

Treatment of Organics in Wastewater Using Electrogenenerated Gaseous Oxidants

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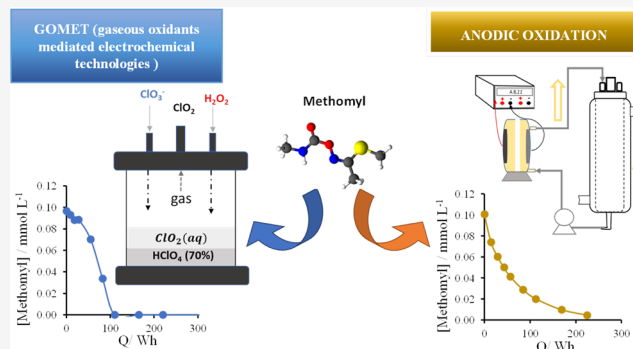
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ABSTRACT: This work focuses on the comparison of the performance of direct electrochemical oxidation with indirect electrolysis mediated by gaseous oxidants in the treatment of diluted wastewater. To do this, energy consumptions of the electrolysis using mixed metal oxide (MMO) electrodes are compared with those required for the production and use of chlorine dioxide in the degradation of methomyl contained in aqueous solutions. Results demonstrate the feasibility of the mediated oxidation process and that this process is competitive with direct oxidation. The oxidants are produced under optimized conditions using the same anodic material applied for the direct degradation of organics, thus avoiding efficiency losses associated with mass transfer limitations in the degradation of dilute organic solutions. Thus, using the ClO_2 gaseous oxidant, a concentration of 0.1 mM of methomyl from a solution containing 500 mL is completely removed with an energy consumption as low as 50 Wh. The application of the same energy to a direct electrolytic process for treating the same wastewater can only reach less than half of this removal. These findings may have a very important application in the use of electrochemical technology to achieve the remediation of persistent pollutants in wastewater, where their low concentrations typically make direct processes very inefficient.



1. INTRODUCTION

The removal of pollutants from wastewater has been a topic of wide interest for decades.^{1–7} Many technologies have been evaluated and, among them, electrochemical oxidation has been shown to be one of the most promising according to the scientific literature.^{8–17} In this context, once the viability of the electrochemical technology for treating organic compounds contained in wastewater was demonstrated at the turn of the century, other challenges were faced looking for improving efficiency and sustainability, including the development of new electrode materials,^{18–24} the synergistic effect and integration of electrolytic processes with other oxidation technologies,^{25–30} and the powering of electrochemical processes with green energies.³¹ More recently, technological advancement is focused on the development of more efficient electrochemical cells, with the final aim of increasing the technology readiness level (TRL) of these processes.³² In addition to this technological progress, fundamental studies that demonstrate the important role of hydroxyl radicals were considered extremely important to understand oxidation mechanisms and optimize their performance. The key role of these radicals has contributed to classify electrochemical oxidation as an advanced oxidation process (AOP).^{33,34}

One of the most important facts that must be evaluated regarding the application of the electrochemical technology is

the concentration of the organic pollutants that should be removed from wastewater.³⁵ Typically, this technology is very efficient when treating wastewater with concentrations within the range of 1000–20,000 mg L⁻¹ COD where, using diamond electrodes and tailored cells, Coulombic efficiencies near 100% can be reached.³⁶ However, below this range, the efficiency decreases almost linearly with the concentration that needs to be removed. Thus, a typical efficiency when degrading wastewater with a COD content of 100 mg L⁻¹ is around 5–10% and, in treating waste with a COD of 10 mg L⁻¹, it is difficult to reach efficiencies over 2–3%, unless the bare electrolytic process is combined with other processes (Fenton, ultraviolet (UV) irradiation, application of ultrasounds, etc.).³⁷ This is explained because the efficiency of the direct electrochemical processes depends importantly on mass transport within the electrochemical cell and below the range 1000–2000 mg L⁻¹, this transport becomes the limiting stage

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(bottleneck), and it is necessary to change the primary oxidation mechanisms from direct transfer of electrons to a mediated process, to achieve a more efficient treatment.

