



Remediation of soils contaminated with methomyl using electrochemically produced gaseous oxidants

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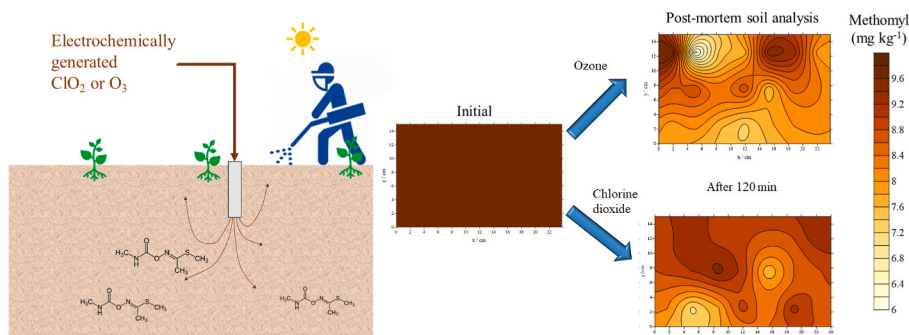
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HIGHLIGHTS

- High efficiencies in the electrochemical production of ozone and chlorine dioxide.
- Gaseous oxidants produced electrochemically suitable for soil treatment.
- Integrated soil washing with ClO_2 achieves complete removal of methomyl.
- Integrated soil washing with ozone results in low removals of methomyl.
- Outstanding performance in direct dosing of ClO_2 and O_3 through perforated pipes.

GRAPHICAL ABSTRACT



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ABSTRACT

This prospective work focuses on the use of two different gaseous oxidants (chlorine dioxide and ozone) to remediate soil polluted with methomyl in two different applications: *ex-situ* and *in-situ*. In the first, the soil washing is integrated with the bubbling of the oxidant, while in the second, the gas was introduced by a perforated pipe located sub-superficially. Regarding the soil washing treatment, results demonstrate that direct use of ozone is not very efficient, although an important improvement is obtained following activation with hydrogen peroxide or UV light. In contrast, chlorine dioxide exhibited complete methomyl depletion from the soil, although with higher energy consumption and technical complexity compared to ozone. The direct dosing of the gaseous oxidants in perforated pipes is effective, achieving methomyl removals of 7.8 % and 9.2 % using ozone and chlorine dioxide, respectively. In these cases, soil conditions are not significantly modified, which becomes an important advantage of the technology as compared with other electrochemically assisted soil remediation process, in which large regions of the treated soil are affected by important changes in the pH or by depletion of ions. This lower impact makes these novel technologies more promising for further evaluations.

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1. Introduction

The removal of pollutants contained in soil in an efficient and sustainable way is one of the challenges that must be faced. Among pollutants, pesticides pose a global problem, due to their necessity in agriculture. Methomyl (S-methyl N-[(methylcarbamoyl)oxy]thioacetimidate) is a highly toxic and hazardous carbamate insecticide (Hayat et al., 2021), that can produce hepatotoxicity, cytotoxicity, and neurotoxicity in animals (Lin et al., 2020), being its use forbidden in Europe. Although methomyl removal in water has been widely studied (Fan et al., 2013; Oller et al., 2007; Tomašević et al., 2010), its removal from soil has been poorly rated. This fact encourages researchers for investigating alternative ways to attack pollutants. For soil treatment polluted with methomyl, different physicochemical and microbial degradation methods have been studied (Lin et al., 2020). Electrochemical technologies are demonstrating important advantages as compared to other technologies in the remediation of polluted soil and wastewater, such as soil washing, bioremediation or thermal desorption (Dionisio et al., 2019; Malpass et al., 2006; Muñoz-Morales et al., 2019; Pointer Malpass and de Jesus Motheo, 2021; Silva et al., 2021). However, many of the studies found in the literature lack novelty, as they often reiterate the same technologies, with only minor variations focusing on nuances in performance or application. Thus, it is important to find new technological approaches that encourages companies for the development of real applications.

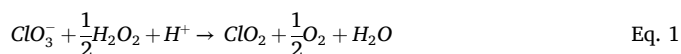
The production of oxidants is one of the most significant topics of research within the electrochemical technology field (de Mello et al., 2022; Dionisio et al., 2019; Escalona-Durán et al., 2020; Li et al., 2019; Sales Monteiro et al., 2022a). In addition to the large number of processes that are being exploited at the full-scale level (among which the chloralkaline industry outstands), there are many other interesting processes whose performance has been evaluated during recent years. Although peroxyanions are among the most interesting oxidants (Rodríguez-Peña et al., 2022b), recently, the production and use of two gaseous oxidants has been proposed as extremely promising: chlorine dioxide and ozone.

The main difference as compared to other oxidants is that both compounds (ClO_2 and O_3) are gases and can be dosed to liquid and solid medium by flowing the gaseous streams in which they are contained. Problems associated with solubility of the oxidants in water can be a disadvantage to be overcome; however, readability for use in different locations is a notable advantage, worth to be explored.

The use of PEM electrolyzers for ozone production (Rodríguez-Peña et al., 2021a; Rodríguez-Peña et al., 2022a) has been demonstrated to be a relevant innovation that helps to obtain extremely high efficiencies. These efficiencies are associated with the use of divided cells with enhanced fluid dynamics and tailored formulations for the anolyte and catholyte that avoids the effect of scavengers (Özdemir and Taymaz, 2022). In addition, PEM electrolyzers can operate with solutions of very low conductivity (Pushkarev et al., 2016), due to the membrane can act as a solid electrolyte, avoiding high ohmic losses (Isidro et al., 2020; Rodríguez-Peña et al., 2021b). With this, the choice of electrode material is quite important, as it can allow the optimization of ozone production and avoid damage to the membrane. In this sense, boron-doped diamond (BDD) coatings have been settled as the most efficient electrodes for ozone production (Aricò et al., 2013; Cognard et al., 2017; Rodríguez-Peña et al., 2021a).

