Electrocoagulation: simply a phase separation technology? The case of bronopol compared to its treatment by EAOPs

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Paper submitted to be published in *Environmental Science & Technology*

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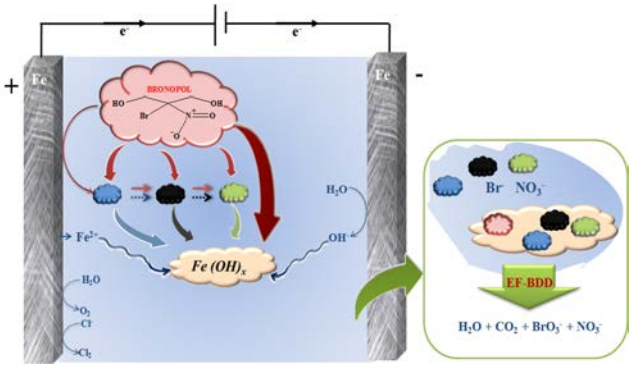
ABSTRACT

Electrocoagulation (EC) has long been considered a phase separation process, well suited for industrial wastewater treatment since it causes a quick, drastic decay of organic matter content. This research demonstrates that EC also behaves, at least for some molecules like the industrial preservative bronopol, as an effective transformation technology able to yield several breakdown products. This finding has relevant environmental implications, pointing to EC as a greener process than described in literature. A thorough optimization of EC was performed with solutions of bronopol in a simulated water matrix, yielding the complete disappearance of the parent molecule within 20 min at 200 mA (~20 mA/cm^2), using Fe as the anode and cathode. A 25% of total organic carbon (TOC) abatement was attained as maximum, with bronopol being converted into bromonitromethane, bromochloromethane, formaldehyde and formic acid. N atoms were accumulated as NO_3^-, whereas Br^- was stable once released. This suggests that mediated oxidation by active chlorine, as well as by hydroxyl radicals resulting from its reaction with iron ions, is the main transformation mechanism. Aiming to enhance the mineralization, a sequential combination of EC with electro-Fenton (EF) as post-treatment process was proposed. EF with boron-doped diamond (BDD) anode ensured the gradual TOC removal under the action of $^{\bullet}OH$ and BDD($^{\bullet}OH$), also transforming Br^- into BrO_3^-.

TABLE OF CONTENTS (TOC) ART



INTRODUCTION

Since its first application for sewage treatment in 1889,[1] electrocoagulation (EC) has been considered by the scientific and industrial communities as a mere separation technology that does not alter the structure of the parent organic molecules, simply causing their removal by agglomeration with metal hydroxide flocs to form a contaminated sludge.[2,3] Recently, there has been renewed scientific and technological interest in this process owing to the increasing demand of simple but highly effective water treatment technologies, as well as its suitability to be powered by renewable electricity sources[4] and be conceived as small-scale decentralized units.[5] Companies like Powell Water, WaterTectonics or Elgressy offer solutions based on EC for mining and oil and gas markets, among others, whereas several projects including REWAGEN, EColoRo and ECOWAMA have been funded as part of Europe's FP7 and Horizon 2020 research programs. EC has therefore been brought to the forefront and a more thorough investigation of its particularities is needed.

It has been shown that during EC in Cl^--containing media, this anion can be oxidized at the anode surface to form active chlorine (Cl_2, $HClO/ClO^-$), which is widely used as oxidation and disinfection agent. For example, it has been mentioned that it contributes to dye decolorization.[6] This assumption has been rarely verified by measuring the transformation products, although in a recent study some of us showed the accumulation of chlorobenzene derivatives during the EC of the dye Tartrazine.[7] To date, this phenomenon constitutes the only evidence that EC behaves as a partial transformation technology.

