Studies on process parameters for chlorine dioxide production using IrO$_2$ anode in an un-divided electrochemical cell

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ABSTRACT

Chlorine dioxide is potentially a powerful oxidant with environmentally compatible application in several strategic areas relating to pollution control typically for water disinfection, and its sustained production is a key factor for its successful application. Although increased attention has been paid for on-line chlorine dioxide generation by several chemical and electrochemical methods, the details are mostly confined as patents. We studied in this work the electrochemical generation of chlorine dioxide from an un-buffered solution of sodium chlorite and sodium chloride mixture in an *un-divided electrochemical cell* under constant current mode, with a view to optimize various process parameters, which have a direct bearing on the chlorine dioxide formation efficiency under laboratory conditions. The effect of feed flow rate (10–150 ml min^{-1}), feed solution pH (2.3–5.0), concentration of sodium chloride (0–169.4 mM), concentration of sodium chlorite (0–7.7 mM), and the applied current (100–1200 mA) on the formation of dissolved ClO$_2$ gas in solution and the pH of the product-containing solution was investigated by performing single pass experiments, with no circulation, in a cell set-up with Ti/IrO$_2$ anode and Ti/Pt cathode. The current efficiency and the power consumption were calculated for the optimized conditions.

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1. Introduction

Chlorine dioxide (ClO$_2$) is one of the most powerful oxidants hitherto known, and has been used widely in various industrial processes for the drinking water purification [1], disinfection [2], food processing [3] and odor elimination from rotten food wastes [4], medical treatment and sanitation [5], aquiculture [6], removal of phenol [7] and cyanides from industrial wastewater [8], fouling control in sea water [9], pulp bleaching [10], simultaneous SO$_2$ and NO removal from fuel gas [11], etc. The main features of chlorine dioxide are that it functions not as a chlorinating compound but as a very strong oxidizing agent; it is freely soluble in aqueous solutions and, unlike Cl$_2$, it remains as a gas when dissolved and does not ionize to form weak acid; it has high selectivity and reactivity with regard to a number of specific environmentally objectionable waste materials, including phenols, sulphides, cyanides, thiosulfates, mercaptans, and structures including secondary and tertiary amines; also, it is highly effective in a wide range of pH (5–9.5) [12,13]. The major advantages of chlorine dioxide in the drinking water treatment are that, in contrast to more frequently used

chlorinating agent Cl$_2$, the ClO$_2$ does not form trihalomethanes (THMs), haloacetic acids (HAAs) [14], and organo-bromine compounds [15], which are considered cancer promoters in humans. Moreover, ClO$_2$ is a highly effective microbiocide at concentrations as low as 0.1 ppm over a wide pH range. A recent study showed that ClO$_2$ is a powerful disinfectant for controlling even the most resistant *Mycobacterium avium* microbial pathogen [2]. Therefore, ClO$_2$ is being increasingly employed as an alternative oxidant and disinfectant for water treatment.

Generally, chlorine dioxide is generated by several chemical methods always from acid solutions of either chlorite or chlorate. Reaction of sodium chlorate (NaClO$_3$) involves relatively concentrated sulfuric acid solution with a reducing agent, such as, sulfur dioxide [16], methanol [17], hydrogen peroxide [18], or sodium chloride [19,20], etc. Chlorate–chloride process yields Cl$_2$ gas as a major by-product, and thus it has been traditionally used in applications that do not require high purity water, such as, pulp and paper industry, which also need large quantities of chlorine dioxide [20]. On the other hand, several chlorite-based methods have been reported for generation of relatively high purity (i.e., Cl$_2$-free) ClO$_2$. Some of the efficient operational processes are (i) chlorite–acid process, (ii) chlorite–chlorine process, (iii) chlorite–hypochlorite process, (iv) chlorite–peroxydisulphate process, (v) chlorite–acetic anhydride process, and (vi) chlorite–carbon dioxide process. Chlorite-based processes are mostly used in small

scale- and medium-scale generators particularly for water treatment, chemical oxidation, and disinfection applications because they require high purity water. Further to this, it has been reported to be more easy to control the conditions for the production of ClO_2 from sodium chlorite than from sodium chlorate. A recent review by Deshwal and Lee [21] gives a comprehensive account of various aspects of these processes.

Certain difficulties are encountered with the use of chlorine dioxide, however. It can be toxic to humans at concentrations greater that 1000 ppm, and it can be explosive at partial pressures above about 0.1 atm. Additionally, it is quite unstable and easily decomposed by UV light; all of which make it inconvenient to transport or storage over a long period. For these reasons, on-site generation, at the point of use, which allow for controlled and sustained release of ClO_2 gas has been preferred. Although some of the chemical methods discussed above have been developed for this purpose [22,23], electrochemical methods for ClO_2 generation have been considered more suitable, and attractive especially as a small scale generator. Moreover, electrochemical processes do not require the use of any chemical activators, and do not generate any unique impurities or by-products, since "electron", a clean reagent, is used to achieve oxidation and reduction. All the more, regulation and automation are easier to achieve with electrochemical methods in comparison to the chemical techniques. The electrolytic production of ClO_2 is widely conducted by three methods starting with the anodic oxidation of chlorite or cathodic treatment of chlorate or electrolysis of chloride containing solutions [24]. Several electrochemical generation methods have indeed been reported [25–29] using *divided electrochemical cells* in which the anode and the cathode compartments are separated by a porous diaphragm or an ion exchange membrane, which could permit ion transport but prevent mixing-up of anolyte and catholyte solutions and the reaction products generated at the two electrodes. Considering the membrane cost and the complex cell set-up involved in *divided cells*, simple and inexpensive systems for generating ClO_2 without membranes and resigns have also been reported [30,31]. The main difficulty concerning with these studies is that all of them are as patents, and explicit details on cell design, experimental parameters and conditions, etc., are not accessible. Some of the available literature from publications by Gordon and his co-workers [32–36] and Bergmann group [24,37–39] are mainly related to analyzing chlorine chemistry and problems of by-product analysis for chlorination, or in liquors of chlorine disinfectants produced electrochemically.

