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Efficiency and mechanisms of chlorine dioxide generation by electrocatalytical process

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ABSTRACT

Owing to its higher efficiency and better control of disinfection by-products compared with chlorine (Cl_2), chlorine dioxide (ClO_2) have been widely applied to disinfectation in public water system, cooling system control and wastewater treatment in the past decades. ClO_2 of high purity and high concentration can be electrochemically produced using anolyte composed of specific chemical compounds. Electrochemical process has the advantages of simple dosing, ease of operation and onsite continuous production. In this study, different parameters of membrane electrolysis are varied to determine the appropriate conditions for ClO_2 generation. Experimental results show that at operation voltage of 12 V, membrane electrolysis using anolyte composed of 2% NaCl and 6% $NaClO_2$ with initial temperature of 30 °C and NaOH catholyte of 0.5% concentration can yield ClO_2 of 906.5 mg/L cocentration and 98.4% purity. Moreover, electrolytic reaction accelerates with increase in NaOH catholyte concentration and decrease in initial pH of anolyte. The production rate of ClO_2 is also found to be positively correlated with initial temperature of anolyte.

1. Introduction

Chlorination is the most economical and effective disinfectant of drinking water, and hence has been widely applied to public water system in Taiwan. However, its disinfection effectiveness is restricted by the pH of the water. In addition, reactions between Cl_2 and natural organic matters present in the water yield disinfection by-products, such as trihalomethanes (THMs) and haloacetic acids (HAAs) [1], posing not only adverse health effects on humans but also negative impacts on the environment [2].

Compared with Cl_2, chlorine dioxide (ClO_2) has better control over the yield of disinfection by-products [3], and is thus considered to possess great potential for development into an alternative disinfectant for drinking water. In addition, it is also known that ClO_2 maintains its high effectiveness even at low concentration over a broad pH range [4]. Nevertheless, the use of ClO_2 is not without drawbacks or risks. The potential hazard is attributed to its inorganic toxic by-products, namely chlorite (ClO_2^-) and chlorate (ClO_3^-) [5,6], which has toxicological effects on both the environment and humans [7,8]. There has been active research on removal of toxic disinfection ClO_2 by-products by granular activated carbon and ferrous salts [5,9].

In view of the risks involved in storage and transportation of ClO_2, in situ generation is the preferred mode of production. Compared with the traditional chemical approach to ClO_2 generation, electrochemical production method using the electrolysis technology offers advantages of simple dosing, ease of operation and onsite continuous production. In the past decades, ClO_2 generation by electrochemical techniques has been widely studied with patents granted for its commercialized production. However, the literature comprises mainly studies on ClO_2 application and effects. In contrast, reports on ClO_2 generation by electrocatalytical process have been scarce. Among the few studies on ClO_2 generation by electrocatalytical process [10,11], the focus is on the efficiency of ClO_2 production and not much has been said concerning the purity of ClO_2. Most of the commercially available high-purity ClO_2 is produced with $NaClO_2$ as anolyte. In this study, the anolyte used for ClO_2 generation is made up of both NaCl and $NaClO_2$ to reduce the production cost. Different parameters of membrane electrolysis are varied to determine

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the appropriate conditions for generation ClO_2 of high purity and high concentration. Moreover, the electrochemical reactions involved are also examined.

2. Materials and methods

Fig. 1 is the schematic diagram of the electrolysis cell system used in this study. The system is made of high-strength polypropylene (PP). As can be seen, it is a divided electrolysis cell comprising an analytic half-cell and a catholytic half-cell separated by a cation-exchange membrane. Each of the half-cell has a capacity of 1 L, containing NaCl as the anolyte and NaOH as the catholyte. Note that during electrolysis in an undivided cell, Cl_2 and H_2 are produced in the area near the anode and cathode, respectively. Mixing of these two gases will lead to thermal reaction which may cause explosion if inappropriately handled. Moreover, in an undivided electrolysis cell, disproportionation reaction will occur between the Cl_2 produced near the anode and the OH^- present in the cell [12]:

$$Cl_2 + 2OH^- \rightarrow H_2O + OCl^- + Cl^-, \quad (1)$$

thus undermining the efficiency of Cl_2 generation. Hence, the cation-exchange membrane used in the proposed electrolysis cell system serves to prevent direct mixing of Cl_2 and H_2. In addition, the membrane also enables the Na^+ ions not participating in Cl_2 generation to pass into the catholytic half-cell for charge balancing and for reacting with OH^- to produce NaOH.