Usually, total organic carbon (TOC) removal is not feasible by EC, thus being required a post-treatment. EC has been combined with ozonation[8] and photocatalysis,[9] but a better suited combination arises from coupling with Fenton-based processes to take advantage of the metal ions dissolved during the EC step.[10] On the other hand, great progress has been made in developing the so-called electrochemical advanced oxidation processes (EAOPs). The effect

of the main operation parameters on their performance has been thoroughly evaluated.[11-13] Among them, electro-Fenton (EF) process has shown large ability to oxidize organic matter within a shorter time. In EF, H_2O_2 is electrogenerated on site in acidic solutions from the two-electron O_2 reduction at a suitable cathode material. In the presence of Fe^{2+}, the occurrence of Fenton's reaction yields $^{\bullet}OH$ in the bulk.[14] In undivided electrolytic cells, M($^{\bullet}OH$) is also generated on the anode surface (M),[15] which can be a boron-doped diamond (BDD),[16-22] Pt,[16,17,20] graphite[19,23] or dimensionally-stable anode (DSA).[17,18,24,25] As demonstrated from studies on integrated water networks,[26] EC is an optimum candidate for coupling strategies. It has been employed as a pre-treatment before use of electro-oxidation (EO).[27-29] Recently, we reported for the first time the sequential combination of EC and EAOPs based on Fenton's reaction. EC induces the large coagulation of organic matter as well as the accumulation of metal ions, which can be further used to oxidize the remaining organic matter by EF as post-treatment.[7,30]

Bronopol is widely used as antiseptic and preservative in products like cosmetics and toiletries since it prevents bacterial growth. It is readily soluble in water, which justifies its use in aquaculture.[31] However, under certain conditions it decomposes, thus being considered a formaldehyde releaser[32] that can eventually yield nitrosamines. All these products are known human carcinogens and, moreover, bronopol is considered a skin chemical sensitizer that causes allergic contact dermatitis.[32] Formaldehyde is subject to regulation due to its toxic properties, which has triggered the use of formaldehyde-releasing agents as surrogates that are also under restriction in Europe.[33] Preservatives have been found in concentrations up to mg/L and μg/L in industrial effluents as well as in influents of wastewater treatment facilities,[34] although no much information is available on their occurrence and toxicity. Bronopol may be hydrolyzed in water to yield several products, but it is only slowly degraded at certain pH values and usually requires a few days or weeks.[35,36] Temperature and sunlight/UV radiation

may affect the decay rate of bronopol as well.[36] To our knowledge, no investigation has addressed the use of advanced oxidation processes and electrochemical technologies for treating bronopol in water, whereas only some irrelevant study reported its redox activity in environmental samples. Ergo, it is an optimum candidate to gain further understanding on EC.

The present contribution gives detailed insight into the potentialities of EC as a transformation technology, which could confer a greater environmental compatibility because of a cleaner sludge. Solutions of bronopol in a simulated water matrix have been electrocoagulated under different conditions to optimize the process. The decay of the pollutant as well as its mineralization and fate of heteroatoms has been studied by high-performance liquid chromatography (HPLC), TOC analysis and ion chromatography (IC), whereas transformation products have been identified by gas chromatography-mass spectrometry (GC-MS). Likewise, bronopol has been degraded by EF using an air-diffusion cathode and different anodes, which was followed by coupling between EC and EF to achieve a greater conversion of the pollutant and products. Comparative electrolyses were performed in Na_2SO_4 as an inert electrolyte and a reaction route for the sequential treatment is proposed.

EXPERIMENTAL SECTION

Chemicals. Bronopol (2-bromo-2-nitro-1,3-propanediol, 98%), bromonitromethane (90%) and 2-bromoethanol (95%) of reagent grade were purchased from Sigma-Aldrich and used as received. Formaldehyde, formic acid, perchloric and sulfuric acids (used to adjust the pH prior to EF treatment), anhydrous sodium sulfate (background electrolyte), Fe(II) sulfate heptahydrate (catalyst source for single EF) as well as ammonium oxalate, potassium bromate and sodium nitrate, nitrite, chloride and bromide employed in IC and salts needed for the simulated water matrix were analytical grade from Fluka, Acros Organics and Sigma-Aldrich. All solutions used for calibration of instruments were prepared with ultrapure water from a

Millipore Milli–Q system (resistivity >18 MΩ cm at room temperature). A simulated water matrix mimicking the ionic content of real water from a wastewater treatment facility located near Barcelona (Spain) was used for the electrolyses of bronopol. For this, pure salts accounting for 1.3 mM SO_4^{2-}, 11.5 mM Cl^-, 0.02 mM NO_3^-, 1.5 mM NH_4^+, 11.6 mM Na^+ and 1.0 mM K^+ ions were added to ultrapure water, yielding a solution of 1.7 mS/cm at pH 6.5 (hereby called natural pH). For comparison, some electrolyses were performed in 10 mM Na_2SO_4 (same conductivity).