Thus, we have undertaken detailed systematic studies on the electrochemical generation of ClO_2 oxidant from an aqueous solution of sodium chlorite and sodium chloride mixture in an *un-divided electrochemical cell* under galvanostatic constant current mode with a view to optimize the experimental parameters for optimum generation of dissolved ClO_2 gas in solution under laboratory conditions. In the present work, the effect of various experimental parameters ca. the feed flow rate, initial feed pH, the concentration of NaCl salt, the concentration of $NaClO_2$ precursor, and the applied current on the generation of ClO_2 was studied at a IrO_2-coated–Ti as the anode. Un-buffered solutions of NaCl and $NaClO_2$ mixture as feed in single pass mode were employed in the present work, and buffered solutions were not used in order to avoid possible interference by the buffering agents. Separate studies are being conducted with various buffers in order to gain a step-by-step insight into possible interference by the buffering agents, and these results will be communicated later. The results of the present study allowed us to derive useful information on the efficiency of the electrochemical experimental set-up and the effect of each individual parameter in achieving ClO_2 generation under laboratory conditions.
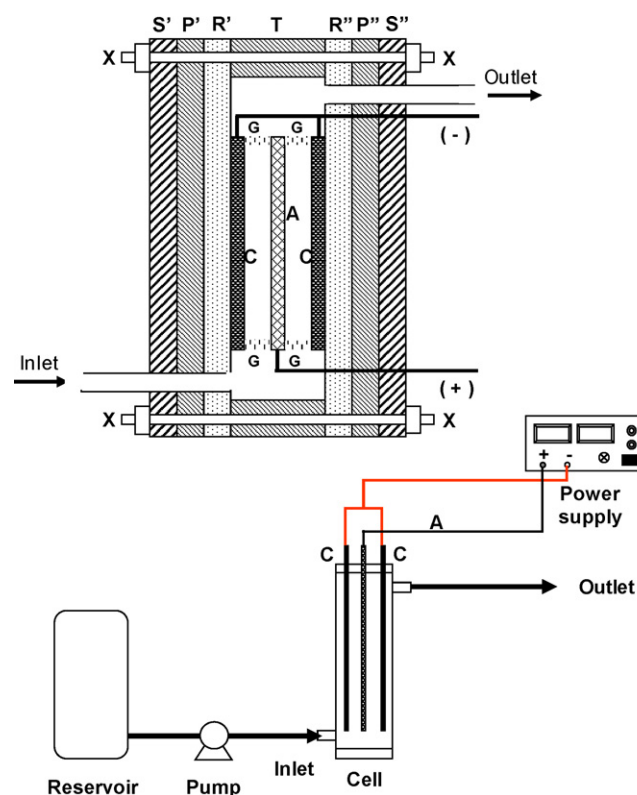

Fig. 1. Schematic view of the experimental set-up and details of electrochemical cell design used in this Study. (A) Anode; (C) cathodes; (G) rubber gaskets; (T) teflon cell housing; (R′, R″) silicon rubber sheets; (P′, P″) teflon plates; (S′, S″) stainless steel plates; (X) clamps.

2. Materials and methods

2.1. Materials

Sodium chlorite (79%) from Kanto Chemical Co. Inc., Japan, and sodium chloride (99%) from DaeJung Chemicals & Metals Co. Ltd., Korea, were used as received. Solution pH was adjusted using sulfuric acid (95%) from DC Chemicals Co. Ltd., Korea. All solutions were made using water purified by reverse osmosis (RO) (Human Power III plus, Korea). Mesh type IrO_2-coated–Ti (Ti/IrO_2) and Pt-coated–Ti (Ti/Pt) plates of dimensions 2 cm × 3.7 cm × 0.2 cm with 0.8 roughness factor were purchased from Wesco Electrodes and Systems, Korea.

2.2. Equipment

The electrochemical cell was an un-divided filter press type as shown in Fig. 1. The anode and cathode were 2 mm thick mesh type Ti/IrO_2 and Ti/Pt plates, respectively. Two cathodes (C) were arranged on either side of an anode plate (A), and rubber gaskets (G) were used to maintain an inter-electrode gap of 1 mm. The C–A–C unit was set in side a Teflon cell housing (T) provided with channel medium by which the electrolyte solution flowed across the electrode assembly. The two cathodes were hard-pressed against two 3 mm thick (5 cm x 14 cm) silicon rubber sheets (R′, R″), which were in turn clamped tightly to Teflon plates (P′, P″) and outer stainless steel plates (S′, S″) with the help of clamps (X) at four corners of the rectangular module. The effective surface area of the electrode was 11.84 cm². The other accessories of the experimental set-up consisted of a peristaltic pump (Cole-Parmer Instrument Company-MasterFlex® Model 7518-10), a reservoir and silicon

tubing. A schematic diagram of the experimental set-up is also shown in Fig. 1.

2.3. Experimental procedure

Feed solution containing a mixture of $NaClO_2$ and $NaCl$ was directly introduced in to the electrolytic cell assembly by the peristaltic pump, and ClO_2 generation experiments were performed by single-pass system without recirculation. Constant current electrolyses were performed by a locally made constant current source from Korea Switching Instrument. All the measurements were conducted at $19 \pm 1\,^\circ C$.

