Electrochemical disinfection of groundwater for civil use — An example of an effective endogenous advanced oxidation process

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HIGHLIGHTS

• Groundwater was electrolyzed in a CabECO® reactor in batch and continuous mode.
• A CabECO® reactor equipped with BDD electrode allows effective disinfection.
• Disinfection is due to the concomitant production of ozone and free chlorine.
• Chlorate and perchlorate formation can be controlled by process parameters.
• Results show the potential application of the CabEco® reactor in disinfection.

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ABSTRACT

Lab-scale experiments using real groundwater were carried out using the CabECO® reactor system in order to evaluate its suitability for producing safe water, acceptable for civil purposes. Trials were carried out in discontinuous and in continuous mode, analyzing the influence of electrical and hydraulic process parameters on the quality of treated water. The use of highly boron-doped diamond electrodes in the reactor allowed the electrosynthesis of considerable amounts of ozone. Because of the relatively high amount of chloride in the groundwater samples, a mixture of HOCl/ClO2 was also synthesized. Somewhat unexpectedly, the increase in the current density in the explored range 100–1000 A m−2 was accompanied by an increase in the faradic yield of the electrosynthesis of oxidants, which was more pronounced for ozone than for free chlorine. As reported in literature, the main radical intermediate in the relevant reactions is ·OH, which can lead to different oxidation products, namely ozone and HOCl/ClO2. The electrolytic treatment also caused a decrease in the concentration of minor components, including NH4+ and Br−. Other byproducts were ClO3− and ClO4−, although their concentration levels were low. Moreover, due to alkali formation at the cathode surface, the precipitation of calcium and magnesium carbonates was also observed.

In addition, the experimental investigation showed that even Pseudomonas aeruginosa and Legionella could be completely removed in the treated stream, due to the unique capacity of the reactor to...
1. Introduction

Water which is unsafe in terms of microbiological contamination, is responsible for different waterborne diseases, which represent the main causes of world mortality (WHO, 2017). Therefore, the disinfection of water is a mandatory step in any treatment procedure, in order to provide water which is adequate for civil use and thus safe from a microbiological viewpoint. This is clearly set out in most national regulations, including Germany (Trinkwasserverordnung and TrinkwV, 2001; D. Lgs. 31/2001; SANS 241), Italy (D. Lgs. 31/2001), South Africa (SANS 241), and Canada (Health Canada, 2017) as detailed in Table SM-1 in the Supplementary Material section.

Groundwater and surface water may be polluted due to the presence of metals, carbonates, ammonia, microorganisms, pesticides, and polycyclic aromatic hydrocarbons of natural or anthropic origins (Paul et al., 1995; Calijuri et al., 2012; Ahoulcides, and polycyclic aromatic hydrocarbons of natural or anthropic presence of metals, carbonates, ammonia, microorganisms, pesticides (Kapalka et al., 2009). Under these conditions other solution components, typically anions like sulfates and carbonates, may be converted into oxidizing oxo-anions. When chloride ions are also present, their conversion to species with a higher oxidation state, e.g. $\text{Cl}^-$ in the case of hypochlorous acid, will also take place. Due to these features, water oxidation at BDD electrodes is an ideal reaction cage, which is determined by the chosen electrolysis parameters (Kapalka et al., 2009). Under these conditions other solution components, typically anions like sulfates and carbonates, may be converted into oxidizing oxo-anions. When chloride ions are also present, their conversion to species with a higher oxidation state, e.g. $\text{Cl}^-$ in the case of hypochlorous acid, will also take place. Due to these features, water oxidation at BDD electrodes is an ideal reaction cage, whose features are determined by the chosen electrolysis parameters (Kapalka et al., 2009). Under these conditions other solution components, typically anions like sulfates and carbonates, may be converted into oxidizing oxo-anions. When chloride ions are also present, their conversion to species with a higher oxidation state, e.g. $\text{Cl}^-$ in the case of hypochlorous acid, will also take place.