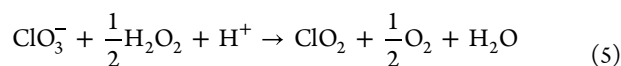
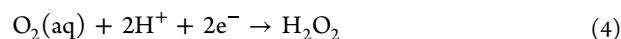
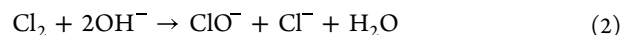
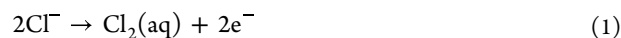
The combination of electrochemical technologies with other advanced oxidation processes (AOPs) is this objective. The first works,^{38,39} made at a very low TRL of 2–3, aimed to clarify the effect of the salts contained in wastewater on the degradation of different pollutants (in fact, many of them were not real wastewater, but solutions containing the pollutant and salts in nonrealistic concentrations). Many works demonstrate the feasibility of removing the organic species in most cases, but the resulting effluent was not suitable for use in any case due to the difficulties in the separation of the oxidants and the salts contained in the electrolyte, as cited by Sirés et al.⁴⁰ Then, the target of the research shifted from the evaluation of the effect of salts to the clarification of the role of other species such as hydrogen peroxide that do not leave an unaffordable fingerprint in the treated waste. The main disadvantage observed was the significant increase in cost when several technologies are combined, possibly associated with the fact that those works were carried out at a low TRL.³²

Recently, interest has arisen in the electrochemical production of oxidants off-site from the waste treatment process, looking for higher efficiencies in this production, in which the electrolyte is not the waste but a special solution made on purpose to produce the oxidant.

Once formed, this oxidant is applied to the waste and it is let to oxidize the organic pollutants chemically, either alone or activated by chemical, photolytic, or ultrasound mechanisms.^{41–47} The main problem associated with this application is that, along with the addition of the oxidant, other compounds contained in the electrolyte where the oxidant was manufactured, are added to the water.^{48–50} Among these oxidant solutions, those containing peroxo species like peroxocarbonates, peroxosulfates, peroxophosphates, and hydrogen peroxide are worth to be mentioned. Also, and although used in much lower extension, hypochlorite solutions are also included. Thus, the main limitation in their use is the composition of the electrolyte used to manufacture them, because of the difficulties in the separation of the oxidants and the salts contained in the electrolyte in a cheap and efficient way.⁴⁰

This problem can be detached when the oxidant produced is a gas, like in the cases of chlorine, ozone^{51,52} and chlorine dioxide,^{53,54} because in those cases, the electrolyte used for the production is not added to the waste that is expected to be treated, but simply a gaseous stream containing the oxidant gas, because they can be easily stripped from the electrolyte solution by flowing air and this becomes a very important advantage. This means that the fingerprint of this technology is going to be less important than that obtained with other more aggressively mediated processes. This approach is very new, especially in the case of chlorine dioxide, which is an oxidant whose electrochemical production has been the target of research only very recently. Although there are several approaches to produce this important oxidant,^{55–58} the most interesting path seems to be the combination of the production of chlorate (which is a well-known electrochemical process in which the raw matter can be brine or a salty chloride solution) (eqs 1–3) with the electrochemical production of hydrogen peroxide (in which a great development is being reached recently with the development of more and more efficient cells) (eq 4).^{48,59,60} In the combined process, the oxidation

state of chloride (−1) is raised to that of chlorate (+5) electrochemically, and then hydrogen peroxide decreases it down to +4 (chlorine dioxide) (eq 5).^{60–61,63}



The ease in the change of oxidation state of chlorine species increases the difficulty of this process, which in addition needs highly acidic media. However, the good prospects of chlorine dioxide made it interesting to go further in the development of this electrochemical production.

Considering this background, the main aim of this paper is to make a preliminary comparison of the direct and mediated (using chlorine dioxide) degradation of pollutants at very low concentrations, especially in terms of energy demand. To do this, the degradation of a diluted solution containing methomyl is evaluated when the pollutant is degraded by direct electrolysis using mixed metal oxide (MMO) electrodes or when using for this degradation the oxidant chlorine dioxide, produced from chlorate and hydrogen peroxide, formed electrochemically with the same electrodes.

2. MATERIALS AND METHODS

2.1. Chemicals. For the generation of oxidants, deionized water (Millipore Mili-Q system, resistivity 18.2 MΩ·cm at 25 °C, TOC:2 ppb) and the following analytical standard reagents were used: sodium chloride, sodium perchlorate, 70% perchloric acid, and 1.9–2.1% of titanium(IV) oxysulfate solution (CAS:13825–74–6/Sigma-Aldrich) as an indicator for H₂O₂ measurement and oxidants analysis, and the samples were acidified with 20% sulfuric acid for subsequent reaction with sodium thiosulfate. For the effluent preparation, 16.21 mg L^{−1} methomyl from its commercial compound was used, whose composition is 215 g L^{−1} methomyl, 420 g L^{−1} ethanol, and 324 g L^{−1} other ingredients.

