

## Article

# Full and Sustainable Electrochemical Production of Chlorine Dioxide

Ángela Moratalla <sup>1</sup>, Mayra K. S. Monteiro <sup>1,2</sup>, Cristina Sáez <sup>1</sup>, Elisama V. Dos Santos <sup>2</sup>  
and Manuel A. Rodrigo <sup>1,\*</sup>

<sup>1</sup> Department of Chemical Engineering, Faculty of Chemical Sciences and Technologies, University of Castilla-La Mancha, 13005 Ciudad Real, Spain; angela.moratalla@uclm.es (Á.M.); mayra.kerolly@gmail.com (M.K.S.M.); cristina.saez@uclm.es (C.S.)

<sup>2</sup> Environmental and Applied Electrochemical Laboratory, School of Science and Technology, Federal University of Rio Grande do Norte, Lagoa Nova, Natal 59078-970, Brazil; elisamavieira@ect.ufrn.br

\* Correspondence: manuel.rodrigo@uclm.es

**Abstract:** With the final purpose of manufacturing electrochemically-based devices that produce chloride dioxide efficiently, this paper focuses on the production of chlorates and hydrogen peroxide in two different electrochemical cells, in which operation conditions are selected to obtain high efficiencies, and in the subsequent combination of both electrochemically manufactured solutions to produce chlorine dioxide. Results demonstrate that suitable reagents can be produced by electrolyzing 20 g L<sup>-1</sup> sodium chloride solutions at 50 mA cm<sup>-2</sup> and 50 °C, and 3000 mg L<sup>-1</sup> NaClO<sub>4</sub> solutions at 5.0 mA cm<sup>-2</sup> and 15 °C with current efficiencies of 30.9% and 48.0%, respectively. Different tests performed with these electrolyzed solutions, and also with commercial hydrogen peroxide and chlorate solutions, demonstrate that the ratio between both reagents plays a very important role in the efficiency in the production of chlorine dioxide. Results clearly showed that, surplus chlorate should be contained in the reagent media to prevent further reduction of chlorine dioxide by hydrogen peroxide and consequently, losses of efficiency in the process. During the reaction, a gas with a high oxidation capacity and consisting mainly in chloride dioxide is produced. The results contributed to the maximum conversion reached being 89.65% using electrolyzed solutions as precursors of ClO<sub>2</sub>, confirming that this technology can be promising to manufacture portable ClO<sub>2</sub> devices.

**Keywords:** chlorine dioxide; hydrogen peroxide; chlorate; electrolysis; electrochemical cells



**Citation:** Moratalla, Á.; Monteiro, M.K.S.; Sáez, C.; Dos Santos, E.V.; Rodrigo, M.A. Full and Sustainable Electrochemical Production of Chlorine Dioxide. *Catalysts* **2022**, *12*, 315. <https://doi.org/10.3390/catal12030315>

Academic Editor: Vincenzo Baglio

Received: 8 January 2022

Accepted: 7 March 2022

Published: 9 March 2022

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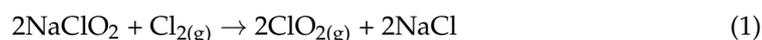


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## 1. Introduction

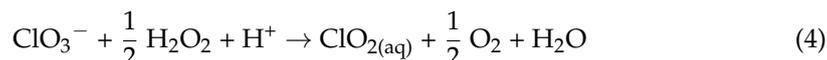
Chlorine dioxide is a very efficient bleaching reagent widely used in the pulp and paper industry [1,2]. In addition, based on the existing literature, ClO<sub>2</sub> is emerging as a powerful disinfectant because of its strong capacity as an oxidant [3–6]. It shows important advantages with respect to chlorine, because of its higher efficiency and the nil formation of chlorinated organics during its application to water samples containing organics [7]. Because of that, its use in the disinfection of drinking water is increasing and, currently, it has been proposed for new applications, such as the disinfection of surfaces [7–10], in trying to find an effective solution to the transmission of COVID-19 [11].

In the last decades, the development of efficient methods capable of producing chlorine dioxide (ClO<sub>2</sub>) has been a topic of primary concern [11–18]. ClO<sub>2</sub> can be formed from the reaction of chlorite with chlorine gas (Cl<sub>2</sub>), hypochlorous acid (HClO) or hydrochloric acid (HCl), according to Equations (1)–(3). These methods have major disadvantages of producing high amounts of chlorides, which can be avoided by the substitution of hydrochloric by sulfuric acid, although in those cases, the processes become less efficient [5,13,16,19–24].





An interesting alternative for chlorine dioxide production is the combination (Equation (4)) of strongly acidic chlorate ( $\text{ClO}_3^-$ ) media and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) [18,25–27]. Hydrogen peroxide is used here as a reductant reagent, a role in which there are other competing processes that use methanol and sulfur dioxide [23,28] instead of hydrogen peroxide. However, from an environmental point of view, this route is more eco-friendly because the main by-product formed is oxygen.



In addition to its higher atomic economy in terms of chlorine and the products being hazardless, this option has another important benefit: both reagents can very easily be produced electrochemically and this opens the possibility of developing portable devices for the production of chlorine dioxide from chloride and air. That is, chloride dioxide could be generated from natural sources by a sustainable and environmentally friendly electrochemical process.

The electrosynthesis of  $\text{ClO}_3^-$  is an efficient and very well-known process that uses electrodes consisting of coatings of mixed metal oxides (MMO) to oxidize chloride to hypochlorite in one-compartment cells, where later disproportionation reactions, promoted by different chemicals, such as chromate, lead to the production of this commodity [29–34]. Its efficiency depends importantly not only on electrochemical parameters, such as the operation current density, but also on chemical inputs, such as the pH and temperature. Recently, the substitution of MMO coatings by diamond coatings has been proposed [35,36], but, despite the improvement in the oxidation capacity achieved by this electrode (associated to the promotion in the production of hydroxyl radicals), a major handicap is that with these anodes the oxidation of chlorides does not stop in the formation of chlorate but in the perchlorate oxoanion. Thus, selection of the operation conditions is even more important than in the industrial process [35–38].