Chlorine dioxide formation experiments for optimization of process parameters were conducted by varying them as follows: feed solution flow rate = 10–150 ml min^{-1}; feed solution pH 2.3–5.0; NaCl concentration = 0–169.4 mM; $NaClO_2$ concentration = 0–7.7 mM; applied current = 100–1200 mA.

Prior to each experiment, the electrodes were cleaned by dipping in 1 M HNO_3 for 30 min duration followed by profuse washings with RO water. During the continuous electrolysis, 20 ml aliquots of samples were collected at the drain at regular intervals, and concentration of chlorine dioxide electrochemically produced was measured by UV–vis spectrophotometer model HACH DR/2500 (λ = 445 nm). The outlet samples were also analyzed for pH.

3. Results and discussion

3.1. General electrochemical reactions in ClO_2 formation

The formation of chlorine dioxide from chloride (Cl^-) and chlorite (ClO_2^-) containing aqueous solution by electrochemical mechanism can be considered to occur according to the following equations [24,33–36]:
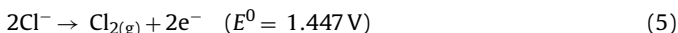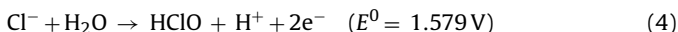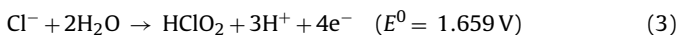
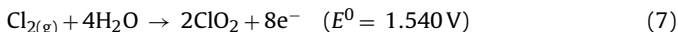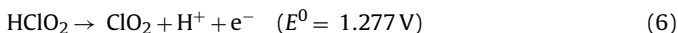The Cl^- ions in solution can be oxidized at the anode directly to ClO_2 (Eq. (1)).

$$Cl^- + 2H_2O \rightarrow ClO_2 + 4H^+ + 5e^- \quad (E^0 = 1.599\,V) \tag{1}$$
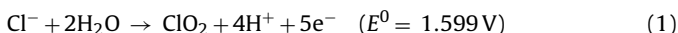
Similarly, ClO_2^- ions in solution can be directly oxidized to ClO_2 at the anode (Eq. (2)).

$$ClO_2^- \rightarrow ClO_2 + e^- \quad (E^0 = 1.039\,V) \tag{2}$$
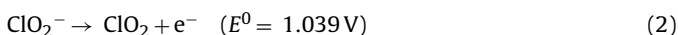
However, there are several additional electrochemical and chemical reactions occurring probably as consecutive or in parallel, also producing ClO_2. For example, Cl^- ion can be oxidized at the anode to various inorganic by-products, e.g., chlorous acid ($HClO_2$) (Eq. (3)), hypochlorous acid (HClO) (Eq. (4)), Cl_2 (Eq. (5)), etc., as follows:

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

$$Cl^- + H_2O \rightarrow HClO + H^+ + 2e^- \quad (E^0 = 1.579\,V) \tag{4}$$

$$2Cl^- \rightarrow Cl_{2(g)} + 2e^- \quad (E^0 = 1.447\,V) \tag{5}$$

and, each of the products of the above reactions can become a source of ClO_2 by their electrochemical oxidation. For instance, $HClO_2$ can be electro-oxidized to ClO_2 (Eq. (6)), and Cl_2 can be electro-oxidised to ClO_2 (Eq. (7)).

$$HClO_2 \rightarrow ClO_2 + H^+ + e^- \quad (E^0 = 1.277\,V) \tag{6}$$

$$Cl_{2(g)} + 4H_2O \rightarrow 2ClO_2 + 8e^- \quad (E^0 = 1.540\,V) \tag{7}$$

The product of the reaction (4) ca., HClO, is known to get oxidized to $HClO_2$ as in Eq. (8) [24], which can form ClO_2 following reaction (6).

$$HClO + H_2O \rightarrow HClO_2 + 2H^+ + 2e^- \quad (E^0 = 1.645\,V) \tag{8}$$
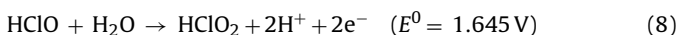
A typical chemical reaction well known in ClO_2 generation in solution is that the dissolved ClO_2 can take part in reactions forming ClO_2^- and ClO_3^- preferably in alkaline solution [40] as follows (Eq. (9)):

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O \tag{9}$$
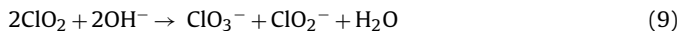
The ClO_2^- ion on protonization can form $HClO_2$, which, as described in reaction (6), can form a cycle of newly produced ClO_2. Similarly, chlorate ion is known to undergo electroreduction to ClO_2 gas (Eq. (10)).

$$ClO_3^- + H_2O + e^- \rightarrow ClO_2 + 2OH^- \quad (E^0 = 1.645\,V) \tag{10}$$
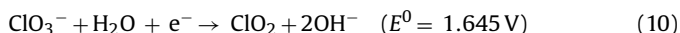
However, the electrogeneration of ClO_2 from chlorate electrolysis was minimal [24] due to low rate constant for the ClO_3^- electroreduction reaction [33,35].

Yet another chemical complexity that may arise is from a rapid reaction between liberated Cl_2 with ClO_2^- ion in solution producing ClO_2 gas (Eq. (11)) or ClO_3^- ions (Eq. (12)) depending on the pH of the solution [21,41].

$$2ClO_2^- + Cl_2 \rightarrow 2ClO_2 + 2Cl^- \tag{11}$$

$$ClO_2^- + Cl_2 + H_2O \rightarrow ClO_3^- + Cl^- \tag{12}$$
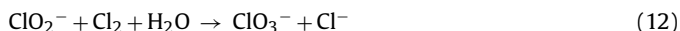
Acidic solutions were reported to favor the formation of chlorine dioxide, while alkaline conditions tending to produce chlorate [41].