Electrolytic systems. The experiments were done in an open, undivided glass cell of 150 mL capacity with a double jacket for circulation of water thermostated at 35 ºC, under vigorous stirring provided by a magnetic PTFE follower. For the EC trials, the anode was a pure Fe, pure Al or stainless steel (AISI 304 and 316L) plate with immersed dimensions of 3.0 cm × 1.5 cm, 0.25 cm thickness (all sides exposed to solution). The same materials with analogous dimensions were tested as cathode. One or more electrode pairs were placed alternately in parallel with an interelectrode gap from 1.0 to 4.0 cm, employing a monopolar parallel electrical configuration. This connection mode was preferred because, at laboratory scale, it avoids issues with bypass current. At industrial scale, it allows controlling the anode consumption and its periodic replacement, although bipolar connection is also widespread since it requires the use of fewer connections and a high voltage / low current power supply. Before first use, all electrodes were properly cleaned and then activated with a 0.1 M NaOH or H_2SO_4 solution. For the EF process, the anode (3 cm^2) was either a Pt sheet of 99.99% purity supplied by SEMPSA (Barcelona, Spain), a BDD thin-film electrode supplied by NeoCoat (La-Chaux-de-Fonds, Switzerland) or a DSA-O_2 (IrO_2-based anode) or DSA-Cl_2 (RuO_2-based anode) plate from NMT Electrodes. The cathode was a 3 cm^2 carbon-PTFE air-diffusion electrode supplied by E-TEK (Somerset, NJ, USA), mounted as described elsewhere and fed with air pumped at 1 L/min for continuous H_2O_2 generation.[14] The interelectrode gap

was about 1.0 cm. Before first use, a preliminary polarization was done in 0.05 M Na_2SO_4 at 100 mA cm^{-2} for 180 min to remove the impurities of the BDD surface and the activation of the air-diffusion electrode.

Analytical procedures. The electrical conductance and pH were measured with a Metrohm 644 conductometer and a Crison 2000 pH-meter, respectively. Constant current electrolyses were performed with an Amel 2049 potentiostat-galvanostat and the potential difference between the anode and cathode (E_{cell}) was provided by a Demestres 601BR digital multimeter. The mineralization of solutions was assessed from their TOC abatement, determined on a Shimadzu TOC-VCNS analyzer (Text S1 of the Supporting Information, SI).

The time course of the concentration of bronopol was followed by reversed-phase HPLC upon injection of 10 μL aliquots into a Waters 600 LC fitted with a Waters Spherisorb ODS2-C18 5μm, 150 mm × 4.6 mm, column at 25 ºC and coupled to a Waters 996 photodiode array detector set at 210 nm. All the samples withdrawn from treated solutions were filtered with Whatman 0.45 μm PTFE filters. The analyses were carried out isocratically using a 5:95 (v/v) acetonitrile/water (0.1% H_3PO_4) mixture as mobile phase at 1.0 mL/min. The corresponding retention time (t_R) for bronopol was 9.8 min. Generated aliphatic carboxylic acids were identified and quantified by ion-exclusion HPLC using the same chromatograph, fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm, column at 35 ºC and the detector set at λ = 210 nm. A 4 mM H_2SO_4 solution eluted at 0.6 mL/min was used as mobile phase. In these chromatograms, a well-defined peak appeared at t_R = 13.6 min for formic acid. Inorganic anions accumulated in the electrolyzed solutions were determined by IC upon injection into a Shimadzu 10Avp LC, using an anion-exchange column (Text S2 in SI).

For a more complete identification of reaction products, GC-MS analysis was performed with an Agilent Technologies system composed of a 6890N gas chromatograph coupled to a

5975C mass spectrometer operating in EI mode at 70 eV. A non-polar Teknokroma Sapiens-X5ms and a polar HP INNOWax column, both of 0.25 µm, 30 m × 0.25 mm, were used (Text S3 in SI).