Disinfection by-products (DBPs) are frequently observed in developing countries, such as in the sub-Saharan countries, where fecal contamination is one of the major causes of water source deterioration (Obi et al., 2002; Hay et al., 2012). In such cases, water treatment must include a disinfection step able to guarantee the removal of the occurring pathogens. In general, the disinfection is an end-of-pipe treatment that consists of the application of physical processes such as rapid filtration and/or UV irradiation or chemical processes such as chlorination or ozonation. It also has to guarantee water which is safe during its storage and along the distribution system to its different users.

Chemical disinfection is extensively used worldwide: in the past, chlorine was the most used disinfectant, but nowadays its compounds (sodium and calcium hypochlorite, chlorine dioxide) are preferred. In the Southern African region, active chlorine is still the most widely used disinfectant, followed by sodium and calcium hypochlorite and chlorine dioxide (Momba et al., 2009). However, despite its effectiveness, chlorine may not guarantee total water sanitation. For example, the protozoan parasite Cryptosporidium and some viruses are not inactivated by the usually applied chlorine doses (White, 1999). This adds to other disadvantages such as unfavorable taste and odor, difficulties in handling and management, and the generation of toxic DBPs.

On the other hand, physical processes only allow water disinfection in their immediate surrounding and do not provide any residual effect which is able to guarantee the distribution of safe water to different users. Therefore, studies on alternatives have been conducted and a number of other disinfectants have been suggested (Jeong et al., 2009; Luukkonen and Pehkonen, 2017).

In this context, during the last two decades, active research has been carried out on the electrochemical properties of boron-doped diamond (BDD) electrodes showing, in particular, that due to their extremely poor catalytic activity towards the oxygen evolution reaction (OER), the latter takes place at very positive potentials, close to the reduction potential of the hydroxyl radical (Iniesta et al., 2001; Tröster et al., 2002, 2004; Ferro and De Battisti, 2003). As hydroxyl radicals are intermediates in the OER process, formed during its first stage (which, logically, is rate determining), it is generally admitted that their concentration can consistently increase in the near-anode surface region, i.e. a sort of reaction cage whose features are determined by the chosen electrolysis parameters (Kapalka et al., 2009). Under these conditions other solution components, typically anions like sulfates and carbonates, may be converted into oxidizing oxo-anions. When chloride ions are also present, their conversion to species with a higher oxidation state, e.g. $\text{Cl}^-$ in the case of hypochlorous acid, will also take place. Due to these features, water oxidation at BDD electrodes is an ideal example of an advanced oxidation process which is easy to control and which requires practically no addition of chemicals for the effective sanitization of natural waters.

The extensive studies carried out by different research groups (Haenni et al., 2002; Martinez-Huitle and Brillas, 2008; Lacasa et al., 2013; Mascia et al., 2013; Bruguera-Casamada et al., 2016) have shown that electrolysis at BDD electrodes represents an effective process for the removal of microorganisms. This is extremely important, as safe quality water is needed in numerous different applications.

This study presents the results collected during an experimental investigation within the Horizon 2020 “SafeWaterAfrica” EU project, aimed at evaluating the technical feasibility of an electrochemical decontamination step in the treatment of polluted groundwater. Investigations focused on the effectiveness of the
removal of various contaminants present in real groundwater, particularly of different types of bacteria and, at the same time, on the possible formation of undesired byproducts in the different operational conditions.

2. Materials and methods

2.1. The electrochemical reactor

The experiments were conducted using a CabECO® unit provided by CONDIAS GmbH, Germany (WO 2015128077 (A1); WO 2015128076 (A1), WO 2015128077 (A1)), shown schematically in Fig. 1 and in greater details in Fig. SM-1 (in the Supplementary Material section). The CabECO® reactor consists of a couple of mesh electrodes (a total active area of 24 cm²) separated by and directly in contact with a perfluorinated ion-exchange membrane (zero-gap-technology). In this scheme, electrochemical reactions mostly take place at the outer surfaces of the electrode system while the ion-exchange polymer guarantees ion transportation (see Fig. SM-1). This set-up allows the electrochemical treatment of low-conductivity solutions, which natural groundwater generally is.