Note that the above electrochemical reaction schemes are predicted from thermodynamic consideration, and the real mechanism can be different based on the electrode kinetic factors, such as, polarization characteristics, overpotential, exchange current density and transfer coefficient of the individual electron transfer reactions [42,43]. Apart from these factors, the solution pH is of paramount importance in the electrochemical reactions of ClO_2 formation, since the type of the species and their distribution in solution are deeply decided by the pH. Moreover, with the usage of traditional industrial oxide-based electrodes, which contain outermost surface covered by layer of hydroxyl groups forming hydroxylated species in aqueous solutions [44,45], electrode surface charge and their consequent interaction with reactant species are highly pH dependent, which could lead to much larger complexity of reactions.

3.2. Effect of feed flow rate

In the first instant, a set of measurements was conducted with various feed flow rates in the range 10–150 ml min^{-1}, keeping all other conditions constant: [$NaClO_2$] = 3.5 mM, [NaCl] = 169.4 mM, initial pH 2.9, applied current = 600 mA. Fig. 2 shows the concentration of dissolved ClO_2 gas electrochemically generated in solution as a function of electrolysis time for various feed flow rates. In all the cases, ClO_2 generation was initiated instantly with an increase up to 5 min, and then remained constant until 30 min studied. The steady state concentration of ClO_2 was found to increase with flow rate, and maximum at 90 ml min^{-1}, as shown in the inset of Fig. 2. Beyond 90 ml min^{-1} flow rate, the ClO_2 production decreased somewhat, which might be a consequence of lesser contact time for the reactants with the electrode for the reaction. The maximum amount of ClO_2 generated at the highest optimized 90 ml min^{-1} flow rate was 284 ppm.

The formation of chlorine dioxide from chloride and chlorite containing aqueous mixture solution by electrochemical mechanism could be from several of the steps considered above [24,33–36].
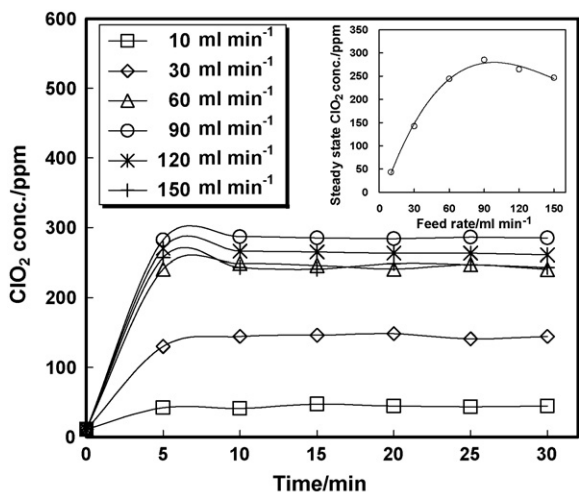
Fig. 2. ClO$_2$ concentration versus time at different feed flow rates (ml min^{-1}): (□) 10; (◇) 30; (△) 60; (○) 90; (*) 120; (+) 150. Inset: dependence of ClO$_2$ concentration measured at 20 min as a function of feed flow rate. (Electrolysis conditions: [NaClO$_2$] = 3.5 mM; [NaCl] = 169.4 mM; initial feed pH 2.9; current = 600 mA).

3.3. Effect of feed pH

The pH of the solution is well known to play a key controlling effect in the generation of ClO$_2$ both in chemical and electrochemical methods [24,40]. In order to understand the relation between solution pH and dissolved ClO$_2$ gas generation in solution, electrolysis to generate ClO$_2$ was carried out at 90 ml min^{-1} flow rate with solutions of different initial feed pH in the range 2.3–5.0. In this set of experiments, the concentration of NaClO$_2$ and NaCl was kept to a value of 3.5 and 169.4 mM, respectively, and 600 mA current was used. Both ClO$_2$ concentration and the pH of the outlet solution (pH of the product-containing solution) were measured under steady state condition at 20 min, and the results are plotted in Fig. 3.

It can be noticed in Fig. 3 that the steady state values of ClO$_2$ concentration produced and the pH of the product-containing solution varied with initial feed pH showing three characteristic zones. Now, the quantity of ClO$_2$ evolved and the pH of the product solution as the electrolysis proceeded were plotted as a function of time for a specific initial feed pH in each zone, and are shown in Fig. 4.

When the feed solution was highly acidic, say, pH 2.3 in zone 1, the ClO$_2$ quantity continuously increased up to 5 min and then
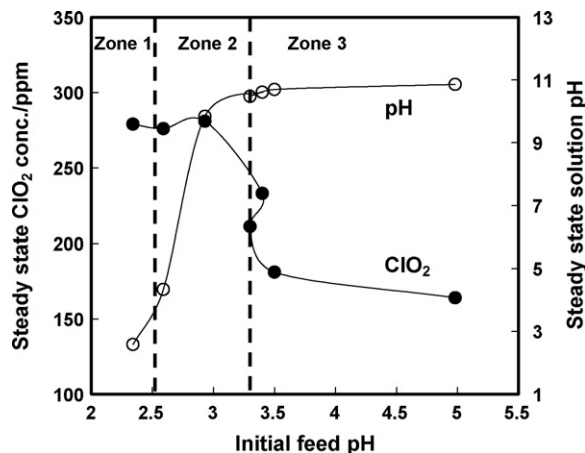

