodic overpotential of overpotential of hydrogen evolution, it can get anodic overvoltage was approximately 0.033 V, cathodic overpotential was about 0.40 V.

Formula of ion-exchange membrane voltage drop:\( V_M = D \cdot P \quad (V) \). \( D \) - current density (A/cm\(^2\)).

\( P \) - The membrane resistivity ( \( \Omega \cdot \text{cm}^2 \)). Experiment current density was set to \( D \), the current was set to \( I \). The effective area of electrolyzer was 2000 cm\(^2\). The current expressed as \( I = 2000D \).

DuPont ion-exchange membrane resistivity was about 3.5 \( \Omega \cdot \text{cm}^2 \). Bringing all the values into formula, it got \( V_M=3.5D \quad (V) \).

The formula of metal conductor voltage drop:

\[
IR_m = \rho K \frac{L}{S} \cdot I \quad (V)
\]

\( \rho \) – The resistivity of the metal conductor under a certain temperature.

\( L \) - Length of the metal conductor, cm

\( S \) - The conductive area, cm\(^2\)

\( I \) - The current intensity, A

\( K = 1 + \alpha(t - t_0) \), the temperature coefficient correction value

\( \alpha \) - The temperature coefficient.

The copper resistivity was 0.017\( \Omega \cdot \text{cm}^2 \) under 20\(^\circ \)C.

The copper temperature coefficient was 0.004(\(^\circ \)C). Bringing all the values into formula, \( IR_m=0.083D \quad (V) \).

The formula of electrolyte ohmic voltage drop:

\[
IR_e = \frac{KAI}{S} \quad (V)
\]

\( K \) – Electrolyte conductivity. \( A \) – The plate distance. \( I \) – The current. \( S \) – The plate area.

The temperature was 75\(^\circ \)C. The salinity was 4.5%. The electrolyte conductivity was 0.0225s/cm. The plate distance was 1 mm. The plate area was 0.2 m\(^2\). Bringing all the values into formula, \( IR_e=4.44D \quad (V) \).

According to the above formulas, the theoretical cell voltage \( E = 2.561+0.8022D \quad (V) \), where \( D \) is current density (KA/cm\(^2\)).

System design

The schematic diagram of the ballast water treatment system presented in this paper is shown in Fig. 1. The system is composed of the following parts: seawater tank, seawater pump, electrolyzer, ballast tank, gas-liquid separator tank, low concentration lye tank and high concentration lye tank. Seawater will enter the electrolyzer from the bottom of electrolytic anode compartment (position a in Fig. 1). The products of the electrolytic anode (available chlorine solution) outflow from the top of the anode compartment (position b in Fig. 1) to the ballast water tank. These available chlorine solutions were used for the ballast water treatment. The low concentration NaOH enters the electrolyzer from the bottom of the cathode compartment (position c in Fig. 1). The products of the electrolytic cathode (high concentration NaOH) outflow from the top of the cathode compartment (position d in Fig. 1) to the high concentration lye tank. These high concentration NaOH was used for the flue gas desulfurization treatment.

Algae preparation

This algae cell Chlorella vulgaris, Nitzschia closterium f.minutissima, Platymonas subcordiformis, Dunaliella solina, Isochrysis galbana, and Prorocentrum micans were obtained from the Marine Fisheries Research Institute of Liaoning Province, China. They were cultured by f/2 medium in bottles at the following conditions\(^{22} \). The temperature was 24\(^\circ \)C\(^{23} \), Illumination was 3000lux and light dark than 12:12\(^{24} \). Bottles were shaken four times every day.
Results and Discussion

The current efficiency and cell voltage are the main effect factors for improving the electrolyzer efficiency. The fluctuation of cell voltage not only affects the normal electrolysis production but also causes a certain degree of damage to electrical equipment. Therefore, they are the key points for this study.

Effect of current density on cell voltage

Anolyte mass fraction of NaCl is set to 4.5%, catholyte mass fraction of NaOH is 15%, temperature is 75°C and electrolyte flow rate is 40 L/h. Also, the pressure difference between anode and cathode is 230 mm H₂O column (anode pressure is greater than the cathode pressure). The current increases up to 20 A/min (0.1 KA/m²) and keep a stable voltage value. The relationship between cell voltage and current density is shown in Fig. 2.