The experimental setup consists of a cell, whose volume is around 45 mL, a peristaltic pump, a 5 L tank and a power supply (Fig. 1). The system was operated in either discontinuous or continuous mode. In the first case, the cell effluent was recirculated into the water tank feeding the cell (Fig. 1, left); in the second case, the water only passed through the cell once and was sent directly to the storage tank (Fig. 1, right).

The main operational conditions adopted during the investigation in discontinuous and continuous mode are reported in Table SM-2 and Table SM-3, respectively; all experiments were carried out at room temperature (20–25 °C).

Electrolysis current and electrode (anode) potential are the parameters that most influence the production rate of strong oxidants via electrolysis. In this investigation, galvanostatic conditions for the electrolytic treatment were chosen, and the anodic current density (j), directly related to the anode potential, was used as the measure of electrode polarization.

2.2. Feeding

The system was fed with real groundwater, drawn from wells at the waterworks situated on the banks of the River Po in Ro Ferrarese (44.9477° N, 11.7572° E, Ferrara Province, Italy). The main characteristics of the water used for the experimental investigation are collected in Table SM-4, together with the corresponding analytical methods (APAT - IRSA/CNR, 2003).

Groundwater presents a low level of microbiological contamination and a low value of COD. Some electroactive species, like ammonium, are present, although at low concentrations, while the more significant content of chloride ions is typical of groundwater drawn in the Po Valley. Bromide ion concentrations, too, are characteristic of this area and could be affected by a modest seawater intrusion (water samples come from a well which is about 20 km far from the Adriatic Sea) or the large application of fertilizer on rural area (Brindha and Elango, 2013). Under ordinary electrolysis conditions, the chloride concentration may guarantee a consistent faradaic yield for chloride oxidation, primarily to the +1 oxidation state. In general terms, the water oxidation reaction is expected to be the dominating process, but Cl-, Br-, and NH4+ are also electroactive, as are some of their oxidation products.

In order to better assess the disinfecting performance of the electrochemical treatment, experiments were performed on water inoculated with controlled amounts of selected pathogens: strains of E. coli, Enterococci, P. aeruginosa, and Legionella were added as discussed in sections 3.1.4 and 3.2, in order to mimic contamination that may occur in sub-Saharan countries.

2.3. Preparation of bacteria suspension

Bacteria strains of Escherichia coli (ATCC 25922), Enterococcus fecalis (ATCC 29212), Pseudomonas aeruginosa (ATCC 27853), and Legionella pneumophila (ATCC 33152) were provided by Microbiology, in the form of lyophilized organisms in pellets. The contaminated aqueous solution was prepared by mixing 200 L of groundwater with 60488 UFC of each strain, in order to obtain the following initial concentrations: > 200 MPN/100 mL (Coliforms and E. coli), >28 CFU/100 mL (Enterococci), <10 CFU/100 mL (P. aeruginosa) >100 CFU/230 mL (Legionella) an initial concentration of approximately 300 CFU/100 mL for each type of microorganism. After mixing, the solution was continuously shaken for 30 min in order to activate all the microorganisms whose activities could have been slowed down by the low groundwater temperature (around 14 °C). As anticipated, tests were then carried out at ambient temperature (between 20 and 25 °C).

2.4. Microbial analysis

Water samples for microbial analysis were withdrawn in 1 L glass bottles without the addition of sodium thiosulfate as analyses were performed within 1 h of sampling.

Concentrations of Coliform bacteria, E. coli and Enterococci were estimated by using products provided by IDEXX: Colilert-18, Enterolert DW (water with chlorine), and Enterolert E (water without chlorine). Analyses of P. aeruginosa, Legionella and total bacteria count at 22 °C and 36 °C were realized by using a culture media provided by Biolife Italiana: they were either ready for use or dehydrated and they were prepared in a laboratory according to international standard methods (see Table SM-4 for details).

Fig. 1. Diagram of the equipment used for the experimental investigation in discontinuous mode (left side) and continuous mode (right side).
The inactivation rate for the different bacteria was evaluated as the reduction of the ratio between effluent and influent bacterial occurrence \((N/N_0)\), where \(N_0\) represents the initial bacterial concentration and \(N\) the bacterial concentration at the respective sampling time.