Fig. 3. Dependence of ClO$_2$ concentration (-●-) and solution pH (-○-), measured after 20 min electrolysis, on initial feed pH (Electrolysis conditions: [NaClO$_2$] = 3.5 mM; [NaCl] = 169.4 mM; feed flow rate = 90 ml min^{-1}; current = 600 mA).

remained constant around 276 ppm, whereas there was an insignificant change in product solution pH which remained at its initial value around 2.6 (Fig. 4a). As opposed to this behavior, for the feed pH 2.9 in zone 2, along with ClO$_2$ the product pH also increased initially up to 5 min and then remained constant at 9.8 (Fig. 4b). For the solution in the zone 3 with feed pH 3.5, similar increases in both ClO$_2$ and product pH were observed against time (Fig. 4c); but, the final pH were high around 10.7, while the ClO$_2$ generated were quite smaller around 187 ppm, as is evident in Fig. 3.

The drastic increase in product pH towards alkaline values during ClO$_2$ formation at the anode for feed solutions in zone 2 and zone 3 can be understood as due to the H$^+$ reduction at the cathode (Eq. (13)) and the usage of un-buffered solution in the present work.

$$2H^+ + 2e^- \rightarrow H_2 \tag{13}$$

As the solution became alkaline for these feed solutions, the electrochemically generated ClO$_2$ could immediately disproportionate to chlorite and chlorate, as described in Eq. (9) [40], leading to lesser ClO$_2$ yield, as in Fig. 3.
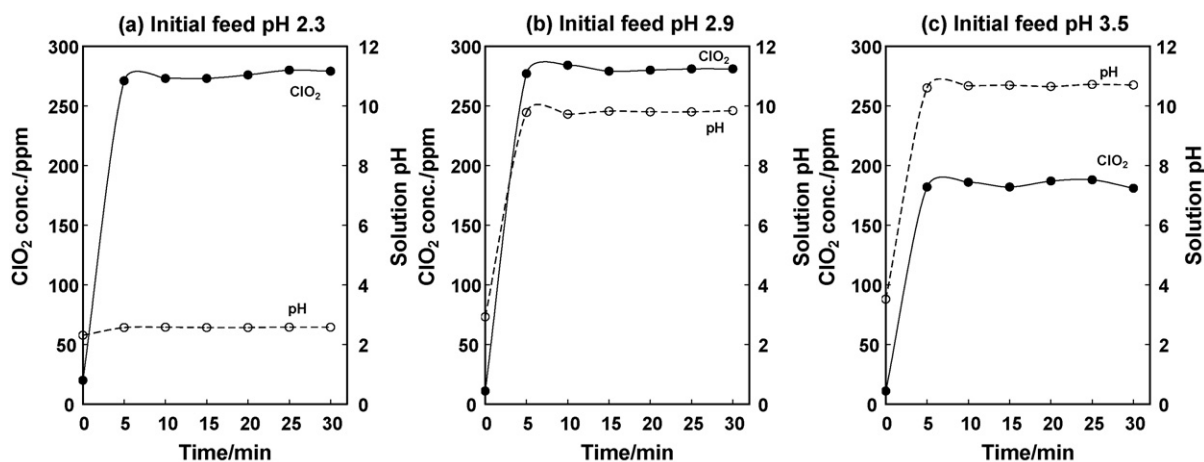
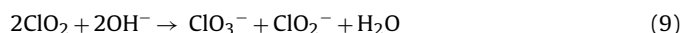$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O \tag{9}$$

Fig. 4. ClO$_2$ concentration (-●-) and solution pH (-○-) versus time for various initial feed pH in different zones of Fig. 3: (a) pH 2.2 in zone 1; (b) pH 2.9 in zone 2; (c) pH 3.5 in zone 3. (Electrolysis conditions: [NaClO$_2$] = 3.5 mM; [NaCl] = 169.4 mM; feed flow rate = 90 ml min^{-1}; current = 600 mA).
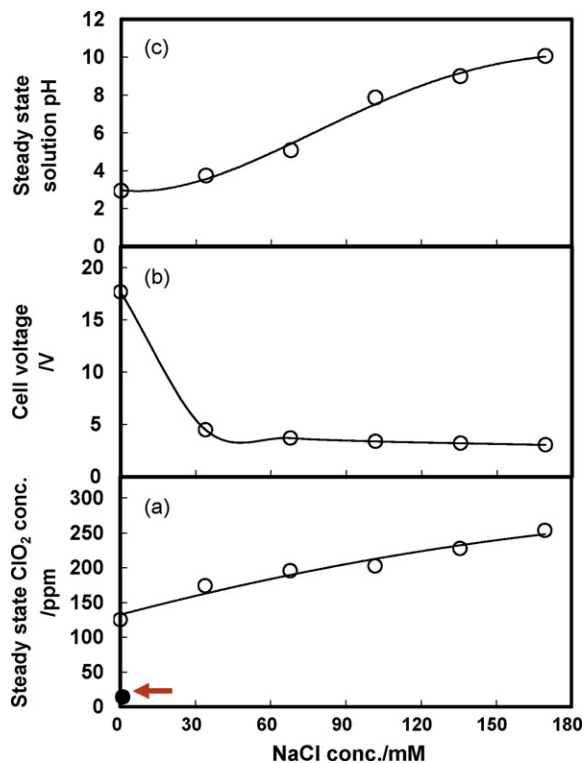
Fig. 5. Influence of NaCl concentration on measured parameters: (a) steady state ClO_2 concentration; (b) steady state cell voltage; (c) steady state solution pH. (Electrolysis conditions: $[NaClO_2] = 3.5\,mM$; initial feed pH 2.9; feed flow rate = 90 ml min^{-1}; current = 600 mA). ($\leftarrow$) Indicates ClO_2 concentration chemically produced from a clean 3.5 mM $NaClO_2$ solution with no NaCl.