H_2O_2 concentration was determined from the light absorption of its Ti(IV) colored complex at λ = 408 nm, measured on a Shimadzu 1800 UV/Vis spectrophotometer at 25 ºC.[37] Active chlorine produced was determined by the *N*,*N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method (Text S4 in SI).[38] Quantitative analysis of soluble iron accumulated in electrocoagulated solutions was performed by inductively-coupled plasma (ICP-OES) using the Optima 3200L spectrometer.

The electrochemical characterization was carried out by linear sweep voltammetry (LSV) with an Autolab PGSTAT30 instrument (Text S5 in SI).

Solutions of 100-150 mL with 100 mg/L TOC (2.78 mM of bronopol) in 10 mM Na_2SO_4 or in the simulated water matrix were treated by single EC (at natural pH) and EAOPs (at pH 3.0). In EC, the effect of electrode material and pair number, interelectrode gap and applied current was thoroughly studied. In the EAOPs, pH was fixed at 3.0 because this was found as optimum for the EF treatment with air-diffusion cathode.[14] To perform the sequential EC/EF, EC-treated solutions were centrifuged for 5 min at high speed to easily withdraw the supernatant to be further treated by EF upon pH adjustment to 3.0.

RESULTS AND DISCUSSION

Separation and transformation ability of EC for bronopol solutions in simulated water. Once the stability of 2.78 mM bronopol solutions in simulated water and 10 mM Na_2SO_4 at natural pH as well as at pH 3.0 was verified for 480 min by TOC and HPLC measurements, we could establish that the changes occurring during the subsequent electrochemical treatments arise from specific phenomena different from hydrolysis or

decomposition that have been reported in natural water after a few days or weeks. A first series of EC experiments was then carried out aiming to find the most suitable anode and cathode materials. In the literature, it has been described that it does not exist a rule to ensure which material may provide larger decontamination for a given pollutant or wastewater. However, focusing on the anode selection, Fe and Al tend are considered as the materials of choice. SI Figure S1 shows the percentage of TOC removal reached at 60 min using different anode/cathode combinations with 1.0 cm of interelectrode distance for the EC treatment of bronopol in simulated water at natural pH and 200 mA. As can be seen in SI Figure S1a, the Fe/Fe pair yielded the greatest TOC removal among all electrode pairs under study (ca. 28%), being much larger than that obtained from other combinations. The use of stainless steel anodes could, in some case, yield around 20% of TOC abatement, whereas the worse results were achieved using an Al anode. Hence, it is clear that freshly formed amorphous iron hydroxide flocs, which are fractal and highly porous,[3] act as "sweep flocs" with large surface areas, being beneficial for a quick adsorption of soluble organic compounds contained in solution. Since bronopol is a charged molecule, electrostatic attraction may also contribute decisively to its enhanced removal, as demonstrated from additional chemical coagulation trials carried out independently using iron hydroxides. On the other hand, the larger tendency of pure Fe to become electro-oxidized to Fe^{2+}, compared to stainless steel anodes, explains its superior performance as the anode material, whereas the use of Fe cathode also favors the larger release of iron ions from its chemical dissolution. The value of the potential difference between the anode and cathode in each system, as well as the local passivation of the electrode surface (no evidences were provided by the potential differences), are also important parameters that may exert large influence on the release of metal ions and the consequent variation of ionic strength and formation of particle aggregates.

Another relevant finding comes from the only partial TOC removal. If bronopol tends to become electrocoagulated, as shown above, a much larger abatement would be expected since coagulants are continuously produced in the presence of Fe^{2+} and OH^- generated at the electrodes. The presence of nitrate ions, which are known to be detrimental for oxidizing an iron electrode, in the simulated water cannot justify the formation of a passive layer because their content is really low. The stabilization of TOC content from 60 min can thus be accounted for by the accumulation of oxidation/reduction by-products that are not readily coagulable and remain in solution, as will be further demonstrated below. In other words, it seems that EC cannot be simply considered a separation technology, but also a transformation one.

