Using membrane electrolysis method to generate chlorine dioxide

Yi-Tze Tsai, Yung-Hsu Hsieh, Chia-Lin Yang
Environmental Engineering
National Chung Hsing University
Taichung, Republic of China (Taiwan)
tsaiyitze@gmail.com

Chen-Yu Chang
General Education Center
National Taitung Junior College
Taitung, Republic of China (Taiwan)
cyc1136@ntc.edu.tw

Shu-Hai You
Safety, Health and Environmental Engineering
National United University
Miaoli, Republic of China (Taiwan)
yoshuhai@ms12.hinet.net

Abstract—Chlorine dioxide(ClO₂) has been known as a powerful disinfectant of water, it is widely used in public water system even in wastewater treatment. A novel membrane electrolysis method for producing ClO₂ has the advantages of simple dosing, easy operation and continuous generation on-site. Hence, the aim of this research was to study the effect of various operation parameters (voltage, anolyte, catholyte, and pH) in producing ClO₂ by membrane electrolysis method. The most important result of this experiment is the maximum concentration and purity of the ClO₂ were 302.01 mg/L and 91 %, respectively, with an analytic mixture of 2 % sodium chloride (NaCl) and 6 % sodium chlorite (NaClO₂). Moreover, the lower pH of anolyte will result in the ClO₂ generate early.

Keywords—chlorine dioxide; membrane electrolysis; sodium chlorite; anolyte

I. INTRODUCTION

Chlorination is the most cost-effective approach of disinfection in public water purification; nevertheless, the formation of organic disinfection by-products (DBPs) is well established when natural organic matter (NOM) presented in the raw water sources, for instance, trihalomethanes (THMs) and haloacetic acids (HAAs) [1-2]. These DBPs are harmful to human body and even have an adverse impact on environment [3]. In reference to the formation of DBPs, the ClO₂ represent a powerful alternative disinfectant of public water systems as it forms fewer DBPs than chlorine [4-5]. The ClO₂ is not only efficient in killing bacteria and also effectively eliminating color and microorganisms [6-7].

In view of the risks about storage, transportation and instability, ClO₂ is required to generate in situ by chemical method. In this regard, the electrolysis technology has made progress recently as it performs the advantage of continuous operation on-site. Based on the above mentioned, this study attempted to figure out the optimum operation conditions of ClO₂ generation by membrane electrolysis technology.

II. MATERIALS AND METHODS

This experimentation was carried out in a divided electrolysis cell and it was divided into two half cell by an ion-exchange membrane (Fig. 1). The electrolysis operation was performed using titanium anode containing noble metals and geometry grid to increase its activation. The ClO₂ gas was drawn out and dissolved in the effluent by a Venturi injector during the period of electrolysis operation.

Prior to initiating the electrolysis assays, the parameters were selected as following: operation voltage, constituent of anolyte, concentration of catholyte, and pH of anolyte. The ranges of these parameters are provided in Table I. In the experiments of voltage and catholyte, various values were performed under fixed condition of constituent of anolyte (NaCl 10 %) for figuring out the optimum value of voltage and concentration of catholyte. In the experiment of anolyte, anolytes of various compositions were studied concerning a guidance manual on alternative disinfectants and oxidants [8]. Thus, the NaClO₂ was selected as the compositions of anolyte.

To evaluate the concentration and purity of ClO₂ in the effluent of Venturi injector, the concentration of each chlorine-containing species in the effluent that related to chloride include chlorine (Cl₂), chlorite (ClO₂⁻), chlorate (ClO₃⁻), and chlorine dioxide (ClO₂) were measured. All analyzed items were using Standard Methods for the Examination of Water and Wastewater except chlorine-containing species that using E. Marco Aieta Method [9].

III. RESULTS AND DISCUSSION

Based on the previous test run, the operation time was finished in one hour completely; meanwhile, the general reactions in the cell are posited to follow from the fact.
When using NaCl 10 % as anolyte, the main chemical in the effluent is Cl₂ ((1) and (2)). In the general reaction of electrolysis of NaCl, the chloride in the anolyte will react with the anode to form ClOH⁻ (3). Equation (1) is the main source of Cl₂. In the region proximity to the anode, Cl₂ and O₂ were formed by way of a by-reaction that occurred go alone with the formation of ClOH⁻ (4) [10]. In the meantime, the Cl₂ may react with OH⁻ to form Cl⁻ and OCl⁻ (5) [11].