Opposite to ozone, chlorine dioxide is not produced in a single electrochemical step. ClO_2 is the result of the chemical combination of two electrochemically produced reagents: hydrogen peroxide and chlorate (Sales Monteiro et al., 2022b; 2021; Terhalle et al., 2018). Although there are other routes, ClO_2 can be produced by the reaction of sodium chlorate in a concentrated acidic solution with hydrogen peroxide (Equation (1)). However, this reduction also promotes the formation of chlorine, hypochlorous acid, and hypochlorite in high concentrations, besides the ClO_2 formed. The formation of these side

products can be avoided by optimizing the ratio of hydrogen peroxide to chlorate used to generate, mainly ClO_2 (Moratalla et al., 2022; Terhalle et al., 2018).



The main aim of this work is to evaluate the feasibility of using gaseous oxidants, which can be produced *in-situ* for real applications, in the treatment of soil polluted with methomyl. To do that, ozone and chlorine dioxide will be electrochemically generated by electrochemical cells designed and manufactured by a 3D printer. Both oxidants were bubbled to a soil washing solution and to perforated pipes treatments to remove methomyl from a spike soil in order to determine the best conditions for the treatment of methomyl in soils. Through these investigations, this study aims to contribute to the development of innovative and sustainable solutions for soil remediation challenges.

2. Materials and methods

2.1. Chemicals

Deionized water (Millipore Mili-Q system, resistivity 18.2 MΩ cm at 25 °C, TOC: 2 ppb) was used for electrolytic solutions. Ozone was produced directly using mQ water as electrolyte, however, chlorine dioxide was produced using sodium chloride, sodium perchlorate and perchloric acid (70%). For hydrogen peroxide identification, 1.9–2.1% of titanium (IV) oxysulfate solution (1.9–2.1%, CAS: 13825-74-6/Sigma-Aldrich) was used as indicator. Finally, oxidants concentration has been determined by a iodometric titration of potassium iodide with sodium thiosulfate (0.001 M).

2.2. Electrochemical generation of gaseous oxidants

Ozone was generated in a bicompartamental electrochemical PEM cell (designed and manufactured by 3-D printing) with two mesh electrodes of boron-doped diamond (BDD) (1.5 cm²). These electrodes were assembled to a Nafion® membrane (Membrane Electrode Assembly, MEA), that also act as separator for both compartments. A schematic illustration of the cell was presented in a previous work (da Silva et al., 2023a). In addition, the system comprises two recirculation pumps and two tanks, one for electrolyte circulation in the anodic compartment and the other for the cathodic compartment. The temperature in the electrolytic tanks was maintained by a thermal bath. A flowmeter equipped with a valve was used to control the oxygen gas entry into the anodic tank. A power supply was used to apply the required current density. The assembly is shown in Figure SM1. The generated gas was conducted and bubbled in a test tube containing a solution of KI and sulfuric acid for the measurement of generated oxidants. In the case of the soil washing and soil flushing treatments, the ozone was flowed directly to the treatment tank or to the subsurface of soil through a perforated pipe. ClO_2 generation is produced by mixing two flows of electrogenerated chlorate and hydrogen peroxide continuously in a tank containing an extremely acid medium (HClO_4 , 70%). The gaseous ClO_2 generated was conducted to the soil washing and soil flushing treatment in a similar way as ozone. The experimental devices are shown in the Supplementary Material Section (Figure SM2). For continuous chlorate generation, an electrochemical flow reactor (also designed in the lab and manufactured with a 3D printer) was used (Figure SM2a). This cell was equipped with an MMO (Ru) anode from Tioxide and a titanium cathode, both measuring 78.5 cm². A solution of NaCl (5 g L⁻¹) was used as electrolyte and operation conditions were current density of 150 mA cm⁻², 15 °C, and continuous flowrate of 62.5 mL h⁻¹. For hydrogen peroxide (H_2O_2) generation, an electrochemical gas diffusion cell printed on a 3D printer was used, using MMO (Ru) as the anode (10.9 cm²) and a painted carbon paper 10.9 cm² as the cathode (Figure SM2b). As electrolyte a solution of 14.05 g L⁻¹ of NaClO₄, acidified to pH 3.5, was

used. Operation conditions were current density of 4.6 mA cm^{-2} and continuous flowrate of 90 mL h^{-1} . Schematic illustrations of the cells were presented in a previous work (da Silva et al., 2023b).

2.3. Soil washing and in-situ soil treatments

The soil washing and in-situ (by flowing the oxidant throughout perforated pipes) treatments were carried out using samples of soil spiked with methomyl. For this purpose, a clay soil was spiked with a solution of methomyl with the objective to obtain a concentration of 10 mg of methomyl kg of soil $^{-1}$. Soil washing tests were carried out using by mixing soil and washing at different weight ratios soil/water ranging from 0.25 to $1.00 \text{ g soil g}^{-1}$ of water in a reactor of 500 mL . Then, the gaseous oxidants generated electrochemically were bubbled into the resulting solution for 180 min (Figure SM3a). Moreover, in the case of ozone, because of the refractory behavior observed in the previous tests, additional experiments were carried out looking for the activation of ozone with UV light (introducing a UV lamp of 5 V in the reactor) and H_2O_2 (in the same molar concentration of ozone production). Samples were collected, filtered, and analyzed to determine the methomyl concentration. All these experiments were carried out by triplicate. In-situ soil treatment was evaluated using a flat 3D mock-up simulating the first 15 cm of a soil. In the mock-up the addition of the gaseous species was sub superficially, using a perforated pipe in a depth of 13 cm regarding the surface of the polluted soil (Figure SM3b). Then, the polluted soil was introduced and compacted in the mock-up (around 3000 g of polluted soil). After a first stabilization of the gaseous production, the experiment started when the gaseous oxidants were introduced to the perforated pipe continuously during 120 min . For the postmortem characterization, the mock-up was divided into 21 portions (3 rows, 7 columns) to obtain a 2D surface graph of the methomyl concentration. Portions are weighted and treated to extract methomyl for analysis, mixing 10 g of soil with 20 mL of water and stirring during 24 h . After that, samples were filtered and analyzed.