2.2. Experimental Setup and Procedure. To generate chlorate from a sodium chloride solution, an electrochemical flow reactor (Figure 1A) manufactured with a three-dimensional (3D) printer was used, and it was equipped with an MMO (based on RuO₂/Ti and supplied by Ti anode) anode

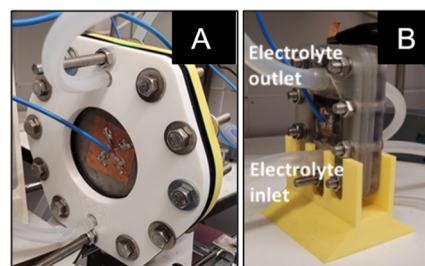


Figure 1. (A) Electrochemical flow reactor used for chlorate generation with a plate of titanium as cathode and DSA as an anode. (B) Gas diffusion cell used for hydrogen hydroxide generation with DSA as anode and painted carbon paper as cathode.

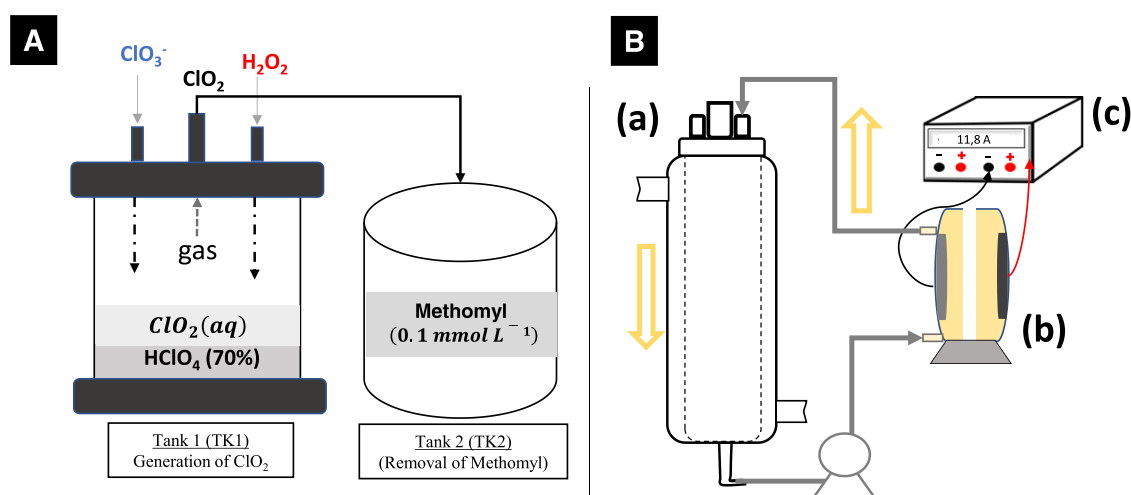


Figure 2. (A) Scheme of ClO₂ production used for the treatment of methomyl in dissolution. (B) Electrochemical oxidation setup with MMO (Ti anode) anode: (a) recirculation tank with Na₂SO₄ (0.05 mol L⁻¹), (b) electrochemical flow reactor, and (c) power supply. $j_{app} = 79.5 \text{ mA cm}^{-2}$, and initial volume of 500 mL.

and a titanium cathode, both measuring 78.5 cm². The optimized conditions for production involved the use of a solution containing 5 g L⁻¹ NaCl, applying 150 mA cm⁻², at 15 °C, using a titanium plate as cathode. From this, it was possible to generate large amounts of ClO₃⁻ continuously at different flow rates. The same MMO electrodes were used to produce chlorates and the direct degradation of methomyl.

To generate hydrogen peroxide (H₂O₂), an electrochemical gas diffusion cell (Figure 1B) printed on a 3D printer was used, using an MMO (based on RuO₂/Ti and supplied by Ti anode) as the anode (10.9 cm²) and a painted carbon paper 10.9 cm² as the cathode. The optimized condition used for methomyl treatment in this work was a solution of 14.05 g L⁻¹ NaClO₄ acidified to pH 3.5, applying 4.6 mA cm⁻², with a continuous average flow of 100 mL h⁻¹.