Note also that the fact that the Fe/Fe couple is the optimum one turns out to be beneficial because: (i) it allows polarity reversal at industrial scale, which prevents electrode scaling and fouling from organic layers, and (ii) iron ions accumulated in solution are the preferred ones for coupling Fenton-based post-treatments, as explained later. Hereby, the effect of experimental variables on EC using a Fe/Fe pair was studied with the same solution composition. Figure 1a depicts the influence of applied current and interelectrode distance using one single pair of electrodes, as well as the effect of the number of electrode pairs on percentage of TOC removal attained at 60 min. In all these trials, conductivity increased from 1.7 to ca. 2.3 mS/cm, whereas pH varied from 6.5 to 8.0-8.5. As can be observed, increasing percentage of TOC removal of ca. 14%, 17%, 28% and 30% were achieved at 50, 100, 200 and 300 mA, respectively, using one pair of electrodes at 1.0 cm. The expected trend is reached within the range 50-200 mA (apparent current density of ~ 5-20 mA/cm^2), since a current increase leads to a greater production of Fe^{2+} and OH^- that ends in larger amounts of coagulant $Fe(OH)_x$. Furthermore, a greater applied current enhances the generation of Cl_2 from Cl^- contained in the simulated water (10 mM) via eq 1. This species, along with

$HClO/ClO^-$ formed in the bulk upon Cl_2 dissolution, might potentially contribute to the transformation of bronopol into molecules with a lower ability to coagulate, as for example organochlorinated products.

$$2\ Cl^- \rightarrow Cl_{2(aq)} + 2\ e^- \quad (1)$$

A much less significant enhancement of decontamination was obtained by applying 300 mA. This can be explained by the excessive production of Fe^{2+} ions, which quickly form massive hydroxide particles without ideal size and porosity and thus, with no time to entrap an additional amount of organic matter. This hypothesis was ascertained from ICP measurements, which yielded only 0.8 mg/L of dissolved iron at 300 mA, whereas up to 11, 22 and 62 mg/L were accumulated at 200, 100 and 50 mA, respectively. Therefore, the optimal current value was 200 mA, ensuring the best dosage of coagulant species and favoring the best growth of aggregates formed between hydroxydes and organic molecules. Based on the anode weight loss upon the electrolysis at this current and according to Faraday's law, current efficiency for anode dissolution was 100%, which suggests a negligible contribution from O_2 evolution reaction.

The influence of the interelectrode distance was subsequently studied using the Fe/Fe couple at 200 mA. Figure 1a shows no amelioration at 2.0 and 3.0 cm, whereas a slightly higher TOC removal of 33% was reached at 4.0 cm. However, this occurred in concomitance with a significant increase of potential difference due to the larger ohmic drop, which is detrimental for future scale-up of this technology. A distance of 1.0 cm was considered to yield the most well-balanced EC treatment, being chosen to test the effect of the number of electrode pairs. Under the same conditions, the use of two Fe anodes and two Fe cathodes in parallel-plate arrangement yielded a very similar TOC abatement of 25% at 60 min. This confirms that, for the electrolytic cell employed in this study, such EC conditions are really preferable since they promote the most efficient formation of coagulants and oxidants. This

latter configuration with four electrodes was then preferred to pursue the investigation, being the most convenient at industrial scale because the anodes will exhibit longer service life due to their slower dissolution. Consequently, the cost related to maintenance and replacement will be significantly lower. Figure 1b shows the TOC vs time profile for the optimum EC treatment with two Fe pairs. As can be seen, TOC content decreases gradually, with no significant additional decontamination after 60 min. ICP measurements confirmed the accumulation of up to 11 mg/L of dissolved iron in the final solution, as explained above.

The vast majority of studies dealing with EC just focus on the evolution of the global organic matter content. Unfortunately, this gives an incomplete idea of the underlying mechanisms occurring in this process. Here, the time course of bronopol concentration during the optimum EC treatment of Figure 1b was evaluated by HPLC. Figure 2 reveals its total disappearance after 20 min, which demonstrates the ability of EC technology to transform the parent molecule into by-products that are accumulated in the solution bulk because they do not coagulate. Although Cl_2 accumulation from eq 1 is thought to be rather slow because current efficiency corresponding to anode dissolution is almost 100% under the adopted conditions, it can be plausibly stated that the main oxidants are: (i) active chlorine, which may promote the formation of chloroderivatives, and (ii) $^{\bullet}OH$ formed in the bulk from Fenton-like reaction between active chlorine (assuming the role of H_2O_2) and iron ions.[39,40] The formation of small amounts of weaker radical species like $HO_2^{\bullet}$, $H^{\bullet}$ and $Cl^{\bullet}$ upon homogeneous and heterogeneous reactions cannot be discarded either. In contrast, additional tests have revealed that neither Fe^{2+} nor Fe^{3+} ions are able to oxidize the parent compound. The oxidants are then able to convert bronopol into other molecules, but they are not powerful enough to further mineralize them, as confirmed from the stable TOC values after 60 min. The analysis of bronopol decay fits quite well to a pseudo-first-order kinetics, which would partly agree with

a constant generation of coagulant and oxidant species from electrode reactions that are directly controlled by applied current.