2.4. Analytical techniques

Methomyl concentration was measured using high-performance liquid chromatography (HPLC), using an Elipse Plus C18 column from Agilent, with a flowrate of 0.3 mL min^{-1} of a mobile phase of acetonitrile: water (20:80, v/v), 25°C , an injection volume of $20 \mu\text{L}$ and $\lambda = 233 \text{ nm}$. The ion chromatography analysis was carried out for the monitoring of ClO_3^- , Cl^- and ClO_4^- , using a Metrohm 930 Compact IC Flex (Madrid, Spain) coupled to a conductivity detector, with a flowrate of 0.8 mL min^{-1} of mobile phase composed of $85:15 \text{ v/v}$ 3.6 mmol L^{-1} Na_2CO_3 /Acetone solution and a Metrosep A. Supp 7 column. The temperature of the oven was 40°C and the injection volume was $20.0 \mu\text{L}$. Hypochlorite was monitored using an automatic titrator with an As^{3+} solution. The H_2O_2 was determined by UV-VIS spectrophotometer (410 nm), using 0.5 mL of sample, 0.5 mL of Titanium (IV) oxysulfate solution ($1.9\text{--}2.1 \%$, Sigma Aldrich), and 4.5 mL of water, based on the methodology developed by (Eisenberg, 1943) and modified elsewhere (Cordeiro-Junior et al., 2022). The chlorine dioxide (ClO_2) in the liquid phase was monitored by spectrophotometry using a Spectroquant® Prove 300 from Merck KGaA, D-64293 Darmstadt, with wavelength absorbance in 360 nm . The calibration curve of standard ClO_2 was based on previous work reported elsewhere (Monteiro et al., 2021). Then, 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 iodide, producing its transformation into iodine. In this last case, the iodine solution was titrated with sodium thiosulphate for oxidant quantification. For determination of O_3 , the ozone gas was bubbled into 5 mL of $30 \times 10^{-3} \text{ mol L}^{-1}$ of KI, and 2.5 mL of H_2SO_4 20% during 3 min , for further oxidant quantification with sodium thiosulphate.

3. Results and discussion

3.1. Use of electrogenerated ozone

Fig. 1 shows the rate of electrochemical production of ozone, obtained by electrolysis of Mili-Q water, in which it can be seen that it increases rapidly up to a steady state of nearly $0.534 \text{ mg min}^{-1}$, which means a current efficiency of 35.8% and an energy efficiency of $6.21 \text{ mg (Wh)}^{-1}$, which are outstanding values as compared to others reported in the literature (Mena et al., 2023; Rodríguez-Peña et al., 2021), and that are explained not only because of the PEM type of cell used, but also because of the good hydrodynamic of the 3-D printed cell used. The steady-state flow rate was almost constant with time, and this stream was applied directly (as it was produced) in the series of soil treatment tests made in this work.

Regarding the use of ozone to improve results of the soil washing treatment, it can be seen in Fig. 2 that when the gaseous stream produced electrochemically is bubbled into the mixture soil-water, the treatment does not seem to be very efficient (Fig. 2a), regardless of the ratio soil/water used in the washing treatment. The same occurs when only hydrogen peroxide is added to the soil washing process (Fig. 2b) or when it undergoes only UV irradiation (Fig. 2c). These results confirm the refractory character of methomyl regarding ozone and hydrogen peroxide oxidation or UV irradiation, because the ratio between ozone/hydrogen peroxide and methomyl is very high as compared to the stoichiometric one (for example, between 77 and $200 \text{ mmol O}_3/\text{mmol}$ methomyl) and the concentration of oxidant, it is not limiting the process. However, efficiency increases importantly when the processes are combined, especially in the case of the combination ozone-hydrogen peroxide (peroxone), suggesting that the activation of radical mechanisms may help to explain the improvement observed, confirming that soil washing can be combined with this mediated electrochemical process successfully.

Once verified that ozone attacks the methomyl formed in the liquid phase during soil washing treatment (although efficiency is importantly improved with hydrogen peroxide) a step further is to verify its use *in-situ*. Previous work based on the use of ozone for in-situ remediation have been studied efficiently (Clayton et al., 2011; Karpenko et al., 2009; Ranc et al., 2016), being more effective in soil presenting iron compounds whereas organic matter act as finite ozone consumer (Zucker et al., 2021). Three tests were carried out, and the results are shown in Fig. 3. Thus, when ozone is applied to the soil throughout a perforated pipe, it seems that the methomyl starts to be removed and

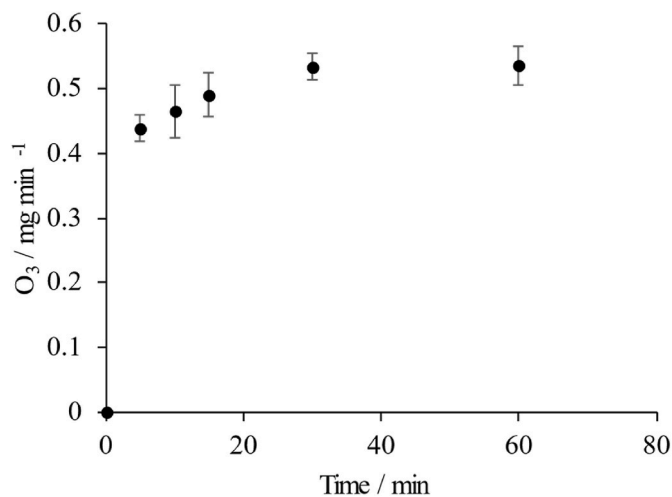


Fig. 1. Production of ozone (mg min^{-1}) in the gaseous phase. Using a current density of 200 mA cm^{-2} , 15°C , O_2 flow of 20 mL h^{-1} , and Mili-Q water as solution.