Different to chlorate, hydrogen peroxide is not produced massively using electrochemical methods, but by the chemical anthraquinone process [39]. However, efficiencies in the electrochemical processes are increasing fast, and nowadays, electrochemical processes are starting to be considered as serious real alternatives [40–43]. Although there are two electrochemical routes for  $\text{H}_2\text{O}_2$  production, i.e., via anodic and cathodic reactions [44,45], only the cathodic path is feasible because the anodic oxidation of water proceeds mainly to oxygen and it is difficult to find operation conditions in which the reaction stops in the formation of  $\text{H}_2\text{O}_2$  as shown in Equation (5). The cathodic route is based on the  $\text{O}_2$  reduction in an aqueous medium (Equation (6)) using electrode material based on noble metals, noble metals alloys or carbon [46] and special gas diffusion electrodes (GDE) or flow-through electrodes, because the massive contact between the oxygen, the electrolyte and the electrocatalyst is required for an efficient process. Recently various strategic options to enhance the high-yield production of  $\text{H}_2\text{O}_2$  have been developed, including modifying the catalytic structure of the carbonaceous electrodes carbon black/PTFE (CB/PTFE), reticulated vitreous carbon (RVC), carbon felt (CF), foam after the deposition of (CB/PTFE) or innovative reactor designs (pressurized-jet microfluidic flow-through), looking to enhance  $\text{O}_2$  solubility, maximizing reaction efficiency and reducing energy consumption [47,48].



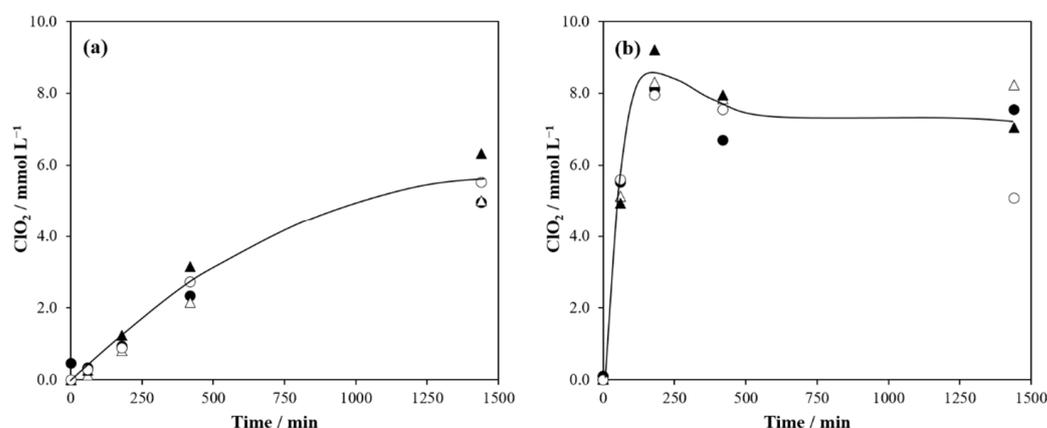
Based on the two electrochemical processes, this work focuses for the first time on the production of chlorine dioxide from the combination of electrochemically produced hydrogen peroxide and chlorates. Trying to approach a most sustainable process perchlo-

rate electrolytes are used with the aim of obtaining higher efficiencies in the production of hydrogen peroxide avoiding the effect of scavengers, such as peroxosulfate, and to obtain a less reactive supporting media which will be easier to be recirculated. To obtain more information, firstly the chemical interaction between commercial hydrogen peroxide and chlorates will be evaluated to establish the optimum reagent ratio and after that, electrolyzed solutions will be manufactured and mixed in suitable ratios to produce this important oxidant. Reaction will be followed by UV-vis spectrophotometry so as not to interfere with the reaction mixture with other chemicals used in the measurement of the chlorinates species. Mechanistic information and ways to improve the processes in the search of manufacturing portable chlorine dioxide devices will also be evaluated.

## 2. Results and Discussion

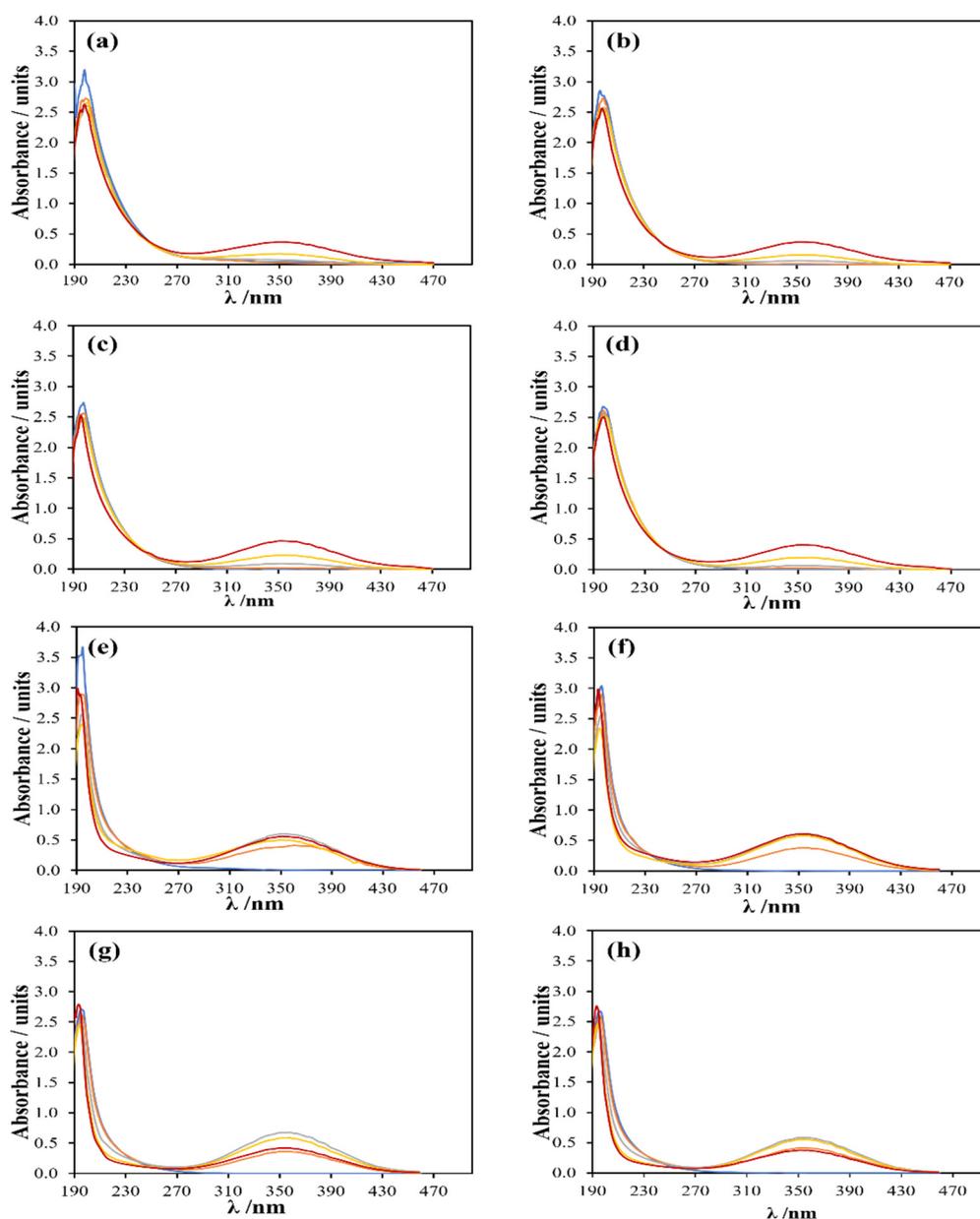
### 2.1. Chemical Production of Chlorine Dioxide