We can see that the cell voltage gradually increased with increasing the current density with the higher energy consumption. The reason is that the increased current density lead to decrease of the anodic overvoltage, cathodic overpotential, the ion-exchange membrane voltage, the metal conductor voltage and the electrolyte ohmic voltage. This variation will increase the cell voltage. In the ion-exchange membrane electrolysis industry, the high current efficiency and low cell voltage are the targets of the ion-exchange membrane electrolysis. Experiences have indicated that cell voltage plays an important role in the process of electrolysis.

Higher current density is easier to cause a bubble produce and movement, which will affect the transport process when Na⁺ pass through the ion-exchange membrane. Bubble attachment on ion-exchange membranes during electrolysis is of great concern because it has a marked influence on the cell voltage. So, we should not choose the larger cell voltage due to keeping the higher efficiency of electrolytic cell and a better safe operation.

In this measurement, the maximum security cell voltage is set to the DC4.5V to keep easier equipment safe running, maintenance and the protection for ion-exchange membrane. As it was seen in this figure, when the current density is less than 1.5 KA/m² under the safe cell voltage conditions, the simulated results are better agreements with measurements. But, when the cell voltage value is larger than the maximum safe...
value, the current density is greater than 1.5 KA/m² and the larger error will be produced to great extents. Therefore, the optimized parameters are as follows: current density is 1.5 KA/m², testing cell voltage is 4.27V and theory cell voltage is 3.76V.

As a matter of fact the actual value curve slope changes, the reasons can be explained that the concentration of experiment NaCl was lower, which could lead to increase the membrane moisture content and cause the reverse osmosis speed of OH⁻ increased. When transfer speed of Na⁺ begin to slow down under high current density condition, the anode of Na⁺ is lacked and caused the Na⁺ local "vacuum". This result will increase the resistance of ion through the membrane and produce a larger cell voltage.

The effect of current density on the current efficiency

In general, we tend to use the current efficiency to indicate the effective use of electric quantity in the electrolytic reaction. The current efficiency can normally calculate the anodic product Cl₂ and the cathodal products NaOH or H₂. Due to the Cl₂ and H₂ were gas in normal, it were difficult to calculate its weight. So the current efficiency (η) can be calculated by formation amount of NaOH.

\[ \eta_{OH} = \frac{J_{NaOH}}{(I/F)} \]

where \( J_{NaOH} \) - Formation speed of NaOH, mol/h. \( I \) - Electrolytic current, A. \( F \) - Faraday constant.

The experimental conditions were same with above 3.1. The current density set gradient for 1, 2, 3, 4 KA/m². At each current density, the NaOH was sampled after the operation of the equipment stability. We calculated the current efficiency by formula. The concentration of NaOH was determined by acid-base titration with phenolphthalein as the indicator. The relationship between current efficiency and current density is shown in Fig. 3.

Fig. 3—The relationship between current density and current efficiency

The figures shows that the diffusion leakage ratio of OH⁻ gradually increases when the current density below 1 KA/m², which results in current efficiency reducing. Current efficiency depends on many factors such as current density, electrolyte composition, hydrodynamic conditions, pH and temperature of the solution. Current efficiency was reduced when the current density was more than 4 KA/m², which shows the current density over a certain critical value, the efficiency of electrolyzer can not be increased even if current density increased. Within a certain range, the current density had little effect on the current efficiency. From the Fig. 3, we can see that the current efficiency curve change was smaller when the current density was between 1-4 KA/m², which shows that the current efficiency had little influence on the current density within the wide range change. It was of great significance that electrolyzer had high turndown ratio. Current efficiency reached the maximum value when the current density was 2 KA/m² from the experiment result. But from the curve relation of the current density and the cell voltage, it was known that the cell voltage value exceeded the maximum security value in 2 KA/m². It was necessary to maintain cell voltage, current density and current efficiency within a suitable range in order to make the cell to achieve optimal operating condition. So that the current density was 1.5 KA/m² for the best, the corresponding current was 300A, the current efficiency was 80%, the cell voltage was 4.27V. Bringing optimum current into theoretical calculation formula, the cell voltage was 3.7613V. The difference between practical cell voltage and the theoretical calculation cell voltage was 0.5087V. Operating the equipment in the best condition, the available chlorine concentration of the anode was 800 ppm.

Killing algae affect test

The respective configuration of Chlorella vulgaris, Nitzschia closterium f.minutissima, Platymonas subcordiformis, Dunaiella solina and Isochrysis galbana whose initial concentrations were all 5×10⁵ cell/ml, the initial concentration of Prorocentrum micans was 5×10³ cell/mL. Accessing to different concentrations of saturated chlorine water after electrolysis, the effect on condition of killing the algae with different available chlorine concentration were research, and the time were 0.5, 1, 24, 48, 72 h. Algae were counted using blood count slabs. The available chlorine was determined by iodimetry. Operating the equipment in the best
condition, the anode product was diluted with different concentration and added into algae solution. Lethal curve to different concentrations of six kinds algal by available chlorine was shown in Fig. 4.