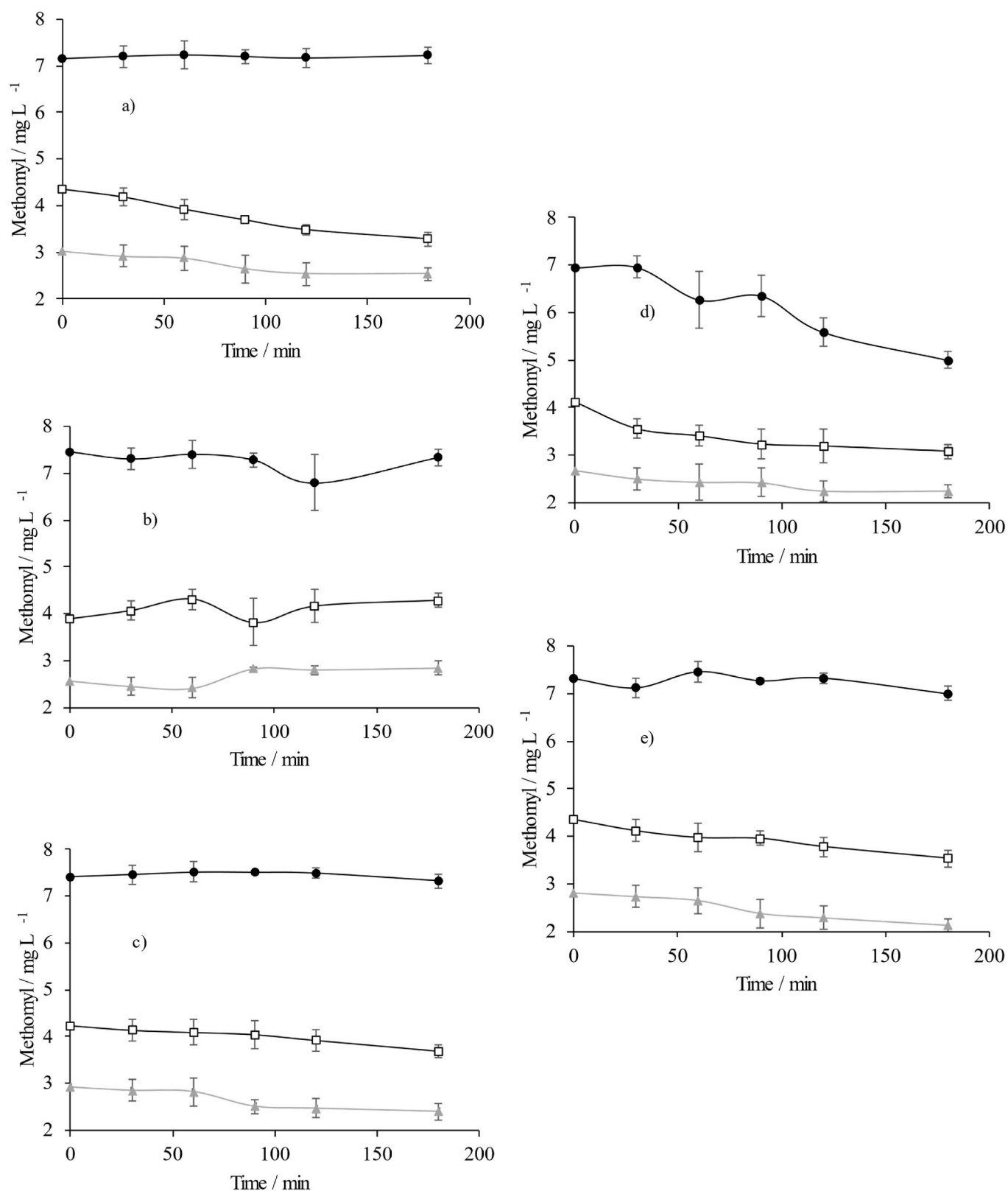


Fig. 2. Soil washing treatment for Methomyl removal by a) electrogenerated ozone, b) hydrogen peroxide, c) UV light in liquid, d) electrogenerated ozone activated by hydrogen peroxide and, e) electrogenerated ozone activated by UV light in liquid. Soil washing at different proportions of soil/water (black circles: 1 g soil g⁻¹ of water, white squares: 0.5 g soil g⁻¹ of water, gray triangles: 0.33 g soil g⁻¹ of water). Ozone cell conditions: 0.3 A, 15 °C, Milli-Q water as the solution.