Figure 1a shows the production of chlorine dioxide in the liquid phase obtained after mixing 10 mL of a solution containing commercial chlorate ( $5000 \text{ mg L}^{-1} \text{ NaClO}_3$ ) with 6 mL of commercial hydrogen peroxide ( $3300 \text{ mg L}^{-1}$ ) and 25 mL of sulfuric acid (5.0 M), keeping the temperature at  $50 \text{ }^\circ\text{C}$ . In addition, Figure 1b also shows this production at a temperature of  $83 \text{ }^\circ\text{C}$ , after mixing 10 mL of commercial chlorate ( $5000 \text{ mg L}^{-1} \text{ NaClO}_3$ ) with 4 mL of commercial hydrogen peroxide ( $3300 \text{ mg L}^{-1}$ ) and 25 mL of sulfuric acid (5.0 M). As seen, chlorine dioxide is produced in the reaction media in both cases and the rate of production depends on temperature, being faster at  $83 \text{ }^\circ\text{C}$  where the maximum concentration of chlorine dioxide is reached after 3 h of reaction. Conversely, at  $50 \text{ }^\circ\text{C}$  the reaction is slower, and this steady-state value is not reached after one complete day of reaction, the concentrations still increasing. Another important point is the reproducibility of the tests, which were made in quadruplicate with standard deviations in the range  $0.082\text{--}0.630 \text{ mmol L}^{-1}$  for  $50 \text{ }^\circ\text{C}$  and  $0.042\text{--}1.350 \text{ mmol L}^{-1}$  for  $83 \text{ }^\circ\text{C}$ .



**Figure 1.** Time-course of the production of chlorine dioxide in the liquid reaction mixture: (a) 10 mL of chlorate ( $5 \text{ g L}^{-1}$ ), 6 mL of hydrogen peroxide ( $3300 \text{ mg L}^{-1}$ ) and 25 mL of sulfuric acid (5.0 M) at  $50 \text{ }^\circ\text{C}$ , (b) 10 mL of chlorate ( $5 \text{ g L}^{-1}$ ), 4 mL of hydrogen peroxide ( $3300 \text{ mg L}^{-1}$ ) and 25 mL of sulfuric acid (5.0 M) at  $83 \text{ }^\circ\text{C}$ . Number of repetitions: 4. Legend Figure 1a: Test Q1 (●), test Q2 (△), test Q3 (▲) and test Q4 (○). Legend Figure 1b: Test Q5 (●), test Q6 (△), test Q7 (▲) and test Q8 (○).

UV-vis spectra of the different samples are shown in Figure 2, where the peak corresponding to chlorine dioxide (c.a.  $360 \text{ nm}$ ) can be seen. No other peaks are as clearly observed. However, the slope of the UV spectra in the range  $200\text{--}270 \text{ nm}$  with a shoulder (where the chlorite absorption peak is found at  $230 \text{ nm}$ ) indicates formation of this species at  $50 \text{ }^\circ\text{C}$  and prevention in its formation at  $83 \text{ }^\circ\text{C}$ . Based on the existing literature, when increase of temperature occurs, the reaction activation energy more easily results in the formation of chlorine dioxide.