As demonstrated in Figure 2A, the experiments of ClO₂ generation were carried out in completely closed glass reactors of 1000 mL (Tank 1), adding different ratios of chlorate (4800 mg L⁻¹) and hydrogen peroxide (46–70 mg L⁻¹) simultaneously at different flow rates for ClO₂ formation (eq 5). To maintain the strongly acidic pH, 100 mL of perchloric acid 70% were added in all cases as initial volume. Also, the H₂O₂ solution added was acid. Samples of the liquid and gas phases were collected to quantify the evolution of ClO₂.

Two initial experiments were carried out with the system shown in Figure 2A. The first experiment (E1) used 2 L of KI (2 mol L⁻¹) in TK2. The second experiment (E2) used 500 mL of a methomyl solution (0.1 × 10⁻³ mol L⁻¹) in TK2. For ClO₂ generation (TK1) was applied a continuous flow of 4.0 and 0.18 mmol h⁻¹ for ClO₃⁻ and H₂O₂, respectively, with an inlet airflow of 10 L h⁻¹. Then, to evaluate the production of chlorine dioxide, the airflow and dosages of ClO₃⁻ and H₂O₂ were varied as indicated in Table 1.

The degradation of methomyl by electrochemical oxidation using MMO (RuO₂/Ti) as anode and Ti anode as cathode was carried out using the system shown in Figure 2B, using a recirculation tank of 500 mL (a) with Na₂SO₄ (0.05 mol L⁻¹), electrochemical flow reactor (b), and power supply (c) to apply 79.5 mA cm⁻².

To calculate energy consumption associated with electrochemical processes, eq 6 was applied using intensity and voltage data obtained during the electrolysis tests. Energy data

Table 1. ClO₂ Generation Conditions, Using 100 mL of HClO₄ (70%), and V_i = 500 mL

ID	airflow (mL h ⁻¹)	ClO ₃ ⁻ flow (mL h ⁻¹)	H ₂ O ₂ flow (mL h ⁻¹)
(1)	50	62.5	92
(2)	30	62.5	92
(3)	10	62.5	92
(4)	30	67.9	187.5
(5)	30	180	64.3

obtained are used to plot the main results of the methomyl removal.

$$W = \int_0^t I \cdot V \cdot dt \quad (6)$$

2.3. Analytical Techniques. The methomyl analysis was performed using a high-performance liquid chromatography (HPLC) method. For this purpose, an Elipse Plus C18 column from Agilent (PN: 959961–902) was used, with a mobile phase of acetonitrile:water (20:80, v/v), a flow of 0.3 mL min⁻¹, 25 °C, injection volume of 20 μL, and λ_{max} = 233 nm. Chlorine dioxide (ClO₂) in the liquid phase was monitored by spectrophotometry using a Spectroquant Prove 300 from Merck KGaA, D-64293 Darmstadt, with a wavelength absorbance of 360 nm. Previous experiments from our research group indicated the calibration curve of standard ClO₂.⁶⁰ For the gaseous phase determinations, samples of 5 mL of gas were taken and bubbled into 10 mL of water for measuring the spectra or into a solution containing potassium iodide, producing its transformation into iodine. In this latter case, the iodine solution was titrated with sodium thiosulfate (0.001 N) to quantify oxidants.

3. RESULTS AND DISCUSSION

3.1. Degradation of Methomyl by the Mediated Electrochemical Process. One of the main challenges in the development of new processes to face the destruction of organics contained in wastewater is to evaluate their performance in continuous operation mode, which is the operation mode in which full-scale treatment should be applied. This is of great significance when the product is a gas, and it is especially important in the case of chlorine dioxide because its

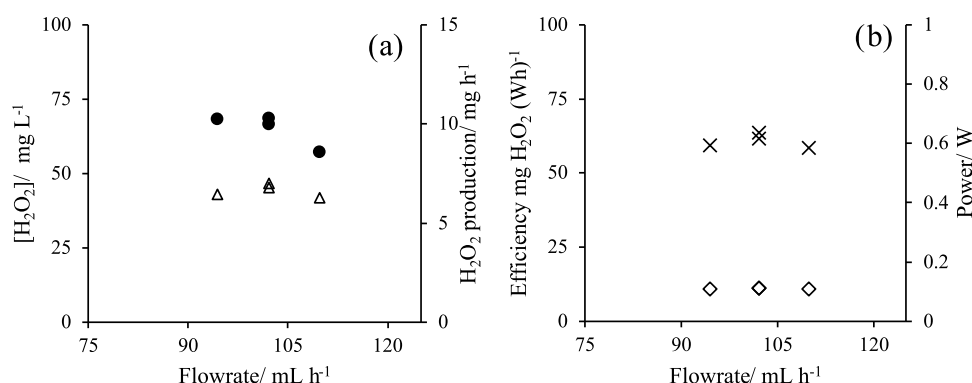


Figure 3. (a) H_2O_2 concentration (●) and H_2O_2 production (Δ) vs continuous flow rate (mL h⁻¹). (b) Efficiency (×) and power (◇) calculated for H_2O_2 production.