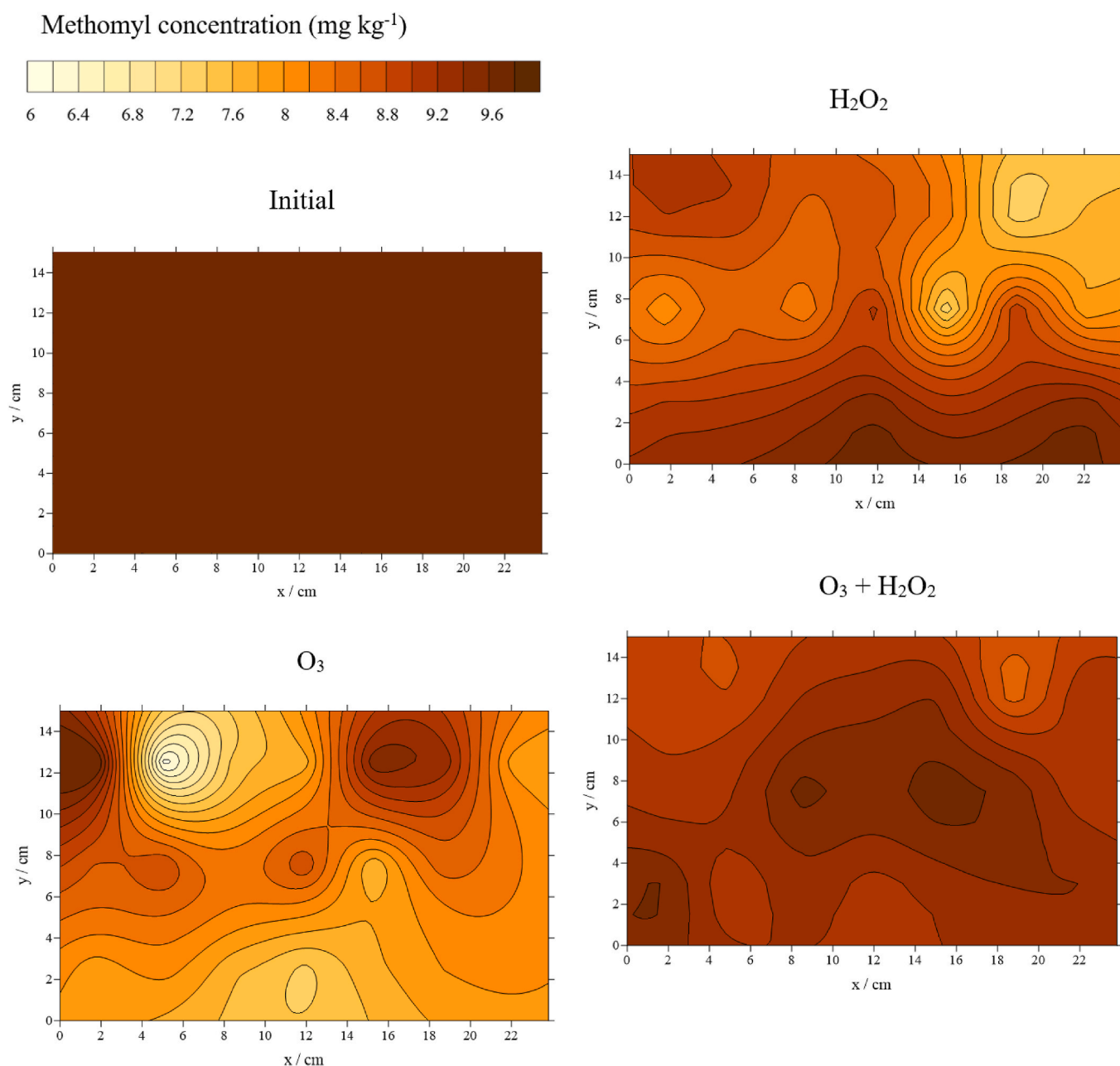


Fig. 3. Removal of methomyl from in-situ treatment with ozone, hydrogen peroxide, and ozone combined with hydrogen peroxide. The initial concentration of methomyl was 9.6 mg kg^{-1} of dry soil. Ozone cell conditions: 0.3 A, 15°C , Milli-Q water as the solution.

after passing 64.1 mg O_3 , just 7.79% of the total methomyl contained in the soil was removed. Total methomyl removal was determined by comparing the initial amount of methomyl (knowing the concentration and the total amount of soil) and the final amount retained in the soil (the summatory of the concentration of each portion taking into account the weight of soil on each portion). Removal takes place mainly near the perforated pipe (which is placed in the y coordinate 2 cm).

In this case, the UV cannot be effectively irradiated, but hydrogen peroxide (molar ratio 1:1 with respect to ozone dosed) has been added at the upper surface of the soil (to allow it to percolate through the soil). The reaction between hydrogen peroxide and ozone can produce peroxone, one of the most aggressive oxidants in dark AOPs (Osgerby, 2006). The removal, in this case, is higher in the zone in which the oxidants are added (ozone at the bottom and hydrogen peroxide at the top). However, the combination of both fluxes does not show the same improvement in performance seen during soil washing. In fact, worse

results are observed as compared to bare ozonation. This worse performance can be explained in terms of the less efficient effect of the radical mechanism in stagnant soil as compared to a liquid mixture. In fact, the peroxone produced with this combination can be wasted in soil because of the lower availability of methomyl to be destroyed. It is important to take in mind that most of the hydrogen peroxide and ozone reacts in the place where they are added, and only the surplus oxidants can reach an intermediate position where peroxone can be activated. In fact, in this case the removal of methomyl was 2.53 % when adding only hydrogen peroxide and, in the case of combining both technologies, it stabilized at an intermediate value of 3.14%, indicating that in this case there is not an improvement as important as that obtained in the soil washing process.

As seen in Figure SM4 the profiles of water content are not altered by the addition of any of the reagents, except that the addition of hydrogen peroxide (as a solution) leads to a higher water content than the system

in which only ozone is added. As well, no relevant impacts are seen on the pH and conductivity of soil for the treatment applied, as shown in Figure SM5. This fact is important because the application of electrokinetic technology modifies importantly the profiles of all these parameters and the low changes detected in this case are promising in terms of going further with this new technology approach: it achieves the removal of organics but does not affect to the quality of soil treated, at least with the same impact of other electrochemical technologies.

3.2. Use of electrogenerated chlorine dioxide

Fig. 4 shows the stabilization in the continuous electrochemical production of chlorate (Fig. 4a) and hydrogen peroxide (Fig. 4b) when applying, in their respective electrolytic productions, current densities of 150 and 4.6 mA cm⁻². It also shows the resulting chlorine dioxide production rate when both electrochemically generated products are mixed in a ratio 62.5 mL h⁻¹ ClO₃⁻/90 mL h⁻¹ H₂O₂, as a function of the air flowrate used to strip chlorine dioxide (Fig. 4c). As seen, the production of chlorine dioxide is primarily influenced by the stripping flow

rate of air used. Part d shows that once stabilized (in a very short period) the production is kept for long application times (with fluctuations associated to the combination of three processes that points out the complexity of the system). A first series of tests demonstrated that in operating at low air flowrates (with chlorine dioxide productions within the same range of those used for ozone, 0.74 mmol h⁻¹), the treatments (soil washing and flowing gas through pipes) were found to be inefficient and thus, a higher stripping air flowrate was used to reach a production of 15 mmol h⁻¹ (no changes in the electrochemical parameters meaning that no relevant extra cost are needed, but just optimization of process conditions), which is kept in the two series of tests carried out in this work. In this lab-scale oxidant production system, the power applied is 105 W, pointing out an energy efficiency of 0.286 mmol (Wh)⁻¹. This gaseous stream used in the different tests was found to be very stable.