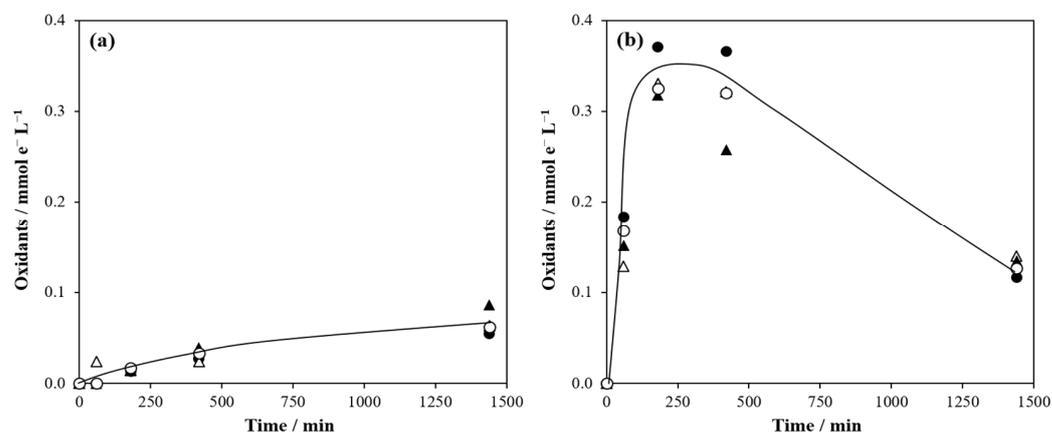


**Figure 2.** Change in the UV-vis spectra recorded during production of chlorine dioxide in the liquid reaction mixture: (a–d) 10 mL of chlorate ( $5 \text{ g L}^{-1}$ ), 6 mL of hydrogen peroxide ( $3300 \text{ mg L}^{-1}$ ) and 25 mL of sulfuric acid ( $5.0 \text{ M}$ ) at  $50 \text{ }^\circ\text{C}$ ; (e–h) 10 mL of chlorate ( $5 \text{ g L}^{-1}$ ), 4 mL of hydrogen peroxide ( $3300 \text{ mg L}^{-1}$ ) and 25 mL of sulfuric acid ( $5.0 \text{ M}$ ) at  $83 \text{ }^\circ\text{C}$ . Number of repetitions: 4. Legend: (—) 0 min, (—) 60 min, (—) 180 min, (—) 420 min and (—) 1440 min.  $50 \text{ }^\circ\text{C}$ : (a) test Q1, (b) test Q2, (c) test Q3 and (d) test Q4.  $83 \text{ }^\circ\text{C}$ : (e) test Q5, (f) test Q6, (g) test Q7 and (h) test Q8.

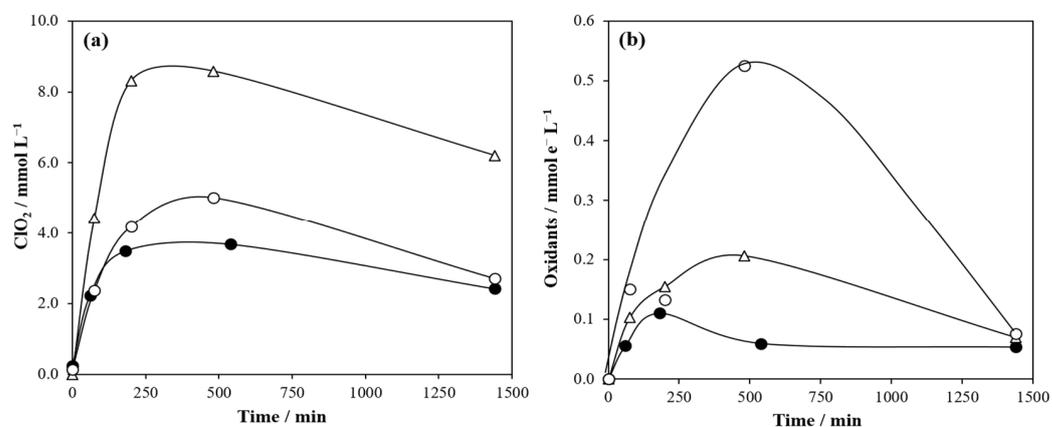
Regarding the stripping of chlorine dioxide, 5 mL of gas produced was bubbled into a 10 mL solution containing  $1 \text{ g L}^{-1}$  of potassium iodide, where the formation of iodine was measured by titration. Oxidation capacity of the gaseous stream is shown in Figure 3 and results confirm the faster and higher production of chlorine dioxide at  $83 \text{ }^\circ\text{C}$  as compared to that obtained at  $50 \text{ }^\circ\text{C}$ .

Significance of the stoichiometry of processes is shown in Figure 4, where the ratio between hydrogen peroxide and chlorate is changed in three tests from 0.2 to  $4.1 \text{ mmol H}_2\text{O}_2/\text{mmol ClO}_3^-$  at  $60 \text{ }^\circ\text{C}$ . Thus, it can be seen that the ratio 1.0 allows reaching a higher amount of chlorine dioxide in the tests. Surplus chlorates at the end of the test were  $79.2$ ,  $323.5$  and  $97 \text{ mg L}^{-1} \text{ ClO}_3^-$  for the ratios 0.2, 1.0 and 4.1, respectively. This means that the

conversion into the desired product increased significantly up to 18.8% in this optimum ratio, while it is remarkable slower for the ratios 0.2 (4%) and 4.1 (7.8%). However, the concentrations of oxidants measured in the gas are higher for the ratio 4.1, in which an important excess of hydrogen peroxide is added. This can be explained in terms of the higher production of chlorine because of the reduction of chlorate up to this species which, as known, is also a powerful oxidant.



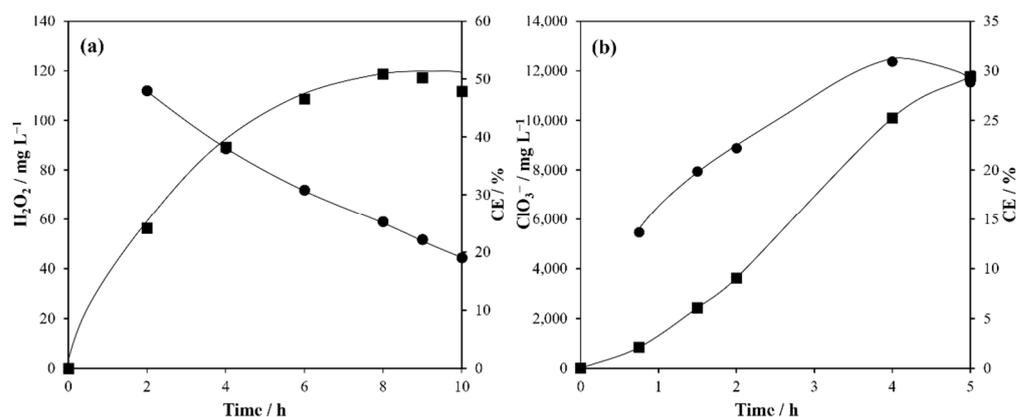
**Figure 3.** Oxidation capacity of the gases produced from the chlorine production reactor: (a) 10 mL of chlorate ( $5\text{ g L}^{-1}$ ), 6 mL of hydrogen peroxide ( $3300\text{ mg L}^{-1}$ ) and 25 mL of sulfuric acid ( $5.0\text{ M}$ ) at  $50\text{ }^{\circ}\text{C}$ , (b) 10 mL of chlorate ( $5\text{ g L}^{-1}$ ), 4 mL of hydrogen peroxide ( $3300\text{ mg L}^{-1}$ ) and 25 mL of sulfuric acid ( $5.0\text{ M}$ ) at  $83\text{ }^{\circ}\text{C}$ . Number of repetitions: 4. Legend Figure 1a: Test Q1 (●), test Q2, test Q3 (▲) and test Q4 (○). Legend Figure 1b: Test Q5 (●), test Q6 (Δ), test Q7 (▲) and test Q8 (○).