Note that the pH range in which ClO_2 could be stable and free from self-decomposition was cited differently by different authors, e.g., Junli et al. [46] reported that ClO_2 could be stable at pH 8.5, whereas Jin et al. [11] indicated that ClO_2 disproportionation started right from the neutral pH.

3.4. Effect of NaCl concentration

In order to investigate on the relationship between the concentration of NaCl and the quantity of dissolved ClO_2 gas generation in solution, specific galvanostatic electrolysis of 3.5 mM of $NaClO_2$ solution of feed pH 2.9 were carried out at different NaCl concentrations, 0–169.4 mM, at 600 mA current and 90 ml min^{-1} flow rate. Steady state concentration of ClO_2 produced was measured at 20 min for each NaCl concentration, and Fig. 5a depicts the trend of these concentrations of ClO_2 as a function of NaCl concentration. As can be observed, the electrochemically generated ClO_2 concentration increased gradually from 125 to 253 ppm with a tendency for saturation, when Cl$^-$ concentration in the bulk solution was increased from 0 to 169.4 mM.

Note that both chloride and chlorite ions in solution were the source for the ClO_2 formation via electrochemical reactions described above in Section 3.1. However, it was possible to evaluate the contribution by the single component, in this case chlorite ion, by considering the first solution consisting of 3.5 mM of $NaClO_2$ with [NaCl] = 0 mM and acidified with H_2SO_4 (for pH maintenance). It is obvious from Fig. 5a that the very low concentration of ClO_2^- ca. 3.5 mM was able to produce appreciable amount of ClO_2 around 125 ppm by electrolysis. A qualitative idea about the individual electrochemical contribution by NaCl could be obtained in the next section involving experiments with fixed amount of $NaClO_2$ but varying NaCl concentration.

Fig. 5a also shows that the pH 2.9 solution containing 3.5 mM $NaClO_2$ alone (free of NaCl) showed around 15 ppm ClO_2 before electrolysis. This was due to acidification of chlorite with sulfuric acid according to Eq. (14) [32,41].

$$4ClO_2^- + 2H^+ \rightarrow 2ClO_2 + ClO^- + Cl^- + H_2O \qquad (14)$$
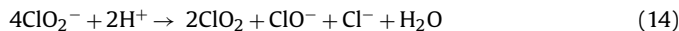
The negligibly small quantity of ClO_2 around 15 ppm produced by chemical reaction of $NaClO_2$ compared to the large quantities of the gas electrogenerated from the $NaClO_2$ and NaCl mixture (Fig. 5a) clearly demonstrate that the contribution by the chemical route to the electrochemical processes was only meager at room temperature.

For each of the NaCl concentrations, the cell voltage and the pH of the outlet stream were also measured under steady state condition at 20 min after electrolysis started, and the values are plotted in Fig. 5b and c, respectively, as a function of salt concentration. Fig. 5b shows that there was a dramatic fall in cell voltage from 17.7 to 4.5 V with the first addition of 33.9 mM NaCl, as a result of increased solution conductivity. There after the cell voltage remained constant around 3.4 V up to 169.4 mM of salt concentration. This beneficial effect of higher salt concentration in terms of low cell voltage was, however, off-set by a raise in the pH of the product-containing solution to 10.1 at the highest NaCl concentration studied, as shown in Fig. 5c. Note that the initial feed pH in these studies was 2.9.

At this point, it can be noticed that when NaCl concentration was in the range 70–100 mM, (i) the pH of the product-containing solution was in the safer region, 5.1–7.9, for stable ClO_2 free from self-decomposition (Fig. 5c), and (ii) the cell voltage already attained its low value $\approx$3.4 V. Realizing that above this 70–100 mM NaCl concentration range, there was only a marginal gain in the ClO_2 concentration (Fig. 5a), and also the product solution pH rose to unsafe alkaline region (8–10), where ClO_2 could be unstable (Fig. 5c), the NaCl concentration in the moderate range, 70–100 mM, could be considered as optimum.

3.5. Effect of $NaClO_2$ precursor concentration

The effectiveness of the $NaClO_2$ precursor on the dissolved ClO_2 gas formation in solution was studied by means of continuous flow (90 ml min^{-1}) galvanostatic electrolysis (600 mA) experiments: 169.4 mM of NaCl solutions of feed pH 2.9 were tested with different $NaClO_2$ concentrations, 0–7.7 mM. Results are illustrated in Fig. 6, where the ClO_2 concentration liberated, the cell voltage and the pH of the product-containing solution, all measured under steady state condition, are plotted.

Results in Fig. 6a show that the electrochemically generated ClO_2 concentration initially increased somewhat sharply, e.g., from 165 to 233 ppm ($\Delta c = 68$ ppm) for an addition of 0–3.5 mM $NaClO_2$. But, in the later part, for the addition of a similar amount of $NaClO_2$ from 3.5 to 7.7 mM (3.4 mM), the gas concentration increased by a smaller amount, $\Delta c = 47$ ppm (from 233 to 280 ppm), suggesting a tendency for saturation at higher $NaClO_2$ additions.