2.5. Analytical methods

The analytical methods for the determination of the selected chemical, physical and microbiological parameters are reported in Table SM-4. Chemical analyses were performed by ICS 1000 and ICS 1100 ionic chromatographs. Standards used for the calibration of chromatographs were provided by ULTRA Scientific (Italy) at a concentration of 1000 \(\mu\)g mL\(^{-1}\) for each analyte. Conductivity and pH were assessed by using a WTW inoLab\textsuperscript{®} multiparametric probe, calibrated with standard buffers provided by VWR srl. COD and ammonium were assessed using a HACH DR 5000 UV—Vis Laboratory Spectrophotometer (see Table SM-4 for the corresponding analytical method).

All analyses were performed either immediately after the withdrawal of the water sample or completed within the following 24 h.

3. Results and discussion

3.1. The electrochemical treatment under discontinuous conditions

3.1.1. Electrosynthesis of strong oxidants and chemical changes in groundwater composition

Although the main anode reaction is water oxidation to oxygen, under the polarization conditions imposed on the CabECO\textsuperscript{®} cell, chloride ions, present in an appreciable concentration, are certainly oxidized to higher oxidation states in accordance with Kerwick et al. (2005) and Kraft (2008). At the pH values measured during the investigation, close to neutrality, the formation of \(\text{Cl}^{+1}\) in the forms of hypochlorous acid and hypochlorite ions takes place; this contribution will be reported as Free Chlorine (FC). In addition, owing to the presence of ammonium ions in groundwater (Table SM-4), chloramines are also expected to form and contribute, together with FC, to the Total Chlorine (TC), as clearly described in the review by Deborde and von Gunten (2008).

On the other hand, the electrochemical and chemical reactivity of hypochlorous acid involves the formation of chlorate, as well as perchlorate anions, in agreement with Polcaro et al. (2008, 2009) and Bergmann and Rollin (2007).

Free and Total Chlorine. Fig. 2 (left) shows the generation of FC versus time \((t)\) at the different applied current intensities, \(I\). It can be seen that the generation rate of FC is modest at the lowest values of \(I\) \((I = 0.31\ A)\, the maximum value is 0.1 mg L\(^{-1}\), while FC reaches 0.2 mg L\(^{-1}\) at \(I = 0.62\ A,\) after the same charge has passed). In general terms, FC concentration increases almost linearly with \(t\), but both the expected conversion of FC into TC and the possible conversion of FC into chlorate may well justify the lack of linearity.

It is interesting to note that at constant charge \(Q(Q = I \times t)\), the initial production rate of FC increases with \(I\), thus suggesting a substantial increase to the faradaic yield with increasing \(I\). This evidence is important, in view of the number of competitive anodic reactions.

Fig. 2 shows on the right the concentration of the TC, as a function of time at the different values of applied current. The TC concentration increases with \(t\) more pronouncedly than in the case of FC.

The concomitant decrease in ammonium concentration (data not shown) supports the idea that the consumption of FC may take place with the formation of chloramines as clearly discussed in Deborde and von Gunten (2008) and Martin de Vidales et al. (2016).

Ozone. The electrosynthesis of \(\text{O}_3\) at high-oxygen-overvoltage anodes (such as BDD) has been documented in a number of papers (see e.g. Katsuki et al., 1998; Meas et al., 2011; Christensen et al., 2013). However, in the presence of interfering species (such as the case of groundwater) and in view of further applications in the field of water disinfection, a detailed analysis of the effects of the parameters of electrochemical treatment is necessary. As shown in Fig. 3, at the highest value of \(I\), ozone concentration can readily reach values close to 0.5 mg L\(^{-1}\) even at low \(t\) values \(<10\ min\). However, it is worth noting that there is no linearity between ozone concentration and time under each operational condition, due to the reactivity and instability of this compound. The initial rate of \(\text{O}_3\) generation is linear in \(I^2\) (see Fig. SM-3), with the exception of the result for \(I = 2.30\ A\).