**Figure 4.** Chlorine dioxide concentration produced in the liquid reaction mixture (a) and oxidants in the gas phase (b) with different ratios of hydrogen peroxide/chlorate at  $60\text{ }^{\circ}\text{C}$ . Legend: (●) ratio  $\text{H}_2\text{O}_2/\text{ClO}_3^- = 0.2$ , (Δ) ratio  $\text{H}_2\text{O}_2/\text{ClO}_3^- = 1.0$  and (○) ratio  $\text{H}_2\text{O}_2/\text{ClO}_3^- = 4.1$ .

## 2.2. Electrochemical Production of Chlorate and Hydrogen Peroxide

Figure 5 shows the production of hydrogen peroxide and chlorate in two different electrochemical cells. The first was used to produce hydrogen peroxide and it was fed with a solution  $3000\text{ mg L}^{-1}$   $\text{HClO}_4$  and operated at  $5\text{ mA cm}^{-2}$ ,  $15\text{ }^{\circ}\text{C}$  and 2 bar. In this cell, the main anodic reaction is the oxidation of water with the subsequent formation of oxygen. The second was used to produce chlorate from a solution containing  $20\text{ g L}^{-1}$  of  $\text{NaCl}$  and it was operated at  $50\text{ mA cm}^{-2}$  and  $50\text{ }^{\circ}\text{C}$ . The main cathodic reaction is the formation of hydrogen from water reduction. Both processes were run in semicontinuous mode with a flowrate of  $13.9\text{ mL h}^{-1}$  for  $\text{H}_2\text{O}_2$  and  $18.0\text{ mL h}^{-1}$  for chlorate.



**Figure 5.** Electrochemical production of hydrogen peroxide in 3000 mg L<sup>-1</sup> HClO<sub>4</sub> (a) and chlorate in 20 g L<sup>-1</sup> NaCl (b). Symbols: (■) concentration (mg L<sup>-1</sup>), (●) current efficiency (CE/%).

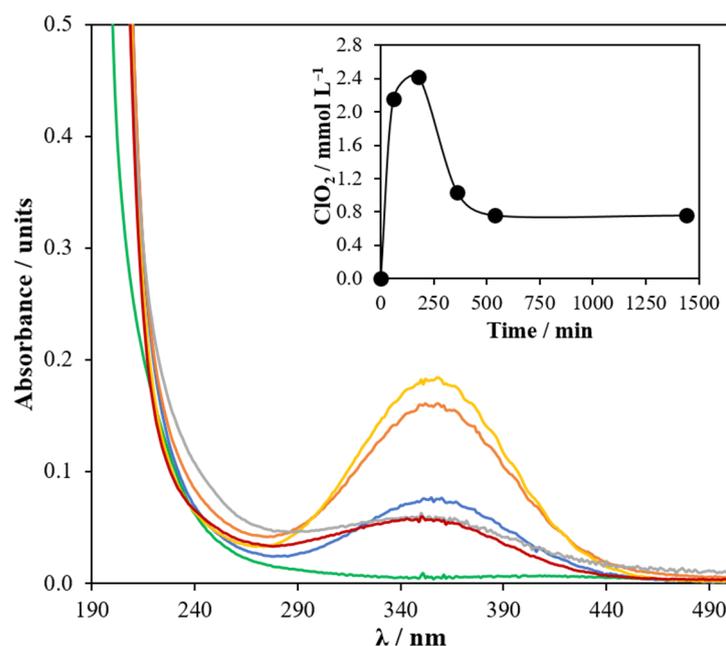
Samples of the hydrogen peroxide produced were taken at applied charges of 0.71 Ah L<sup>-1</sup> (8 h and 118.8 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>) and were mixed with samples of chlorate obtained after passing 48.44 Ah L<sup>-1</sup> (4 h and 10,100.1 mg L<sup>-1</sup> ClO<sub>3</sub><sup>-</sup>). The first also contains perchloric acid (3000 mg L<sup>-1</sup>) while the second is impurified with chloride, chlorine, hypochlorous acid and chlorite. As seen, productions of the two target compounds are important with columbic efficacies in the range 19.0–48.0% for hydrogen peroxide and 13.7–30.9% for chlorate.