Thus, when this stream is bubbled into a soil-washing process, methomyl decreases rapidly down to 0, as seen in Fig. 5a, while the concentration of oxidants increases important after depleting this organic pollutant. Similar results were previously obtained in the degradation of methomyl in water (da Silva et al., 2023b, 2023c), with a

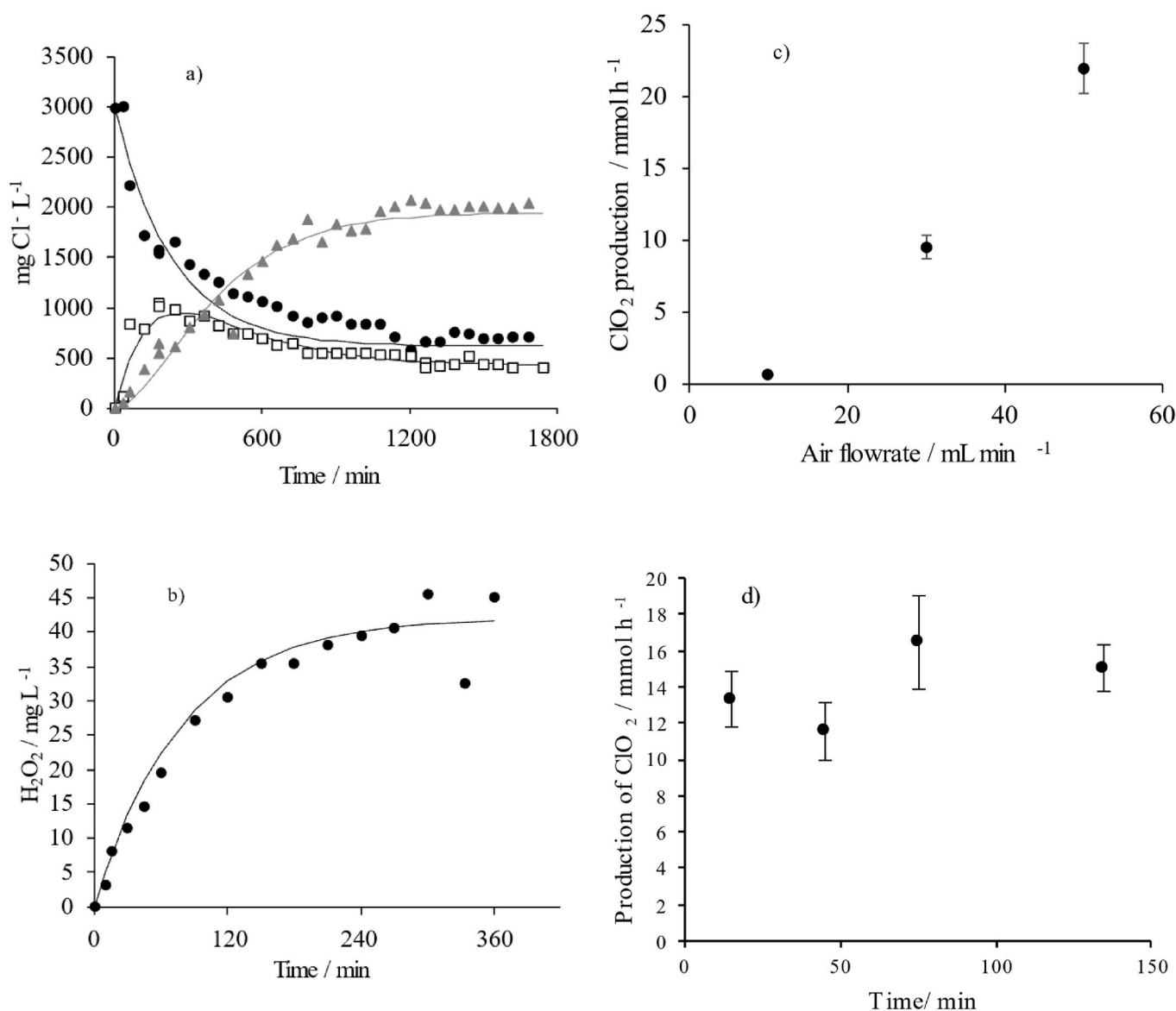


Fig. 4. a) Chlorine species evolution (circles: chloride; squares: hypochlorite; triangles: chlorate) in continuous mode (95.3 mL h⁻¹, 11.7 A, 1.8 L, and 5000 mg L⁻¹ of NaCl of initial electrolyte), b) hydrogen peroxide generation in continuous mode (197 mL h⁻¹, 0.05 A, 0.5 L, 14050 mg L⁻¹ NaClO₄ of initial electrolyte). Lines: theoretical concentrations using a phenomenological model. Production of chlorine dioxide gas (mmol h⁻¹) as a function of airflow rate (c) and time (d).