The disappearance of bronopol at 20 min was corroborated by GC-MS analysis. Bronopol (*m/z* 170, 152, 135), which was not detected after that time, yielded bromonitromethane and bromochloromethane as brominated products that were also removed within 20 min. Note that the formation of chloroderivatives confirms the partial contribution of active chlorine (C_2, $HClO/ClO^-$) to bronopol oxidation. Unlike many studies focused on the environmental fate of bronopol, the formation of 2-bromoethanol was discarded because it was not found by either HPLC or GC-MS. Although no brominated molecules were accumulated at the end of the EC treatment (60 min), GC-MS confirmed the presence of other organic by-products like formic acid and formaldehyde. The formation of the latter compound from bronopol has been reported elsewhere,[32,35,36,41] and it was verified from headspace analysis upon injection without solvent delay at near-ambient temperature, in order to avoid artifacts from GC-MS analysis.

The time course of Br^- ion during the same optimum EC trial depicted in the inset of Figure 2 agrees with the absence of organobrominated compounds after 20 min, as deduced from the gradual accumulation of Br^- along the electrolysis to attain the maximum value of 2.78 mM Br^- at that time, whereupon it remained constant. In addition, the treatment of a solution containing 2.78 mM NaBr instead of bronopol under analogous conditions informed about the stability of Br^- ion in this EC system, which suggests the direct release of the anion from oxidized organobrominated molecules, thus discarding BrO_3^- formation followed by cathodic reduction.

Effect of the anode material on the performance of electro-Fenton treatment of bronopol solutions. Once demonstrated that EC is not simply a separation process, it is interesting to compare its oxidation power with that of two widespread EAOPs, namely EO

with H_2O_2 electrogeneration (EO-H_2O_2) and EF. First, the electrolysis of simulated water at pH 3.0 was performed by EO-H_2O_2 and EF at 100 mA using an air-diffusion cathode and four different anodes in order to compare their ability to accumulate H_2O_2. SI Figure S2 shows the time course of H_2O_2 in EO-H_2O_2, which is < 7 mM at 480 min in all cases. This value is much lower than reported for analogous trials in 0.05 M Na_2SO_4 (i.e., > 15 mM) due to its partial destruction by active chlorine.[42] The largest accumulation was achieved with BDD anode, being much lower with Pt and IrO_2-based anodes. In experiments with the RuO_2-based anode, H_2O_2 became totally consumed by active chlorine, which agrees with the greater active chlorine concentration produced (1-3 mM). It is known that DSA-type anodes are well suited for electrochemical hypochlorite production from very dilute chloride solutions.[43] In contrast, BDD is usually preferred for treating organic pollutants, since it: (i) yields a higher H_2O_2 concentration that is beneficial for EF, and (ii) generates lower amounts of chlorinated radicals that are less oxidizing than hydroxyl radicals formed from eq 2. This anode has then been chosen to study the performance of EAOPs.

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \qquad (2)$$

The ability of EO-H_2O_2 and EF with a BDD/air-diffusion cell to degrade 2.78 mM bronopol was investigated in simulated water, as well as in 10 mM Na_2SO_4 to assess the effect of ion content and determine the fate of released Br^-. Figure 3a illustrates the mineralization ability of both EAOPs in two water matrices at 100 mA. All treatments were able to attain a TOC removal > 90% at 480 min, although two main conclusions can be drawn from these curves: (i) EF with 0.50 mM Fe^{2+} performs better than EO-H_2O_2, which is expected from the concomitant action of hydroxyl radicals formed at the anode surface from eq 2 and in the bulk from Fenton's reaction (eq 3), and (ii) the mineralization is slightly slower in the simulated matrix owing to the partial consumption of H_2O_2, Fe^{2+} and $^{\bullet}OH$/M($^{\bullet}OH$) by active chlorine, as well as to the formation of refractory chloroderivatives.[44]