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\text{Anode: } 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \tag{1}
\]

\[
\text{Cathode: } 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \tag{2}
\]

\[
\text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{ClOH}^- + \text{H}^+ + 2e^- \tag{3}
\]

\[
\text{H}_2\text{O} + \text{ClOH}^- + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{O}_2 + 3\text{H}^+ + 4e^- \tag{4}
\]

\[
\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{OCl}^- + \text{Cl}^- \tag{5}
\]

A. Effect of Operation Voltage

The operating conditions were fixed at catholyte 0.1 % NaOH and anolyte 10 % NaCl in this experiment. After it had been operated 60 minutes and used 12 V as the working voltage, the concentration and purity of ClO₂, ClO₃⁻, ClO₄⁻, and Cl₂ were 17.54 mg/L, 0 mg/L, 2.36 mg/L, 64.16 mg/L (Fig. 2) and 21 %, 0 %, 3 %, 76 %, respectively.

These results revealed that yield of all species were proportioned to the voltage and current density. The maximum production was obtained when using 12 V as the working voltage.

B. Effect of Catholyte concentration

The operating conditions were fixed at working voltage 12 V and anolyte 10 % NaCl in this experiment. After it had been operated 60 minutes and used 0.5 % NaOH as the catholyte, the concentration and purity of ClO₂, ClO₃⁻, ClO₄⁻, and Cl₂ were 32.54 mg/L, 11.64 mg/L, 0 mg/L, 77.76 mg/L (Fig. 3) and 27 %, 10 %, 0 %, 63 %, respectively.

After 50 minutes of operation, the maximum value of total yield has been observed when deionized water was used as the catholyte (Fig. 4). On the contrary, the maximum value of total yield has been observed after 20 minutes of operation when using 0.5% (Fig. 3) and 0.7 % NaOH as the catholyte. These results indicated that reaction rate in the anolyte cell was proportioned to the concentration of catholyte. Therefore, 0.5 % NaOH has been used as the optimum concentration of catholyte for reducing the consumption dose of NaOH.

C. Effect of Composition of Anolyte

The general mechanism of electrolysis cell consists of two kinds of reaction: chemistry and electrochemistry reaction. Furthermore, the guidance manual from USEPA indicates that Cl₂, HOCl, and HCl can react with NaClO₂ to formed ClO₂ (6), (7), and (8)). Consequently, a composite of NaCl and NaClO₂ was used as the anolyte with various proportions in this part of experiment.

The operating conditions were fixed at working voltage 12 V and catholyte 0.5 % NaOH in this experiment. After it had been operated 20 minutes and used a mixture that blended 2 % NaCl and 6 % NaClO₂ together as the anolyte, the concentration and purity of ClO₂, ClO₃⁻, ClO₄⁻, and Cl₂ were 302.01 mg/L, 3.71 mg/L, 0 mg/L, 27.03 mg/L (Fig. 5) and 91 %, 1 %, 0 %, 8 %, respectively.
As resulted above, the concentration of ClO₂ was proportioned to the additional NaClO₂. The ClO₂ can be formed from ClO₂⁻ by direct oxidation (9). Meanwhile, the ClO₂ can also be formed when ClO₂ reacted with Cl₂ (10). Additionally, due to the activated titanium containing noble metals and geometry grid was used as the anode, the Cl₂ and ClO⁻⁻ may be formed and reacts with the anode to form ClO₂ (11), since 2 % NaCl is presented in the anolyte ((3) and (4)) [12].

D. Effect of pH value of anolyte

The operating conditions were fixed at working voltage 12 V, catholyte 0.5 % NaOH, and anolyte blended 2% NaCl and 6 % NaClO₂ in this experiment. After it had been operated 20 minutes and adjusted pH 2 as the pH value of anolyte, the concentration and purity of ClO₂, ClO₂⁻, ClO⁻⁻, and Cl₂ were 242.15 mg/L, 5.06 mg/L, 0 mg/L, 46.65 mg/L (Fig. 6) and 82 %, 2 %, 0 %, 16 %, respectively.

As resulted above, the pH value of anolyte seems no effect on the concentration and purity of ClO₂; nevertheless, after 10 minutes of operation, the optimum purity of ClO₂ has been observed (98 % ClO₂). Hence, the lower pH of anolyte may only accelerate the reaction rate.

IV. CONCLUSIONS

All these results were proceeded for figuring out the feasibility of producing ClO₂ stably by electrochemical technology. The main results of this experiment are listed below:

- The concentration and purity of ClO₂ and reaction rate in the anolyte cell were proportional to the initial concentration of NaClO₂ in the anolyte and concentration of catholyte, respectively. At the meanwhile, the reaction rate was inversely proportional to the pH value of anolyte.
- The maximum concentration and purity of ClO₂ had been observed when using a mixture that blended 2 % NaCl and 6 % NaClO₂ together as the anolyte. The concentration and purity of ClO₂ were 302.01 mg/L and 91 %, respectively.
- In this case, the optimum operation condition of producing ClO₂ by membrane electrolysis method were controlled at working voltage 12 V, catholyte 0.5 % NaOH, and blended 2 % NaCl and 6 % NaClO₂ as the anolyte.
Based on the previous reports and the results in this experiment, the generation of ClO\(_2\) may become more efficient if a cooling system is employed to control the temperature.

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REFERENCES