### 2.3. Production of Chlorine Dioxide by Combination of Electrolytic Solutions

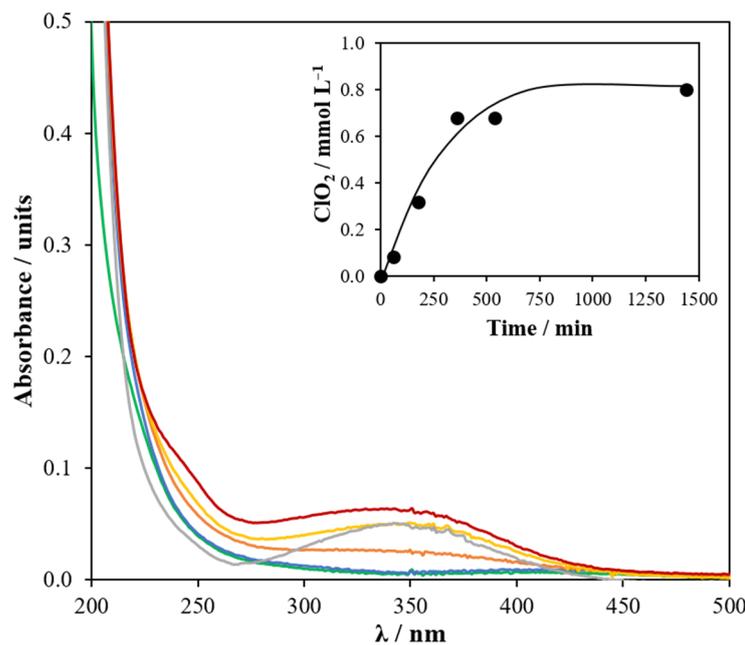
Both solutions were mixed at two different ratios. In test EQI, 13 mL of electrogenerated H<sub>2</sub>O<sub>2</sub> were mixed with 1 mL of electrogenerated chlorate and 25 mL of sulfuric acid (5.0 M) at 68 °C, while in test EQII, 4 mL H<sub>2</sub>O<sub>2</sub> were mixed with 10 mL chlorate and 25 mL of sulfuric acid (5.0 M) at the same temperature. This means that in the first case the ratio was slightly above the stoichiometric (2.66) while in the second case a very important excess of chlorate was added to the system (92.40), trying to prevent further action of surplus hydrogen peroxide when the chlorate is transformed into chlorine dioxide. UV spectra recorded during the following 24 h as well as the concentration of chlorine dioxide reached is shown in Figures 6 and 7 for the two case studies.

In test EQI, the concentration of chlorine dioxide increases up to a maximum around 2.47 mmol L<sup>-1</sup> and then decreases. In the meantime, chlorate decreases from 259.0 to 31.2 mg L<sup>-1</sup>. Thus, consumption of chlorate is 2.75 mmol L<sup>-1</sup> and maximum conversion reached is 89.65%. Decay indicates that this product can be stripped from solution or transformed into less oxidized chlorinated species, such as chlorite or hypochlorite. It is important to take into consideration that after the reaction time that 4.0 mg L<sup>-1</sup> of hydrogen peroxide still remains in the reaction mixture. In experiment EQII, the concentration of chlorine dioxide increases up to stabilization in a value lower than that obtained in test EQI (0.86 mmol L<sup>-1</sup>).

Hydrogen peroxide at the end of the reaction was negligible (0.5 mg L<sup>-1</sup>), suggesting that depletion of this reagent prevents the disappearance of chlorine dioxide. Chlorate decreases from 2590.0 to 2330.1 mg L<sup>-1</sup>, that is a consumption of 3.21 mmol L<sup>-1</sup> and the maximum conversion reached is 26.70%. Again, an excess of chlorate is not found as necessary to reach high conversions. However, higher efficiencies obtained in the two electrochemical tests as compared with chemical production of chlorine dioxide can be explained in terms of the presence of chlorites in significant concentration in the electrolyte added. As seen, the ratio 2.66 is more efficient in the production of chloride dioxide and a shoulder is observed in the region of 230 nm which the peak at 360 nm is broader suggesting the overlapping with the peak of chlorine production at 310 nm. This indicates that stoichiometry plays a very important role in these processes.



**Figure 6.** Changes in the UV-vis spectra during production of chlorine dioxide in the liquid reaction mixture from electrochemically generated hydrogen peroxide and chlorate in test EQI. The inset panel shows the concentration of chlorine dioxide produced in the system during the reaction. Legend: (—) 0 min, (—) 60 min, (—) 180 min, (—) 240 min, (—) 540 min and (—) 1440 min.

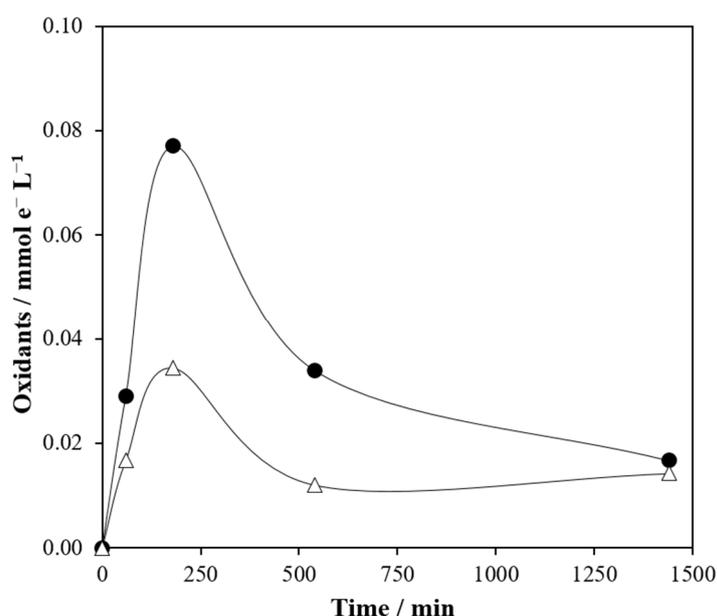


**Figure 7.** Changes in the UV-vis spectra during production of chlorine dioxide in the liquid reaction mixture from electrochemically generated hydrogen peroxide and chlorate in test EQII. The inset panel shows the concentration of chlorine dioxide produced in the system during the reaction. Legend: (—) 0 min, (—) 60 min, (—) 180 min, (—) 240 min, (—) 540 min and (—) 1440 min.