Fig. 6a also shows that the pure NaCl solution (169.4 mM) with no chlorite ([NaClO_2] = 0) gave 165 ppm ClO_2 by electrolysis. By comparing this situation with the performance of pure $NaClO_2$, we already saw in Fig. 5a that even if the $NaClO_2$ concentration was only 3.5 mM, it was able to produce a substantially large quantity of ClO_2 (125 ppm) under similar electrolysis condition. Reaching such high concentrations of ClO_2 gas with minute amounts of chlorite could clearly demonstrate that the electro-oxidation reactions of chlorite anion (reaction (2)) and its acidic form (reaction (6)) were kinetically more facile at the IrO_2 anode; also, the direct electrochemical oxidation of Cl$^-$ to ClO_2 (reaction (1)), as well as the other
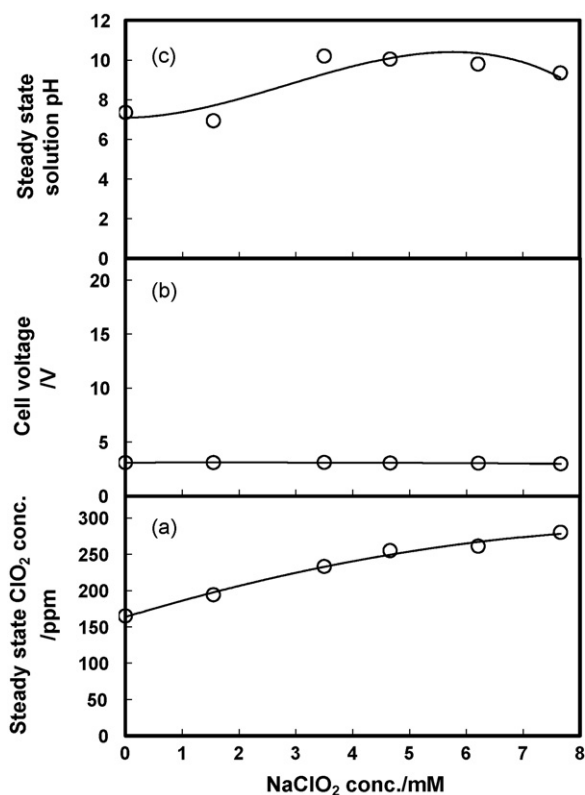
Fig. 6. Influence of NaClO$_2$ concentration on measured parameters: (a) steady state ClO$_2$ concentration; (b) steady state cell voltage; (c) steady state solution pH. (Electrolysis conditions: [NaCl] = 169.4 mM; initial feed pH 2.9; feed flow rate = 90 ml min^{-1}; current = 600 mA).

electrochemical reactions indirectly associated with Cl$^-$ electro-oxidation leading to ClO$_2$ gas formation (reactions (3)–(5), (7) and (8)), were much slower at the oxide electrode under the galvanostatic polarization conditions adopted in the present study. These results were a clear indication that ClO$_2$ could easily be formed from chlorite, and, as an efficient precursor, chlorite could contribute significantly to ClO$_2$ electrogeneration from the chloride–chlorite mixture.

The cell voltage was almost constant at 3.1 V for all the NaClO$_2$ concentrations, 0–7.7 mM, as shown in Fig. 6b, because of the large excess of NaCl salt present in these solutions. However, the pH of the outlet solution, Fig. 6c, increased from 6.9 to 10.0 for a change of NaClO$_2$ concentration from 0 to 3.5 mM; but it remained constant thereafter up to 7.7 mM NaClO$_2$.

Now focusing on identifying optimum NaClO$_2$ concentration, the fact that its concentrations beyond 3.5–4.7 mM did not show any large gain in the ClO$_2$ gas liberation (Fig. 6a), but increased the pH of the product-containing solution closer to 10, where ClO$_2$ could be unstable, clearly implied that 3.5–4.7 mM of NaClO$_2$ could be employed to ensure maximum benefit.

3.6. Effect of applied current

Fig. 7a shows the effect of the applied current on the dissolved ClO$_2$ gas produced in the solution, when the current was varied from 100 to 1200 mA. The tendency is quite clear, the higher the current applied the higher was the ClO$_2$ that could be generated. However, the concentration increase followed a steep rise initially up to around 600 mA, after which it slowed-down.

It may be recalled that such changes in ClO$_2$ formation rate with applied current density was reported by Bergmann and Koparal

[24] during electrolysis of tap water containing 35 mg dm^{-3} of Cl$^-$ (1 mM) and 201 mg dm^{-3} of SO$_4^{2-}$ (2.1 mM) at a mixed oxide (IrO$_2$/RuO$_2$)-coated–Ti anode. Such a behavior was explained as due to a competition amongst several effects, such as (a) removal of ClO$_2$ gas from solution by higher gas production of active chlorine (ClO$^-$, HClO and dissolved chlorine [38]) under the condition that active chlorine was a preliminary stage of ClO$_2$ formation, (b) parallel competition for formation of both ClO$_2$ and active chlorine, when active chlorine was not a preliminary stage of ClO$_2$ formation, (c) reaction of ClO$_2$ with disinfection by-products H$_2$O$_2$ and O$_3$, etc.

Coming to the present system of studies, the mechanisms (a) and (b) could be operative for the trend observed in Fig. 7a, and the mechanism (c) was quite unlikely; since, as well established in the literature [24,38,39,47], active chlorine represents the main electrochemically generated oxidizing species at the conventional transition metal oxide electrodes (IrO$_2$ in the present case), and the formation of reactive oxygen species, such as, H$_2$O$_2$, O$_3$, HO$_2^-$ are negligible at these electrodes. However, an identification, whether the hypothesis (a) or (b) was responsible for the trend in Fig. 7a, is difficult to be envisaged with the limited results available in the present work.