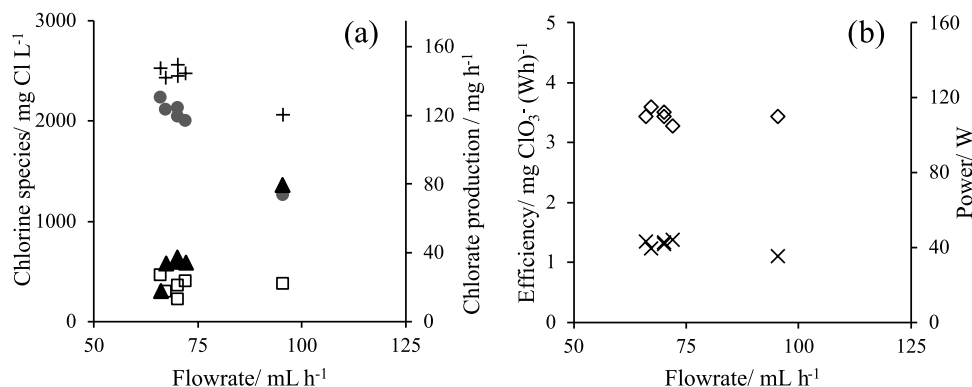


Figure 4. (a) Monitoring of chlorine species (mg Cl L⁻¹), where the chlorine species are hypochlorite (□), chlorate (gray circle solid), and chloride (▲). Chlorate production (+, mg h⁻¹) vs continuous flow rate (mL h⁻¹). (b) Efficiency (×) and power (◇) calculated for chlorate production.

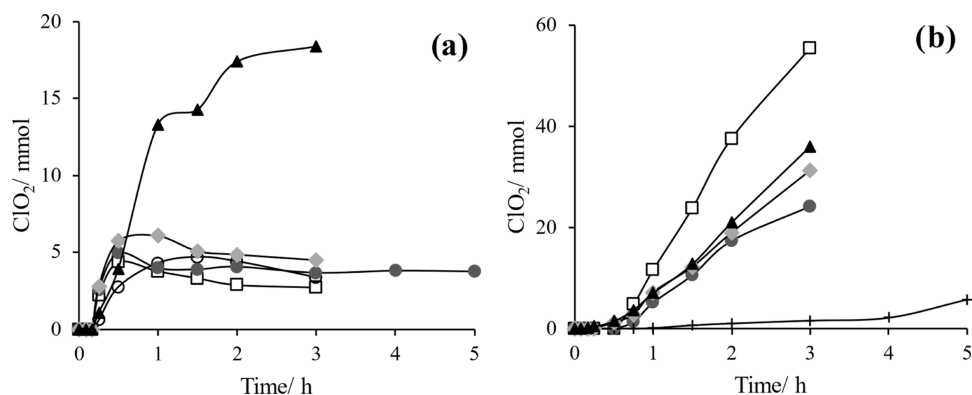


Figure 5. (a) Monitoring of the liquid chlorine dioxide produced (mmol) in the tank of reaction (tank 1) and (b) gas chlorine dioxide (mmol) diluted in the treatment tank with contaminated waste (tank 2). Conditions 1 (□), 2 (●), 3 (+), 4 (gray diamond solid), and 5 (▲) explained in Table 1.

production implies the integration of two electrochemical processes (production of chlorate and hydrogen peroxide) and one chemical step (reaction between both electrogenerated products). In previous works,^{60,63} it was shown how this process yields good results, especially with the use of tailored cells and suitable values of the key operational parameters. In this work, we start from the knowledge acquired in these previous works and design the tests to operate under conditions that were found to reach high efficiencies.