Energy consumption to produce hydrogen peroxide can be estimated by the product of the steady state cell voltage (3.8 V) and the current intensity (0.25 A). Then, to produce 13.8 mL/h of a solution containing 118 mg/L of  $\text{H}_2\text{O}_2$  the power consumption is 0.068 Wh/mL. Similarly, energy consumption to produce chlorate can be estimated by the product of the steady state cell voltage (8.3 V) and the current intensity (3.93 A). Then, to produce 18 mL/h of a solution containing 10,100 mg/L of chlorate the power consumption

is 1.812 Wh/mL. Considering the operation conditions of EQI and EQII and the production of chloride dioxide obtained, the energy efficiencies are 0.775 mg/Wh and 0.114 mg/Wh, respectively, pointing out the relevance of the operation conditions and stoichiometry in the process performance.

Regarding the production of oxidant gases, Figure 8 shows the capacity of oxidation where these streams are used to oxidize a 10 mL KI 1 g L<sup>-1</sup> solution. Again, better results obtained with the ratio 2.66, as it can be easily understood considering the higher concentrations reached in the liquid reaction mixture. The integration of the electrochemically generated ClO<sub>3</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub> and ClO<sub>2</sub> production process was successfully applied as an eco-friendly technology.



**Figure 8.** Oxidation capacity of the gases produced from in the chlorine dioxide reactor. (●) Test EQI, (△) test EQII.

### 3. Materials and Methods

#### 3.1. Chemicals

All aqueous solutions were prepared with double deionized water (Millipore Milli-Q system, resistivity: 18.2 MΩ cm at 25 °C). Perchloric acid (60%) and sodium chloride (food grade) were supplied from Panreac (Castellar del Vallès, Barcelona, Spain) and used as support electrolyte in the generation of hydrogen peroxide and chlorate, respectively. Sodium hydroxide (analytical grade from Merck, Darmstadt, Germany) was used to adjust the pH to the desired value. Sodium chlorate (≥99.0%), sulfuric acid (90–91%), and titanium (IV) oxysulfate (1.9–2.1%) were also supplied from Merck. Hydrogen peroxide (33% w/v) was purchased by Labox (Vilassar de Dalt, Barcelona, Spain). Other chemicals were analytical grade and supplied from Scharlab (Sentmenat, Barcelona, Spain).

#### 3.2. Experimental Setup

##### 3.2.1. Electrochemical Cells

To prove that it is feasible to use chlorate and hydrogen peroxide electrochemically produced for the generation of chlorine dioxide, two electrochemical cells were used, one for hydrogen peroxide generation and the other for chlorate generation. In this way, electrochemical production of hydrogen peroxide experiments were developed by using a microfluidic flow-through cell (MF-FT) with a pressurized-jet aeration (PJA) in a bench-scale experimental set-up as described elsewhere [49]. In this cell, the inter-electrode gap was 150 μm. Mixed metal oxide (MMO-Ir<sub>2</sub>O<sub>2</sub>Ta<sub>2</sub>O<sub>5</sub>, supplied by Tianode) was used as three-dimensional (3D) mesh anode material. In addition, a 3D-titanium mesh electrode

modified with carbon black and polytetrafluorethylene (PTFE) was used as cathode. The modification of the electrode was carried out following the same procedure to the one described by Moratalla et al. [49]. The combination of both electrodes has demonstrated a very good performance in the production of hydrogen peroxide in supporting electrolyte containing sulphate, and here the use in perchloric acid ( $3000 \text{ mg L}^{-1}$ ) media will be assessed. The geometric active areas of both electrodes was  $49.5 \text{ cm}^2$ . The initial pH of the solution was adjusted to 3.0. Experiments were carried out at a current density of  $5.0 \text{ mA cm}^{-2}$  and a temperature of  $11.5 \text{ }^\circ\text{C}$ . To increase the solubility of oxygen in the solution, the system was pressurized to a gauge pressure of 2.0 bar. The volume treated was 2.7 L and the electrolysis time was 10 h. On the other hand, electrochemical production of chlorates experiments was carried out by using a parallel flow cell with an inter-electrode gap of 9 mm in a bench-scale experimental set up. Mixed metal oxide (MMO-RuO<sub>2</sub>, supplied by Tianode) was used as two-dimensional (2D) plate anode material (which was demonstrated to contribute to an outstanding performance in the production of chlorates), and stainless steel (AISI 304) was used as cathode electrode. The geometric area of both electrodes was  $78 \text{ cm}^2$ . Sodium chloride ( $20 \text{ g L}^{-1}$ ) was used as supporting electrolyte. Experiments were carried out at  $50 \text{ mA cm}^{-2}$  (3.93 A) and  $50 \text{ }^\circ\text{C}$ . The volume treated was 0.25 L and the electrolysis time was 5 h. Both electrochemical cells operated under galvanostatic conditions and semi-continuous mode with fresh electrolyte feed rates to the cell of  $13.9 \text{ mL h}^{-1}$  for H<sub>2</sub>O<sub>2</sub> and  $18 \text{ mL h}^{-1}$  for chlorate. Some of the samples collected were subsequently used for the generation of chlorine dioxide.

### 3.2.2. Chlorine Dioxide Assays

The experiments that aimed to examine the formation of chloride dioxide were conducted in 250 mL glass reactors, which were completely closed. The temperature was kept constant throughout all experiments (with a thermostatic bath) and under gentle stirring conditions (350 rpm). The reagents used in this reactor were hydrogen peroxide and chlorate. Since chlorine dioxide production from the reduction of chlorates occurs at extremely acidic pH, 25 mL of sulfuric acid (5 M) was used in all experiments. To quantify the evolution of chlorine dioxide, samples of the liquid and gas phase were collected periodically. In this way, two types of experiment were performed. In the first part, commercial hydrogen peroxide and commercial chlorate were used. Thus, different volumes of hydrogen peroxide ( $3300 \text{ mg L}^{-1}$ ) and sodium chlorate ( $5000 \text{ mg L}^{-1}$ ) were added to the reactor with 25 mL H<sub>2</sub>SO<sub>4</sub> (5M) and working temperatures ranged from 50 to  $83 \text{ }^\circ\text{C}$ . Table 1 summarizes the conditions for each of the experiments.