Chlorate. Fig. 4 (left) shows the time dependence of the concentration of chlorate, at different \(I\). Considerable amounts of \(\text{ClO}_3^-\)
are already generated at low $I$ and $t$ values; moreover, as shown in Fig. SM-4, the initial generation rate of ClO$_3^-$ is linear with $I$.

**Perchlorate.** Data in Fig. 4 (right) show with good approximation that there is a direct proportionality between perchlorate concentration and $t$, at the different applied current intensities.

As expected, the slope increases when the applied current $I$ increases. At the lowest $I$ values, the production of ClO$_3^-$ is modest (for instance, at $I = 0.31$ A, the concentration was 300 $\mu$g L$^{-1}$ after 120 min), but at higher $I$ the concentration increases and at $I = 2.30$ A, a concentration of 1070 $\mu$g L$^{-1}$ was found after only 15 min. The situation is better represented in Fig. SM-5, where perchlorate production is plotted as a function of the charge $Q$: the increase of the faradaic efficiency with increasing $I$ (and therefore $j$) is evident. In particular, looking at data at a constant charge $Q$ of 37 A min, the perchlorate concentration is 303 $\mu$g L$^{-1}$ at $I = 0.31$ A, 343 $\mu$g L$^{-1}$ at $I = 0.62$ A, 458 $\mu$g L$^{-1}$ at $I = 0.93$ A and 539 $\mu$g L$^{-1}$ at $I = 1.24$ A. It is also interesting to observe that, as shown in Fig. SM-6, the perchlorate production rate ($d$ClO$_3^-$/dt) is linear with excellent approximation not in $I$, but in $j^2$.

### 3.1.2. Minor component reactivity

As well as the main components of the groundwater studied, some minor components are also of interest. For instance, as shown in Table SM-4 and in Fig. SM-7, bromides are present at a concentration of 0.46 mg L$^{-1}$ and their oxidation (at least partial) to bromates is to be expected, under the applied experimental conditions (von Gunten, 2003; Ferro, 2005; Deborde and von Gunten, 2008; Barazesh et al., 2016).

In fact, groundwater analyses after electrochemical treatments show a small but measurable decrease in concentration, already at 0.31 A and after 30 min of electrolysis. As expected, the decrease becomes even more pronounced with increasing $I$ and $t$, and a value as low as 0.33 mg L$^{-1}$ was recorded after 15 min when working at $I = 2.30$ A. An interesting consequence of Br$^-$ oxidation is the appearance of chloro-bromo methane in the analysis of electrolyzed samples. Concentration levels are far below the permitted limits for drinkable water, as the occurrence of chloro-bromo alkanes is ubiquitous after the conventional treatments of natural water with hypochlorite (Sharma et al., 2014). In addition, as clearly discussed in White (1999) the occurrence of HOCl, NH$_4$ and Br$^-$ will lead to the formation of bromamines and chlorobromamines, always in very low concentrations. Owing to the low initial Br$^-$ concentration, oxidation most likely takes place through bulk reactions, or within the called “reaction cage”, as a result of the synthesis of strong oxidants such as ozone and free chlorine.

Regarding the behavior of Mg$^{2+}$ and Ca$^{2+}$ ions during electrolysis, it is well known that they are not electroactive and not directly or indirectly involved in electrochemical water disinfection. On the other hand, the formation of insoluble carbonates is unavoidable, under ordinary conditions, with measurable CO$_2$ concentrations in the aquatic medium as a consequence of the contact with the atmosphere, and with high faradaic efficiency of the water reduction at the cathode of the electrochemical reactor, with consequent OH$^-$ production and alkalinization of the near-cathode-surface region. In the present set of experiments, a decrease of about 10% has been found for both cations (Fig. SM-8 and Fig. SM-9), corresponding to the formation of insoluble carbonates. The concentration changes are essentially defined by the consumed charge. The problem of the formation of insoluble carbonates, which does not necessarily occur only on the surface of the cathode, may require some additional electrolysis controls.