Above diagram illustrates that with the increase of the concentration of available chlorine, the effects on algal growth was different. Low concentration of available chlorine can reduce the algal growth rate. Algal appeared death phenomena under the high concentration of available chlorine\(^\text{31}\). The results show that when the effect of available chlorine was 5 ppm, the experiment of six kinds of algal dead after 72 h. Thus, for the six experiment algae, the available chlorine to lethal algal threshold was 5 ppm. In the experimental conditions, the low concentration (1 ppm) of available chlorine can reduce algae growth rate. Figures show that the number of algal cells did not appear recession. However, the algae grow slowly compared with control group. For \textit{Nitzschia closterium f.minutissima} and \textit{Chlorella vulgaris}, the concentrations of available chlorine greater than 2 ppm and for the rest of the algae, the concentrations of available chlorine greater than 3 ppm, the number of all algal appeared recession. This phenomenon was related to the available chlorine decay. In the water, available chlorine decay dependent on many factors, including temperature, initial chlorine concentration, source water quality and biofilm activity\(^\text{32}\). Growth inhibition was not obvious when the concentration of available chlorine was 0.5 ppm. Most of the available chlorine was decay within 24 h when the concentration was less than 2 ppm, but the effect of residual chlorine on algal damage can still last for a period of time. Therefore, the algal grew slowly compared with the control group. The consumption time of available chlorine decay was long when the concentration was greater than 3 ppm. Therefore the effect on algal damage was larger, resulting in the number of the algal in the culture had been in downward stage. Because of the high concentration of the available chlorine (great than 4 ppm) and the effect of the water COD, temperature, pH and light...
and many other kinds of factors, the available chlorine decay time was longer\(^33\). Finally, the number of algal decreased and the algal almost disappeared.

The available chlorine concentration to lethal each algal was different because of different algae structures\(^34\). From the experiment data, the effect of available chlorine concentration for \textit{Chlorella vulgaris} was lowest. Because \textit{Chlorella vulgaris} was about 5 microns which the least in the six experimental algae individual, it was vulnerable to available chlorine attacks when the tolerance of available chlorine concentration was lowest\(^35\). \textit{Nitzschia closterium f.minutissima} took second place for the tolerance the concentration of available chlorine, the reason may be related to the cell wall. The \textit{Nitzschia closterium f.minutissima} had cell wall, adding the available chlorine could induce plasmolysis. It was the void between the cell wall and plasma gap under the microscope, which was plasmolysis for the plant. It was easily caused the algal death. \textit{Nitzschia closterium f.minutissima} belongs to Bacillariophyta, the characteristic of which was each algal cell shell surface side had the keel. There was aulonoraphidiales in the keel. This unique structure was also conducive to the available chlorine penetration cell wall into all cells. Structure of \textit{Platymonas subcordiformis} and \textit{Dunaiella solina} was similar, and both belong to the Chlorophyta of Chlorophyceae. The difference was that \textit{Platymonas subcordiformis} had a thin, smooth cell wall and \textit{Dunaiella solina} had no fiber cell wall. This was mainly due to that \textit{Platymonas subcordiformis} tolerated chlorine concentration was greater than \textit{Dunaiella solina}. \textit{Isochrysis galbana} was easy to form cyst which cloud adverse environmental conditions with resistance ability\(^36\). So \textit{Platymonas subcordiformis} had certain tolerance ability to the available chlorine. The tolerance available chlorine capacity of \textit{Prorocentrum micans} was strongest in six kinds of experimental algae. \textit{Prorocentrum micans} was about 50 microns long, which was the largest in experimental algae. So it needed available chlorine concentration maximum. The cell wall of \textit{Prorocentrum micans} is composed of many small plates with angle, the thorn or papillaryprotrusion and it has strong resistance ability to external interference and was not easy to death\(^37\).

**Conclusion**

A novel ballast water treatment method based on ion-exchange membrane electrolysis is presented and their optimized parameters are also obtained by means of theoretical analysis and experimental measurements, i.e. volt current density, cell voltage, and current efficiency. The six species of algae experiments are carried out using these parameters. The results indicated that it is a higher efficient method to kill the algae.

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