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH \quad (3)$$

The electrochemical characterization by LSV revealed the absence of direct anodic oxidation of bronopol, since no peak appeared before O_2 evolution when using BDD, Pt or DSA as the working electrode. Therefore, hydroxyl radicals are the main oxidant species in trials of Figure 3. The same effects were observed for bronopol decay, as shown in Figure 3a, where EF treatment in Na_2SO_4 yielded the quickest destruction, although quite similar to that found in the other cases. Bronopol disappeared after ca. 300 min following a pseudo-first-order kinetics, with apparent rate constant increasing from 0.014 min^{-1} for EO-H_2O_2 in simulated water to 0.019 min^{-1} for EF in 10 mM Na_2SO_4. GC-MS analysis confirmed the disappearance of the parent pollutant at that time, as well as the formation of bromonitromethane as the main oxidation product. This and other minor compounds are responsible for the residual TOC after 300 min (Figure 3a).

The fate of Br contained in bronopol during the previous trials was investigated by IC. As an example, Figure 3c shows the time course of all inorganic anions during the EF treatment in 10 mM Na_2SO_4. From the early stages, released Br was accumulated as Br^- and BrO_3^-. Br^- concentration reached a maximum value of 0.6 mM at 60 min, whereupon it decreased until disappearing. Simultaneously, BrO_3^- concentration increased up to 2.78 mM at the end of the treatment. This suggests that Br is first released as Br^-, which is further oxidized to bromate by ${}^{\bullet}OH$/M(${}^{\bullet}OH$). This kind of conversion is similar to that of Cl^- to ClO_4^- and that reported under the action of sulfate radicals.[45,46] The formation of bromate can be basically explained by the attack of hydroxyl radicals, being Cl_2/ClO^- irrelevant as deduced from Br^- stability shown in the inset of Figure 2.[47] Note that, at 300 min, the sum of all brominated ions accounted for < 2.78 mM, which confirms the presence of organobrominated by-products until overall mineralization of bronopol solution at 480 min. On the other hand, the entire initial N is transformed into NO_3^-. Figure S3 in SI depicts the

analysis of inorganic anions for EO-H_2O_2. In none of these cases perbromate ions were formed.[48]

To gain further understanding on the behavior of Br^- ion upon application of EAOPs, the four kinds of anodes were used to treat 2.78 mM NaBr by EO-H_2O_2 and EF. From Figure S4a-d in SI, it can be concluded that the quick, total conversion of Br^- to BrO_3^- only occurs with BDD anode, with analogous trends in both EAOPs, thus suggesting that BDD($^{\bullet}$OH) is the main responsible for such transformation. Conversely, the other anodes yielded a much slower conversion, confirming the pivotal role of M($^{\bullet}$OH) to oxidize bromate. Solutions of 2.78 mM $KBrO_3$ were electrolyzed under the same conditions and informed about the total stability of BrO_3^-, which precludes the potential formation of Br^- from cathodic reduction, as also commented for EC.

Enhancement of mineralization of bronopol solutions by a sequential electrocoagulation/electro-Fenton treatment. Based on the evidences discussed so far, which confer a significant dual behavior to EC as a separation and transformation technology and corroborate the high oxidation power of EF to mineralize bronopol by-products, a sequential treatment was proposed.

A 2.78 mM bronopol solution, electrocoagulated in simulated water at natural pH under optimum conditions as in Figure 1b, was filtered to collect the supernatant. Afterwards, the solution pH was adjusted to 3.0 with $HClO_4$ to avoid introducing reactive ions. As can be seen in Figure 4a, TOC was 75 mg/L, whereas ICP measurements confirmed that dissolved iron concentration was 11 mg/L. The EF post-treatment was then carried out in an undivided cell equipped with an air-diffusion cathode and different anode materials at 100 mA. Pt, IrO_2-based and RuO_2-based anodes did not yield a significant TOC removal, which means that the electrocoagulated solution contained very refractory organic compounds. Furthermore, as shown in SI Figure S2, these three anodes yielded the lowest H_2O_2 concentration. Therefore,

not only the M(•OH) formed at these anodes are relatively weak oxidants, but the amounts of •OH formed in the bulk from Fenton's reaction are rather low. In contrast, EC/EF-BDD yielded an 85% TOC removal at 420 min of global treatment. This value is similar to that reported in This value is quite similar to that reported in Figure 3a for EF-BDD at the same time, which is very interesting from an application standpoint, when high organic loads and large volumes have to be treated. Under such conditions, EF finds it difficult to control the stability and progress of the treatment unless the solution to be treated is first diluted, since temperature rises steeply and gas evolves considerably.[49] Hence, EC would act as a convenient conditioning pre-treatment.