The concentration of COD in the withdrawn groundwater is low (around 7 mg L$^{-1}$, Table SM4), as expected for ordinary groundwater where organic contamination should be rather limited. No electrochemical incineration effects could be observed, at any $I$ and $t$; even increasing $j$ towards 1000 A m$^{-2}$, corresponding to $I = 2.30$ A, the COD remained unchanged. One possible reason for this occurrence could be the limited reactivity of the traces of organics present, though the electrolysis parameters explored here are not favorable either, as higher $j$ values and longer times are normally required to achieve a consistent degradation of organic substrates. The extension of natural water decontamination to the abatement of consistent concentrations of organic substrates might require additional treatments to the mere electrochemical approach.

The results described confirm the perspectives of application of the CabECO® technology in water sanitation, with special reference to the case of groundwater of ordinary composition. In fact, under relatively mild polarization conditions (e.g., $j$ around 400–500 A m$^{-2}$, which means $I$ around 1 A), the concentrations of FC, TC and O$_3$ already reach significant values and are expected to exert an effective biocidal action.

### 3.1.3. Analysis of collected chemical data

Due to the fact that groundwater is a very diluted electrolyte solution, the equations of electrochemical kinetics cannot be straightforwardly applied to the study of electrode reactions occurring during groundwater treatment. In the absence of supporting electrolytes, the transfer of charged reactants towards the electrode surface is not only controlled by concentration gradients, but also by electro-migration. In addition, the lack of buffering media (strong acidity or basicity) further complicates the background of electrochemical reactivity for a number of species. A typical example is the result on Cl$^-$ oxidation: its molar concentration is about 2.5 × 10$^{-7}$ M and this very low value would imply fast attainment of diffusion control and limiting current. This, however, is not the case, as the initial FC concentration linearly increases with $I$. The consecutive consumption reactions, leading to chloramines and higher oxidation states of chlorine, inevitably lead...
to a sort of stationary condition in which FC is likely to play the role of intermediate, whose concentration does not change significantly at longer times.

As shown in Fig. 2, under given experimental conditions (including chloride concentration, solution pH and temperature, electrode material, and imposed polarization), the concentration of FC reaches significant values (e.g. ≥ 0.2 mg L⁻¹) only at high \( t \) or high \( I \).

This point is also important with regards to ClO₃⁻ generation (Fig. 4 left) as the fast initial increase of this anion concentration during the first minutes (5–10 min) of electrolysis, even in the presence of very small FC concentrations (Fig. 2), can hardly be explained following the traditional mechanism proposed in literature (Pletcher and Walsh, 1993). Low bulk concentration of FC (polarizations at 0.31 and 0.62 A) and relatively low solution temperatures should not favor chlorate formation, especially through a reaction that might be of second or third order compared to FC. The level of anode polarization, controlled by \( I \), seems to have a much larger effect and no loss of faradaic efficiency is observed (Fig. 4 left and Fig. SM-4).

A possible explanation might be sought in an electrochemical oxidation mechanism, possibly superimposed on the generally accepted chemical path. In this context, it may be useful to recall that mechanisms of complex electrochemical reactions, like the electrochemical incineration of organic substrates at BDD electrodes, have been described by assuming that, under enhanced anodic polarization, a sort of “reaction cage” is formed in the near-electrode region. Within the “reaction cage”, the concentration of hydroxyl radicals is hypothesized to be rather consistent, with the value depending on the anode current density and solution composition (Kapalka, 2008; Kapalka et al., 2007, 2008; 2009; Panizza et al., 2008). Because of the relatively low concentration of potential reactants in this study, the “reaction cage” could be even more extensive than that calculated by Kapalka (2008).