**Table 1.** Experimental conditions for the chemical production of chlorine dioxide.

Test	Volume/mL			T°Reactor/°C	mmol H <sub>2</sub> O <sub>2</sub> /mmolClO <sub>3</sub> <sup>-</sup> Ratio
	H <sub>2</sub> O <sub>2</sub> (3.3 g L <sup>-1</sup> )	NaClO <sub>3</sub> (5 g L <sup>-1</sup> )	H <sub>2</sub> SO <sub>4</sub> (5.0 M)		
Q1	6	10	25	50	1.2
Q2					
Q3					
Q4					
Q5	4	10	25	83	0.83
Q6					
Q7					
Q8					
Q9	0.5	5	25	60	0.2
Q10	2.5	5	25		1.0
Q11	10	5	25		4.1

In the second part, the hydrogen peroxide and chlorate used were from electrochemical production. Samples from the outlet at electrolysis times of 8 h of hydrogen peroxide and

4 h of chlorate was used. In this case, the reactor temperature was set at 68 °C. Hydrogen peroxide and chlorates produced electrochemically were mixed at two different ratios. In test EQI, 1 mL of  $\text{ClO}_3^-$  (10,100.1 mg L<sup>-1</sup>) were mixed with 1 mL of  $\text{H}_2\text{O}_2$  (118.8 mg L<sup>-1</sup>) and 25 mL of  $\text{H}_2\text{SO}_4$  (5.0 M). In test EQII, 10 mL of  $\text{ClO}_3^-$  (10,100.1 mg L<sup>-1</sup>) were mixed with 4 mL of  $\text{H}_2\text{O}_2$  (3300 mg L<sup>-1</sup>) and 25 mL of  $\text{H}_2\text{SO}_4$  (5.0 M).

### 3.3. Characterization Methods

The concentration of chlorate was measured by ion chromatography (IC) using a Metrohm Compact Ion Chromatograph Flex (Madrid, Spain) coupled to a conductivity detector. A Metrosep A Supp 7 column was used as the stationary phase and 85:15 v/v 3.6 mM sodium carbonate/acetone as the mobile phase. The flow rate was 0.8 mL min<sup>-1</sup> and the volume injection of each sample was 20.0 µL. The concentration of hydrogen peroxide was monitored by spectrophotometry, due to the yellow color formed between hydrogen peroxide and  $\text{Ti}^{2+}$  [50] at a wavelength of 410 nm. Chlorine species formed in the chlorine dioxide reactor were also monitored spectrophotometrically using an Agilent 300 Cary series UV-vis spectrophotometer (Madrid, Spain). Chlorine dioxide was detected at a wavelength of 360 nm. Other species, such as chlorite, hypochlorous acid and chlorine, were detected at 230, 323 and 310 nm, respectively. Regarding the production of oxidants in the gas phase, 5 mL of gas taken from the reactor was bubbled in a solution containing 10 mL of KI (1 g L<sup>-1</sup>). Thus, the transformation of iodide to iodine takes place and the solution was titrated with sodium thiosulphate.

## 4. Conclusions

From this work, the following conclusions can be drawn:

- Hydrogen peroxide and chlorate can be efficiently produced by the electrolysis of perchlorate solutions and sodium chloride solutions, respectively. Applying 5.0 mA cm<sup>-2</sup>, 2 bars of a solution containing 118.8 mg L<sup>-1</sup>  $\text{H}_2\text{O}_2$  can be obtained after passing 0.71 Ah L<sup>-1</sup> (8 h of electrolysis). By applying 50.0 mA cm<sup>-2</sup>, a solution containing 10,100.1 mg L<sup>-1</sup> of chlorate can be obtained after passing 48.44 Ah L<sup>-1</sup> (4 h of electrolysis). The first solution contains 3000 mg L<sup>-1</sup> of perchloric acid while the second 20 g L<sup>-1</sup> of sodium chloride.
- The reaction between commercial chlorate and hydrogen peroxide solutions led to the formation of chlorine dioxide. The reaction is highly reproducible, and stoichiometry is very important, because chlorine dioxide is not the final product but an intermediate in the reduction of chlorates to chlorine by hydrogen peroxide. In addition to suitable ratios of  $\text{H}_2\text{O}_2/\text{ClO}_3^-$ , it is important that in the reaction mixture chlorate is not exhausted, in order to prevent further reduction of  $\text{ClO}_2$ .
- Mixing of the two electrochemically produced reagents with sulfuric acid leads to the successful formation of chlorine dioxide. Maximum conversions close to 90% of the chlorate dose are obtained. Using the electrochemically-produced solutions, the significance of selecting a suitable ratio between reagents and the necessity of surplus chlorate in solution to prevent further reduction of chlorine dioxide is also confirmed.
- A gas stream with a high oxidation capacity and consisting mainly of chlorine dioxide is produced either when mixing chemical or electrochemically produced solutions of hydrogen peroxide and chlorates. This confirms the good prospects of the technology for the manufacturing of portable electrochemically-based chlorine dioxide production units.

**Author Contributions:** Conceptualization, Á.M., C.S., E.V.D.S. and M.A.R.; methodology, Á.M.; validation, C.S., E.V.D.S. and M.A.R.; formal analysis, Á.M. and M.K.S.M.; investigation, Á.M. and M.K.S.M.; resources, C.S. and M.A.R.; data curation, Á.M. and M.K.S.M.; writing—original draft, Á.M.; writing—review and editing, C.S., E.V.D.S. and M.A.R.; supervision, C.S. and M.A.R.; project administration, M.A.R.; funding acquisition, M.A.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work belongs to the research projects PID2019-107271RB-I00 and PID2019-110904RB-I00 granted by MCIN/AEI/10.13039/501100011033/ and “Unión Europea NextGenerationEU/PRTR”. M.K.S.M. also acknowledges CNPq-Conselho Nacional de Desenvolvimento Científico e Tecnológico for process number 202069/2019-2 (doutorado sanduíche no Exterior—SWE).

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

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