The electrolysis operation was conducted using a titanium anode composed of iridium (Ir) and ruthenium (Ru) as well as a geometry grid to enhance its activation. During electrolysis, gaseous ClO_2 generated in the anolytic half-cell was drawn out by a Venturi injector and then dissolved in the water inside the injector to form ClO_2 solution. The concentration and purity of the ClO_2 solution thus obtained were analyzed according to the method proposed by Aieta *et al.* [13]. Batch electrolysis was conducted in all experiments and the measurements taken were the instantaneous concentrations of ClO_2 solution flowing out from the Venturi injector. In addition, all experiments were performed in triplicate with the mean measurement used for analysis. All measurements of concentration and purity showed deviations of less than 5%.

Table 1 lists the experimental parameters used in this study to determine the appropriate operation conditions for ClO_2 generation by membrane electrolysis. Except for the experiments on the effect of initial pH and temperature on ClO_2 generation, all other experiments were conducted at an initial pH and initial temperature of anolyte of 7 and 20 °C, respectively. According to the *Alternative Disinfectants and Oxidants Guidance Manual* [14], ClO_2 can be produced through acidification of $NaClO_2$, as expressed in the following reactions:

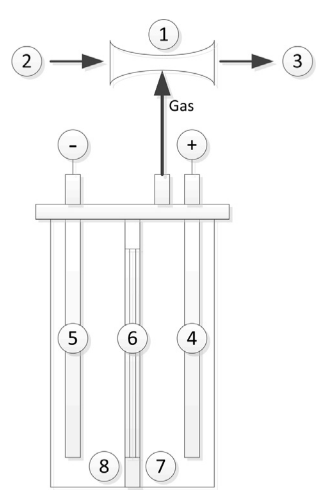

Fig. 1. Schematic diagram of electrolysis cell system.

Table 1
Experimental parameters.

Parameters	Levels
Operation voltage (V)	6, 8, 10, 12
Concentration of catholyte – NaOH (%)	0.1, 0.3, 0.5, 0.7
Concentration of anolyte – NaCl (%)	2, 4, 6, 8, 10
Concentration of anolyte – $NaClO_2$ (%)	0.5, 1, 2, 4, 6
Initial pH value of anolyte	2, 7, 12
Initial temperature of anolyte (°C)	20, 25, 30, 40

$$2NaClO_2 + Cl_{2(g)} = 2ClO_{2(g)} + 2NaCl \quad (2)$$

$$2NaClO_2 + HOCl = 2ClO_{2(g)} + NaCl + NaOH \quad (3)$$

$$5NaClO_2 + 4HCl = 4ClO_{2(g)} + 5NaCl + 2H_2O \quad (4)$$

Hence, this study also explored using anolyte made up of NaCl and $NaClO_2$ in different ratios to determine the most appropriate mix proportions under the experimental conditions. The maximum levels of 10% and 6% for NaCl and $NaClO_2$, respectively were set according to the limits of their current capacities when they are used alone as anolyte. In the experiment on composition of anolyte, the respective maximum levels of NaCl and $NaClO_2$ added were determined by whether the mix proportions would attain the maximum load current of the electrolysis cell system.

3. Results and discussion

3.1. Operation voltage

Fig. 2 shows the results of the 60 min test run. As can be seen, the main reactant generated was Cl_2. Only trace amounts of chlorite and ClO_2 were produced. The highest ClO_2 concentration of 2.47 mg/L was observed after 40 min of electrolysis. With the anolyte containing large quantity of chloride ions (Cl^-), what occurred in the analytic half-cell was the standard reaction of NaCl electrolysis. Moreover, there were other electrochemical reactions generating inorganic by-products, such as hypochlorous acid (HClO) and chlorous acid ($HClO_2$), as expressed by the following:

$$2H_2O + Cl^- \rightarrow HClO_2 + 3H^+ + 4e^- \quad E^0 = 1.659\,V \quad (5)$$

$$H_2O + Cl^- \rightarrow HClO + H^+ + 2e^- \quad E^0 = 1.579\,V \quad (6)$$

In addition, HClO can become the source of Cl_2 and $HClO_2$ through further pure chemical and electrochemical reactions, respectively expressed as follows [10,11,15]:

$$HClO + HCl \rightarrow Cl_2 + H_2O \quad (7)$$

$$HClO + H_2O \rightarrow HClO_2 + 2H^+ + 2e^- \quad E^0 = 1.645\,V \quad (8)$$

Fig. 3 shows the variations in ClO_2 concentration and purity with different operation voltages applied. As can be seen, there exists a positive relationship between ClO_2 concentration and purity with operation voltage. In addition, when the operation voltage was doubled; that is, increased from 6 V to 12 V, the highest ClO_2 concentration at 40 min rose from 2.47 mg/L to 17.54 mg/L. Similarly, the highest purity attained increased from 8.5% to 21%. These results evidence that higher operation voltage