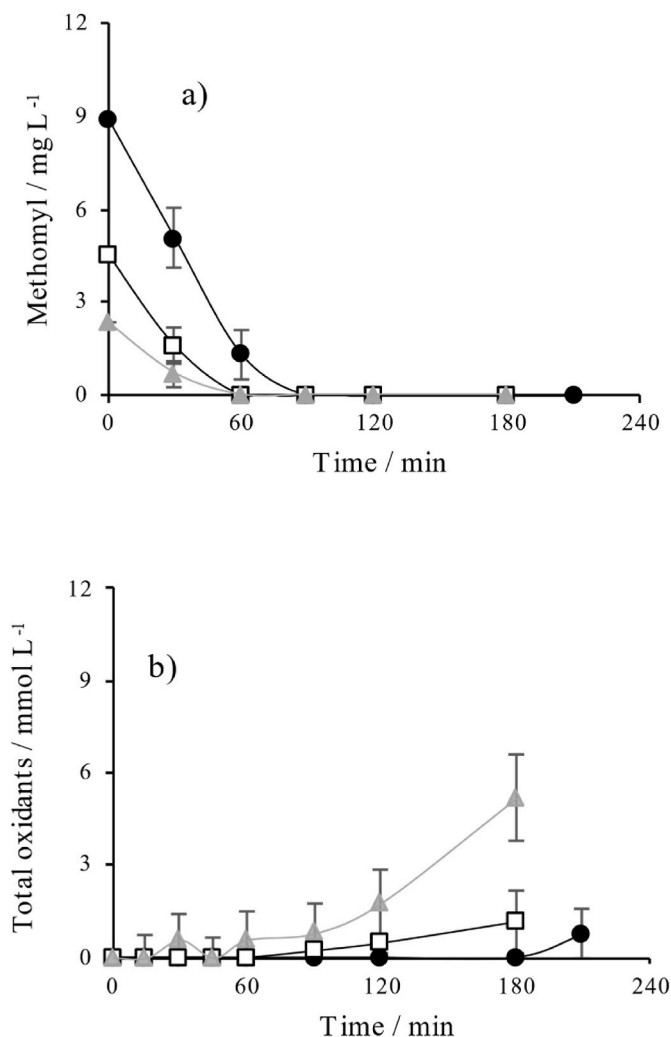


Fig. 5. a) Methomyl removal by the generated ClO_2 at different proportions of soil/water and b) total oxidant concentration measured in the reaction medium (circles: ratio 1 g soil g⁻¹ of water, squares: ratio 0.5 g soil g⁻¹ of water; triangles: ratio 0.25 g soil g⁻¹ of water). The generation conditions of ClO_2 : 100 mL of HClO_4 (70%); Airflow: 30 mL min⁻¹; $[\text{H}_2\text{O}_2] = 28.9 \text{ mg L}^{-1}$; $[\text{ClO}_3^-] = 5022 \text{ mg L}^{-1}$; initial volume: 500 mL.

high decay in the concentration of methomyl when the solution was put in contact with ClO_2 . In this case, the ratios chlorine dioxide/methomyl were even higher than those used in the ozonation tests, because of the unexpected effect of the air stripping flow rate (ranged between 1200 and 3521 mmol chlorine dioxide/mmol methomyl). Efficiencies in the use of chlorine dioxide depend on the initial concentration of methomyl and for the most concentrated solution in methomyl (ratio soil: washing fluid of 1 g soil g⁻¹ of water), the efficiency is $0.026 \text{ g (kWh)}^{-1}$, a value that despite being low is important, because it confirms that this mediated electrochemical production of oxidants can be successfully used to remove species at very low concentrations. In addition, this fact opens the possibility of applying this technology to remediate wastewater/soil contaminated with persistent pollutants.

Comparing the efficiencies of ozone and chlorine dioxide oxidation (Fig. 6), it can be seen that chlorine dioxide is the less efficient oxidant. Larger concentrations needed to be applied to reach a similar efficiency to that obtained by ozone.

Likewise, when chlorine dioxide is dosed to soil (Fig. 7), a final removal of 9.2% is observed after 120 min of application of the gaseous stream. This removal is more important in the bottom zone, just in the place where the perforated pipe is flowing the chlorine dioxide, as can

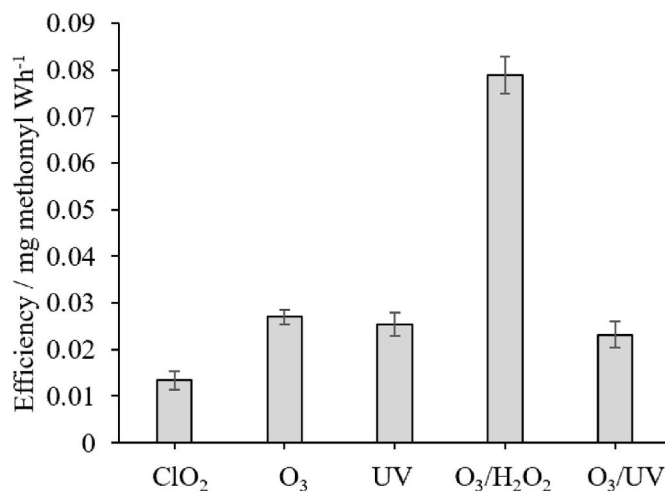


Fig. 6. Energy efficiency of methomyl removal by different technologies at 30 min, with a washing ratio of $0.5 \text{ g soil g}^{-1}$ of water.

be seen in the sequence of maps shown in Fig. 7. Worth to take in mind that they correspond to different mock-ups which underwent to the same treatment and in exactly the same conditions for different reaction times.

In Supplementary Material (Figure SM6) some additional information about the treatment is presented, where it can be observed that there are no changes in the water content, pH, and conductivity during the treatment, which as discussed for the use of ozone, becomes an interesting novelty as compared to electro-kinetic treatments, in which important variations occur in all these parameters. This means that this technologies result in lower impacts in the soil while they can successfully degrade the organic pollutants contained.

Although low removal of methomyl was obtained on in-situ experiments with both oxidants, the results obtained are very promising. On one hand, the methomyl can be completely removed from water, and on the other hand, methomyl removal can be improved with the addition of a high dose of oxidants.