In the case of anodic chlorine oxidation leading to the generation of chlorine species with potentially different oxidation states and chloramines, the initial step could be Cl⁻ oxidation to ClO⁻ or Cl⁻⁻ species. It may be maintained that this electrochemical change takes place via a bimolecular surface reaction, with the rate controlled by chloride-ion discharge (Ferro et al., 2000). A number of reactions would then take place in the “reaction cage”, also involving hydroxyl radicals (first intermediates of the oxygen evolution reaction), with the formation of higher oxidation states for CI: not only chlorates, but also perchlorates (Martínez-Huitle et al., 2008). Within the “reaction cage”, the reaction between ClO⁻ or Cl⁻⁻ with ammonium ions would lead to chloramines; further reactions in the bulk solution would be “frozen” because of the strong dilution effect. Accepting the above assumption, perchlorate formation does not need to be formed through the oxidation of chloride, and different parallel paths may become possible.

A further indication can be obtained from the dependence of the formation rate of a given species on the electrolysis current \( I \) in a galvanostatic regime. In fact, the latter condition imposes a stationary condition on the reacting system in the “reaction cage”, implying in turn substantial invariance of intermediate concentration and, in particular, of hydroxyl radicals. Accordingly, \( I \) may be an indirect measure of the concentration of hydroxyl radicals within the “reaction cage”, and the plot of the initial formation rate of a given species against a suitable power of \( I \) (Fig. SM-4 and Fig. SM-6) should be linear, with the slope of the linear dependence representing the reaction order with respect to the hydroxyl radical. Based on the graphs in Fig. SM-4 and Fig. SM-6, it can be concluded that the reaction order of ClO₃⁻ formation with respect to hydroxyl radicals is 1, while that for ClO₄⁻ formation is 2.

### 3.1.4. Microbiological inactivation in discontinuous mode

**Microbial inoculation.** In this series of experiments, the inactivation of *E. coli*, *Legionella*, *P. aeruginosa*, and Enterococcus was studied using inoculated groundwater samples, in order to simulate the potential contamination of groundwater which frequently occurs in rural and peri-urban areas in the sub-Saharan region (Obi et al., 2002; Momba et al., 2006; Hay et al., 2012; Edokpayi et al., 2015). After the inactivation, *E. coli* and Coliforms concentrations were more than 200 MPN/100 mL, *P. aeruginosa* more than 120 CFU/100 mL and *Legionella p.* More than 100 CFU/230 mL.

In consideration of the results achieved with regard to groundwater contamination, tests on the inoculated sample were only carried out for \( I \geq 0.93 \) A.

The graphs in Fig. 5 depict the reduction (N/N₀) of inoculated bacteria with respect to the residence time within the cell, showing that the complete inactivation of all bacteria was achieved after 30, 10, and 15 min, working with 0.93, 1.24 and 2.30 A, respectively. Interestingly, the inactivation trends for Enterococcus and *E. coli* were always the same and overlap in all the graphs: their complete removal was observed after only 5 min, under all the applied operational conditions.

On the contrary, *Legionella* exhibited the highest resistance among the investigated bacteria and consequently needed a longer treatment time for its complete inactivation. At the lowest current of 0.93 A, no change in *Legionella* and *P. aeruginosa* concentrations was observed during the first 20 min. Under higher current intensities (1.24 and 2.30 A), a significant reduction in their viability was observed just after 5 min of operation: culturable counts (Ferro
et al., 2018) of Legionella decreased to 65–20% of their initial value, while P. aeruginosa showed a complete inactivation. This could be explained by the high level of free chlorine concentration generated during the first minutes in the cell and at high current densities, as highlighted in Fig. 2 (right).

3.2. Electrochemical treatment under continuous mode

Experiments were carried out at different \( q_v \) values, from 0.15 to 4 L min\(^{-1}\), and the effect of polarization within the reactor was analyzed under each hydrodynamic condition.

Data collected by working with \( q_v = 0.15 \) L min\(^{-1}\) confirm that appreciable amounts of free chlorine (in any case limited to about 0.2 mg L\(^{-1}\)) can only be generated with high polarizations, i.e. with currents in the range of 1–2 A. Apparently, Cl\(^{-1}\) \( \text{Cl}^– \) species (originally generated by the anodic oxidation of Cl\(^-\)) are rather quickly converted to combined chlorine and chlorate, as the concentration of this species is significant even at lower polarizations. In a sense, these data are still in agreement with those collected in discontinuous mode, essentially because of the very low imposed flow rate \( q_v \).