It should be noted that Figure 3 shows the effect of the variability of the flow rate on the production of hydrogen peroxide using electrochemical technology within the nearness of the design conditions selected in this work, in which a cell

with an electrode area of 9 cm² was used (100 mL h⁻¹) for the continuous production of H_2O_2 . As seen, results are stable and with a tiny cell and extremely low energy consumption, it is possible to obtain a liquid stream of hydrogen peroxide with an average concentration over 60 mg L⁻¹. Hence, as expected because of the dilution effect, the concentration of H_2O_2 decreases with the increase in the flow rate. This is not the case with the production that it is maintained in values higher than 6 mg h⁻¹ regardless of the flow rate fed to the cell (with Faradaic efficiencies around 22.9%). In those conditions, power consumed is as low as 0.1 W, and thus, outstanding energy efficiencies are reached, in the nearness of 60 mg (Wh)⁻¹.

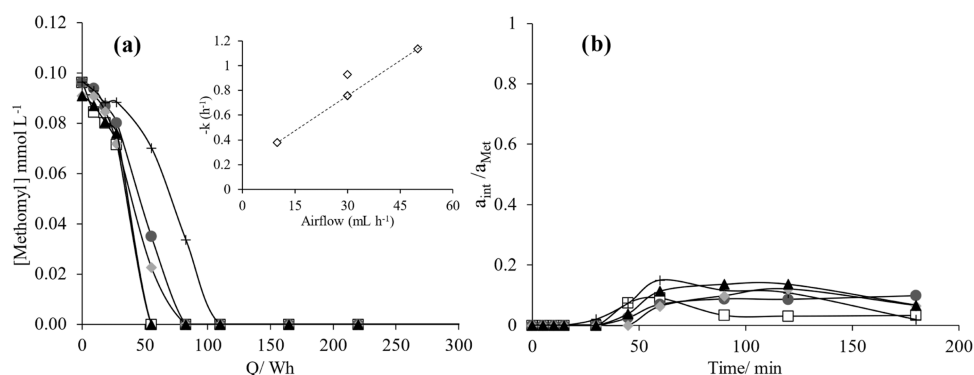


Figure 6. (a) Methomyl concentration decay (C_0 : 0.1 mmol L⁻¹, V_i : 500 mL) due to the ClO₂ reaction under different conditions. *Inset*: The calculated constant rate vs airflow (mL h⁻¹). (b) Chromatogram area of the sum of intermediates during the oxidation of methomyl using ClO₂ produced. Conditions 1 (□), 2 (●), 3 (+), 4 (gray diamond solid), and 5 (▲) explained in Table 1. $a_{\text{int}}/a_{\text{Met}}$ is the area of intermediates divided by the area of Methomyl.

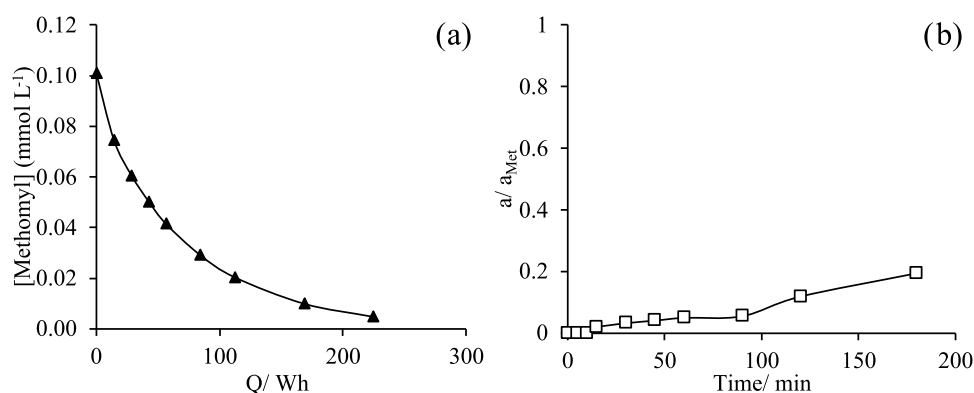


Figure 7. (a) Electrochemical removal of methomyl with the MMO (RuO₂/Ti) anode (▲), using 0.1 mmol L⁻¹ methomyl. (b) Chromatogram area of the sum of intermediates (□) formed during the electrochemical oxidation reaction of methomyl using the MMO (RuO₂/Ti) anode. The supporting electrolyte was 0.05 mol L⁻¹ Na₂SO₄, $j = 79.5 \text{ mA cm}^{-2}$, and V_i of 500 mL.