4. Conclusions

In this work, the use of ozone and chlorine dioxide produced electrochemically for the removal of pollutants contained in soil is evaluated, either through direct in-situ application via a perforated pipe or through ex-situ soil washing processes, wherein the oxidant streams are bubbled into the soil-liquid mixture. The following conclusions can be drawn:

- Both ozone and chlorine dioxide gaseous streams can be produced using electrochemical processes and they can be applied directly in ex-situ (soil washing) or in-situ (dosing from pipes) soil remediation processes, preventing problems associated to electrokinetic and electrochemically assisted soil remediation processes, such as the depletion of ions or the acidification and basification of portions of soil.
- Soil washing using only ozone is not very efficient to remove methomyl, although removals may be significantly improved by activating the ozone with UV light or, especially, with hydrogen peroxide where peroxone can be responsible of the enhancement observed. Peroxone combination is not as effective in the case of the in-situ application, where the ozone is dosed from a perforated pipe, because the reagents are spent before they may be combined and activated. UV combination is not possible in in-situ treatments.
- Chlorine dioxide can destroy methomyl in both, in-situ and ex-situ soil remediation treatments, being able to deplete methomyl when

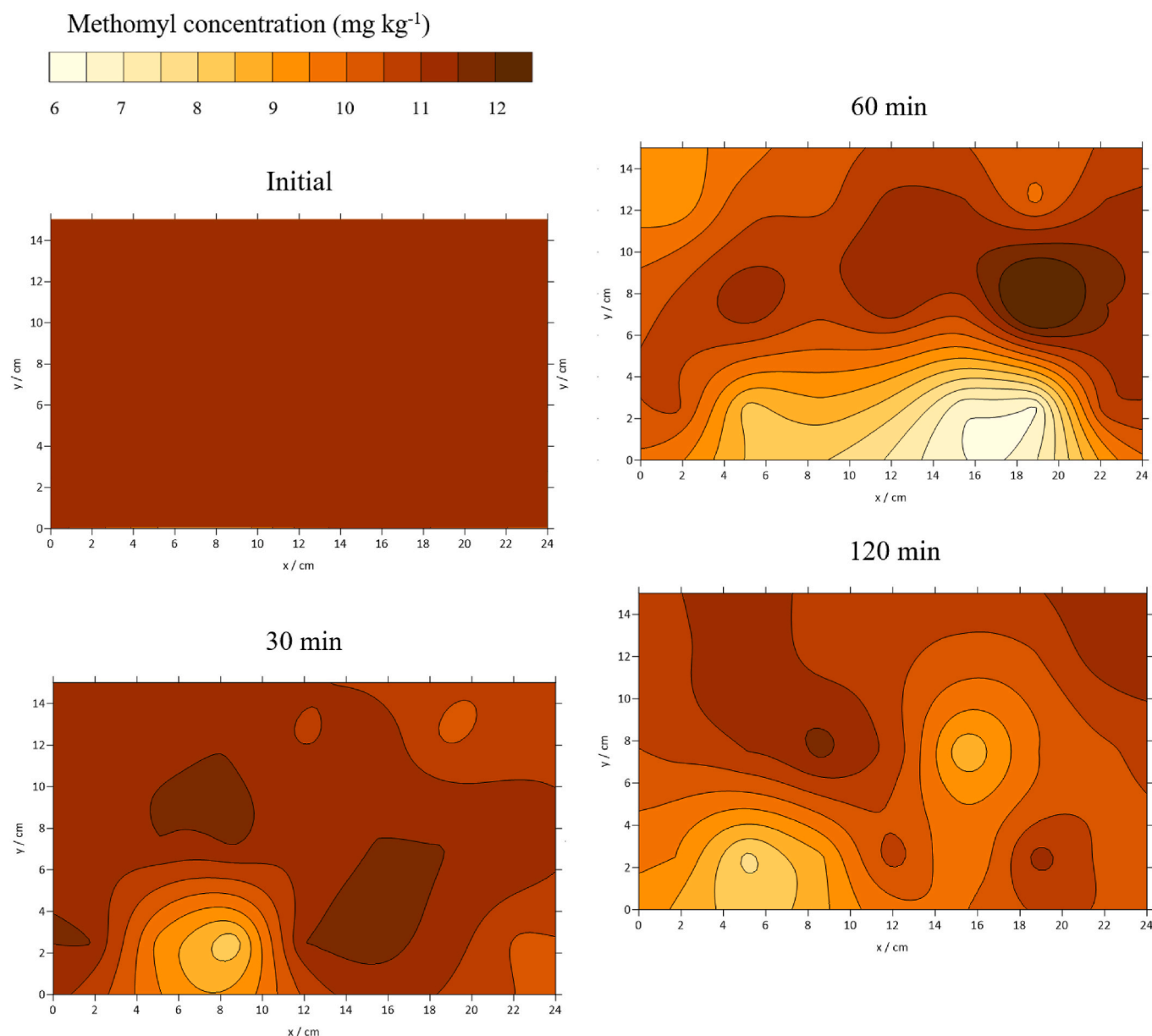


Fig. 7. Removal of methomyl from in-situ treatment with chlorine dioxide by a perforated pipe. The average concentration of methomyl from the beginning was 11.3 mg kg⁻¹ of dry soil. ClO₂ conditions (15 mmol h⁻¹): Airflow: 30 mL min⁻¹; [H₂O₂] = 2 mg h⁻¹; [ClO₃⁻] = 904 mg h⁻¹.

large doses are applied. From the energy point of view, this reagent is less efficient than ozone and from the technical point of view its production requires of the combination of two electrochemical and one chemical process, highlighting a much higher complexity in which many parameters should be accounted (as the air dragging flowrate). However, it does not require any type of activation and destruction of pollutant is complete.

Some important issues deserving more attention in future research in this field are the evaluation in the use of a higher doses of oxidant to achieve complete removal of methomyl, a study of the degradation pathway to determine the intermediates formed and the risk evaluation of the treatment, as well as the real matrix influence in the efficiency of the treatment.

CRediT authorship contribution statement

Leticia Mirella da Silva: Writing – original draft, Investigation,

Formal analysis, Data curation. **Ismael F. Mena:** Writing – original draft, Investigation, Formal analysis, Data curation. **Cristina Sáez:** Writing – review & editing. **Artur J. Motheo:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition. **Manuel A. Rodrigo:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2024.142653>.

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