Data obtained by working with \( q_v = 1.75 \) L min\(^{-1}\) are collected in Table SM-5; the already significant decrease in residence time is reflected by the numerical values.

As shown in Fig. 6, free chlorine concentration increases linearly with the current intensity \( I \) but, in any case, remains around 0.2 mg L\(^{-1}\), even for \( I = 4 \) A. Essentially for the same reasons, ClO\(_3\) concentration remains lower compared to the values detected in experiments in discontinuous mode, though its increase is directly proportional to the current intensity \( I \) up to about 3 A.

With regard to ozone, its concentration reaches 0.07 mg L\(^{-1}\) only at \( I = 4 \) A.

As for minor components, it was found that the concentrations of Br\(^{-}\), NH\(_4\), Mg\(^{2+}\) and Ca\(^{2+}\) remain substantially unchanged, within the limits of reproducibility of experimental data (data not shown).

Without recycling, the increase in \( q_v \) reduces the groundwater residence time within the electrochemical cell causing a consequent decrease in the rate of all of the electrochemically assisted reactions, with special reference to those that are most likely to occur within the “reaction cage”.

A confirmation of the above picture was obtained through the data collected working at \( q_v = 3.0 \) L min\(^{-1}\) and \( I = 4 \) A. Under these operational conditions, the concentration of free chlorine remains around 0.2 mg L\(^{-1}\) while that of O\(_3\) around 0.06 mg L\(^{-1}\), and both values are low with respect to the biocidal demand of the process.

The graph of the concentrations of FC and Chlorate vs. \( I/q_v \), reported in Fig. SM-10, shows the increase in faradic efficiency with increasing \( I \).

With regard to the electrochemical inactivation of microbological species by treatment in continuous mode, collected data are reported in Fig. 7 in terms of their decrease in viability (\( N/N_0 \)) against the applied volumetric charge. A high removal of E. coli, Enterococcus and Coliforms was achieved at a low applied volumetric charge (1.7 A min L\(^{-1}\)); P. aeruginosa was only removed with a high applied volumetric charge (15 A min L\(^{-1}\)); Legionella exhibited higher resistance compared to the other microorganisms, still remaining detectable even with a high applied volumetric charge. These profiles confirm that it is not possible to achieve complete sanitation even at the highest \( I \) values.

4. Conclusions and perspectives

Collected data demonstrate that microbiological decontamination can be readily achieved under discontinuous conditions, provided that the CaBECO® reactor is operated at sufficiently high currents (around 1–2 A). In fact, under these conditions high concentrations of ozone and free chlorine, combined with adequate contact times, guarantee the removal of the different microorganisms and the production of safe water. The generation of undesired DBPs is also observed, e.g. chlorate and perchlorate. Limits for chlorate and perchlorate are under discussion at different levels. In particular, WHO (2017) set as guideline values 700 \( \mu \)g L\(^{-1}\) for chlorate and 70 \( \mu \)g L\(^{-1}\) for perchlorate; in the U.S.A in November 2016, EPA revised the Contaminant Candidate List-4 and included different DBPs, among which chlorate (Richardson and Ternes, 2018), and agreed to set the corresponding limits by 2019 (Morrison, 2016). According to the collected data, chlorate and perchlorate concentration can be kept at values lower than the guidelines thresholds by choosing appropriate electrolysis parameters. Moreover, on the basis of the results achieved by Brito et al. (2015) by using BDD anodes with higher sp\(^3\)/sp\(^2\) ratio, the electro-synthesis of chlorates and perchlorates could be decreased, interestingly.

Under continuous conditions some advantages are observed, compared to the discontinuous mode, with regards to the generation of undesired species, whose concentrations remain low at higher \( q_v \) values. Unfortunately, essentially for the same reasons,
the concentrations of strong oxidants also remain low and, due to the extremely low contact times allowed by the feeding mode, the antimicrobial effects are modest. Higher removal levels were achieved by applying higher currents (>4 A) which, however, led to other performance problems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.05.062.

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