Figure 4 focuses on the continuous production of chlorate (in this case, at different flow rates in the nearness of 75 mL h⁻¹, which was chosen as the design flow rate for an electrode surface area of 78.5 cm²), and it also shows the key parameters to understand this electrochemical process. A mixture of chlorine oxoanions is produced during the process, although in this case the effect of the flow rate is more relevant, and the higher the flow rate, the lower the concentration of chlorate in the resulting stream (same effect of that shown for hydrogen peroxide, although in this case is more clearly observed). Productions decrease with the flow rate, and values over 120 mg h⁻¹ are obtained with power consumptions in the nearness of 110 W and energy efficiencies over 1.10 mg chlorate (Wh)⁻¹, values much higher than those required by hydrogen peroxide production, making the energy required in that process negligible.

Finally, the mixture of streams containing both species (in a strongly acidic perchlorate solution) yields chlorine dioxide both in the liquid and, especially, in a gas stream, as shown in Figure 5. Amounts of produced chloride dioxide largely depend on the dosing between electrochemically manufactured products and the airflow rate used to strip chlorine dioxide from the solution in which it is formed. The most significant parameter is the airflow rate, which informs about the rapid degradation of the chlorine dioxide in the liquid reaction media where it is produced, and of the necessity of exhausting it rapidly after being formed, especially if an efficient process is

looked for. Hence, the most important parameter is not an electrochemical parameter but the flow rate of stripping air used that prevents decomposition of chlorine dioxide in the reaction tank where it is produced.

This gas containing ClO₂ is flowed into synthetic wastewater polluted with methomyl. As seen in Figure 6a, the ClO₂ stream rapidly produced a decay in the concentration of the pollutant, with a rate that is strongly dependent on the flow rate of gas flows (as shown in the onset). Chlorine dioxide is a very good oxidant of organic matter and, opposite to chlorine and hypochlorite, it does not produce chlorinated organic intermediates because the main process responsible for the formation of these species is prevented, as the chlorine addition reaction to the double bonds of organics does not happen with this oxidant as previously reported elsewhere.⁶⁴ Results are plotted versus the energy applied for a later comparison that will be made with a direct electrolytic process (although as the production's power is kept constant during the experiments, this trend is the same as that obtained concerning time). As seen in Figure 6a, energy consumption as low as 50 Wh allows for the total removal in the most efficient conditions, and in the worse conditions, the energy consumption is below 100 Wh. An intermediate is formed during the treatment (Figure 6b) and, as expected, it is rapidly depleted in the conditions in which more chlorine dioxide is added to the reactor. Hence, chlorine dioxide produced electrochemically can be used to degrade efficiently the

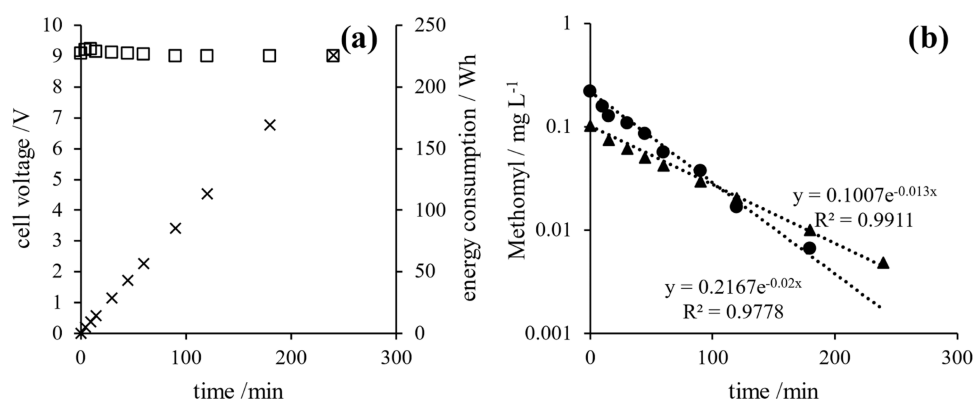


Figure 8. (a) Voltage (V, \square) and energy consumption (Wh, \times) of the electrochemical oxidation process using MMO (RuO_2/Ti) anode ($I = 6.24$ A). (b) Electrochemical removal of methomyl with MMO (RuO_2/Ti) anode, using 0.2 and 0.1 mmol L^{-1} methomyl represented by (\bullet) and (\blacktriangle), respectively. The supporting electrolyte was 0.05 mol L^{-1} Na_2SO_4 , $j = 79.5$ mA cm^{-2} , and $V_i = 500$ mL.

methomyl contained in diluted solutions. TOC was measured for all samples, but no significant changes were observed and, in fact, the small changes detected could be associated with measurement errors rather than with real variations in this globalized parameter. This does not mean that no mineralization was obtained because it may be related to the complexity of the compounds contained in the commercial mixture used and hence their different impact on the TOC value (many different compounds for which the ratio $\text{TOC}_{\text{measured}}/\text{TOC}_{\text{theoretical}}$ is not 1, because of the inefficiencies in the oxidation made by the TOC analyzer).