The cell voltage monitored as a function of the applied current is depicted in Fig. 7b. The cell voltage continuously increased from 2.4 to 4.0 V with increase in the applied current, 100–1200 mA. From Fig. 7a and b, we see that even though higher current produced higher concentration of chlorine dioxide, it was associated with increased power consumption due to the regular increase in cell voltage. Judging from the fact that beyond 600 mA, there was only a marginal increase in gas output, this current could be
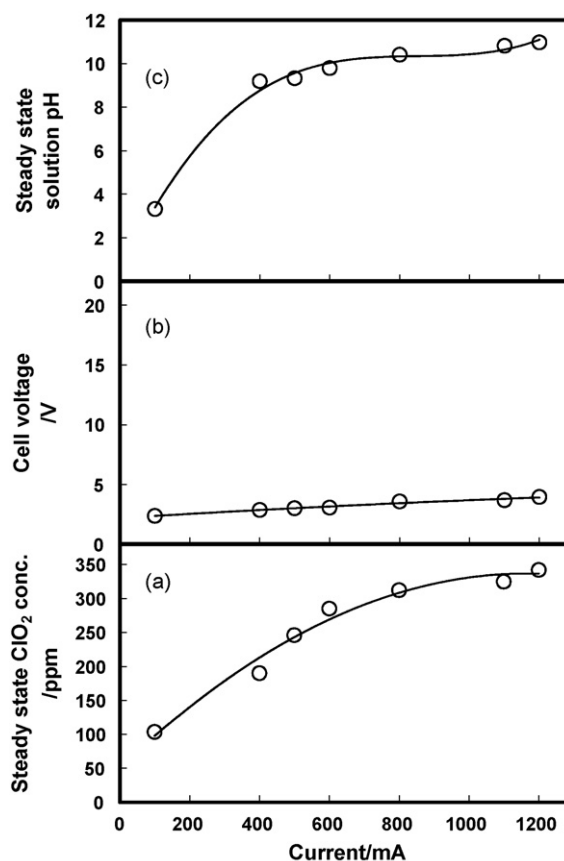

Fig. 7. Influence of current density on measured parameters: (a) steady state ClO$_2$ concentration; (b) steady state cell voltage; (c) steady state solution pH. (Electrolysis conditions: [NaClO$_2$] = 3.5 mM; [NaCl] = 169.4 mM; initial feed pH 2.9; feed flow rate = 90 ml min^{-1}).

considered as maximum for optimum power consumption and maximum quantity of ClO_2 gas produced. The selection of 600 mA as optimum current was further supported from the pH of the outlet stream, Fig. 7c, which indicated that under steady state condition beyond 600 mA the outlet pH moved to enlarged basic pH, 9.8–11.0, which is well known to have adverse effect on the stability of dissolved ClO_2 gas in solution.

The current efficiency and the power consumption under the optimized conditions ($[NaClO_2] = 3.5$ mM, $[NaCl] = 100$ mM, initial feed pH 2.9, feed flow rate = 90 ml min^{-1}, and applied current = 600 mA) were calculated to be 67% and 2.0 Wh g^{-1}, respectively. The following values from Fig. 5, viz., the steady state ClO_2 concentration corrected for chemical reaction = 187 ppm (202–15 ppm), the steady state cell voltage = 3.4 V, and the time of steady state measurements = 20 min, experimentally measured under the optimized conditions, were used in the above calculation. The reason for the current efficiency less than 100% for ClO_2 formation may be related to the concomitant occurrence of oxygen evolution reaction (OER) at the IrO_2 electrode, which is a well known efficient catalytic electrode for OER in acid [48] as well as in alkaline [49] solutions. Our further work in the direction of optimization of experimental conditions for consistently higher ClO_2 electrogeneration is presently underway with a view to achieve higher current efficiency for ClO_2 formation using highly efficient catalytic electrode for the generation of chlorine and its related species, e.g., pure RuO_2 electrode and mixed oxide electrodes [50], and also using $NaClO_2$–$NaCl$ mixture solutions sufficiently buffered to prevent self-decomposition of ClO_2 in solution. These findings will be communicated elsewhere.

4. Conclusions

The following can be concluded from our present work concerning the optimization of process parameters for dissolved ClO_2 gas electrogeneration from an un-buffered $NaClO_2$–$NaCl$ mixture solution in an *un-divided electrolytic cell* using Ti/IrO$_2$ anode under laboratory conditions: (1) the constant current electrolysis of NaCl–NaClO$_2$ mixture solution by single-pass arrangement offers an easy way for on-line generation of ClO_2 gas in solution. (2) Feasible and optimal operating conditions were investigated including feed flow rate, initial feed pH, NaCl salt concentration, NaClO$_2$ precursor concentration, and the applied current. (3) Even when the initial feed pH was slightly acidic or neutral in the range 3.5–5.0, the pH of the ClO_2 product-containing solution during electrolysis was driven to enlarged basic pH range, 10–10.7, affecting the ClO_2 stability. (4) Based on the observation that the pH of the ClO_2 product-containing solution was shifted to safer regions 5.1–7.9 for stable ClO_2 free from self-dissociation, and the cell voltage was shifted to minimum values around 3.4 V, the optimized values for the experimental parameters were evaluated as: feed flow rate = 90 ml min^{-1}; initial feed pH 2.9; NaCl concentration = 70–100 mM; NaClO$_2$ concentration = 3.5–4.7 mM; applied current = 600 mA. (5) Under the optimized experimental conditions, the steady state ClO_2 concentration generated after correcting for chemical reaction = 187 ppm, the current efficiency = 67%, and the power consumption = 2.0 Wh g^{-1}. (6) An analysis of process characteristics indicated the necessity for further detailed systematic work towards enhancing the current efficiency by using highly efficient chlorine generating anodes ca., pure RuO_2 electrode and mixed oxide electrodes, and also by using buffer solutions.

Acknowledgements

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