3.2. Degradation of Methomyl by the Direct Electrochemical Process. Using the same type of anodes that were used to produce chlorate (which was observed to be the bottleneck of the complete process), the electrolysis of the same methomyl solution, evaluated in this work as synthetic waste, was made. Typical operation conditions for this type of treatment were applied with a current density of 79.5 mA cm^{-2} and room temperature. The main results are summarized in Figure 7, where the decay in the concentration of methomyl and the total concentration of intermediates are shown in terms of energy consumption.

As seen, the decay is much less efficient in terms of energy, and more than 4 times more energy is required to complete the degradation of the methomyl solution as compared to the tests in which chlorine dioxide produced electrochemically is used as an oxidant (200 vs 50–100 Wh, respectively). However, it can be confirmed that anodic oxidation can also completely deplete methomyl from the liquid solution. Opposite to what was obtained when bubbling chlorine dioxide in the synthetic solution, the intermediates detected in those tests did not behave as intermediates here but as a final product, although it was produced in the same range of concentrations that reached in the mediated oxidation tests, pointing out again the lower efficiency of the direct electrochemical process.

Figure 8b compares the effect of the initial concentration in a semilogarithmic plot, where it can be seen that the process fits well to a first-order kinetic and that the first-order decay constant depends on the initial concentration as reported in the literature,^{65,66} pointing out the inefficiency in the application of anodic oxidation processes when treating diluted waste. A negligible effect was observed in the resulting cell voltage and energy applied to the system (Figure 8a), confirming that the efficiency of direct anodic oxidation processes increases linearly with the concentration. Thus, in

this case, the energy efficiency of treating a solution with a concentration of 0.2 mg L^{-1} is 0.60 mg (kW h)^{-1} , while in treating a solution with an initial concentration of 0.1 mg L^{-1} the efficiency decreases down to 0.268 mg (kW h)^{-1} , both values much below the typically reported in studies in which concentrations are much higher.^{67,68} Also, Coulombic efficiencies considering an exchange of 26 electrons (nitrogen and sulfur as final products in the oxidation) lead to values of 1.81 and 0.78%, respectively, for the degradation of the solutions containing 0.2 and 0.1 mg L^{-1} , values which can be explained in terms of the dilution, as the kinetics of the oxidation processes typically fits to a pseudo-first-order kinetics.

These results confirm the good prospects of the mediated electrochemical technology proposed for the treatment of dilute solutions and that they can become a real alternative to anodic oxidation, being less sensitive to the effect of dilution than the commonly evaluated direct electrochemical processes.

4. CONCLUSIONS

From this work, the following conclusions can be drawn:

- Methomyl can be removed electrochemically either in direct processes or from electrochemically produced chlorine dioxide. Direct removal fits well to a first-order kinetic model, but decay kinetic constants depend on the initial concentration of methomyl in the wastes.
- Chlorine dioxide can be produced from the mixture of chlorate and hydrogen peroxide streams produced electrochemically in continuous mode. The airflow rate used to strip chlorine dioxide was found to be a very important parameter in reaching high efficiencies.
- The efficiency of the anodic oxidation of methomyl solutions depends almost linearly on the initial concentration of pollutants in the treated wastewater. Chlorine dioxide gaseous oxidants mediated electrochemical technologies (GOMET) are more efficient than anodic oxidation for the remediation of diluted wastewater. It is possible to degrade methomyl with the same anode material and concentration in the synthetic wastewater with 4 times less energy. This indicates that the development of GOMETs is a topic worthy of further research.

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L.M.d.S.: investigation, data curation, formal analysis, writing—original draft. I.F.M.: investigation, data curation, formal analysis, writing—original draft. C.S.: writing—review and editing. A.J.M.: writing—review and editing, funding acquisition, project administration, supervision, validation, writing—review and editing. M.A.R.: conceptualization, funding acquisition, project administration, supervision, validation, writing—review and editing.

Notes

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