Figure 4b depicts the time course of the main reaction by-product accumulated during the sequential treatment with BDD. After 60 min of optimal EC, formic acid attains 43 mg/L, but this value increased during EF because other organic by-products were progressively oxidized to this acid. Its maximum concentration in EF is 79 mg/L, whereupon it gradually disappeared under the action of •OH and BDD(•OH). Note that other organic by-products are also accumulated in solution, since the maximum amount of formic acid only accounted for 21 mg/L TOC. Glycolic acid was reported in the literature,[36] but it was not formed during the present trials. Oxalic, tartronic, ketomalonic, acetic and malonic were not formed either.

Based on all the information, the reaction pathway for the degradation of bronopol in simulated water by the best sequential electrochemical treatment is proposed in Figure 5. The pollutant is transformed into bromonitromethane in EC, with release of formaldehyde. The former by-product can be converted into bromochloromethane by active chlorine, whereas formaldehyde is oxidized to formic acid, which remains in solution along with Br^- and NO_3^- at 60 min. Coupling EC and EF-BDD allows the gradual mineralization of both, formic acid to CO_2 and H_2O, and Br^- to BrO_3^-, under the action of hydroxyl radicals.

It is then evident from this article that, despite more than a century of technological development, some of the fundamentals of EC still remain unknown, which is mainly due to the purely heuristic approach.[50] Although the viability of EC has been proven even at industrial scale, gaining understanding on the mechanisms and reactivity will open the door to a more rigorous scale-up, with new devices like the sequential EC/EAOPs that is foreseen as a powerful solution to water treatment.

ASSOCIATED CONTENT

Supporting Information (SI) contains Text S1-S5, and Figures S1-S4. This information is available free of charge via the Internet at http://pubs.acs.org.

ACKNOWLEDGMENT

Financial support from project CTQ2013-48897-C2-1-R (MINECO, FEDER, EU), as well as from excellence network E3TECH under project CTQ2015-71650-RDT (MINECO) is acknowledged. The authors also thank financial support from MINECO under the FPI grant and the mobility grant EEBB-I-15-10094 to E. Bocos.

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Figure captions

Figure 1. (a) Effect of experimental variables (electrode pairs and interelectrode gap) on percentage of TOC removal vs. applied current for the EC treatment of 150 mL of 2.78 mM bronopol in simulated water at natural pH using Fe as the anode and cathode. (b) TOC abatement with electrolysis time for the optimum EC treatment with 2 Fe/Fe pairs separated 1.0 cm at 200 mA.

Figure 2. Time course of bronopol content for the optimum EC process shown in Figure 1b. The inset panel presents the evolution of Br^- concentration during the trial.

Figure 3. (a) TOC decay vs. electrolysis time for the EO-H_2O_2 and EF (with 0.50 mM Fe^{2+}) treatments of 100 mL of 2.78 mM bronopol in simulated water and in 10 mM Na_2SO_4 at pH 3.0 using a BDD/air-diffusion cell at 100 mA. (b) Bronopol concentration abatement and pseudo-first order kinetic analysis in the inset panel for the above assays. (c) Evolution of inorganic ions released during the above EF treatment with 10 mM Na_2SO_4.

Figure 4. (a) Variation of TOC with electrolysis time for solutions of 2.78 mM bronopol degraded by sequential treatment: EC (150 mL simulated water, natural pH, 2 Fe/Fe pairs separated 1.0 cm, 200 mA) followed by EF (100 mL, pH 3.0, 100 mA) with several anodes and an air-diffusion cathode. (b) Time course of formic acid detected during this sequential EC/EF-BDD process.

Figure 5. Reaction pathway for total bronopol mineralization by the best sequential treatment (EC/EF-BDD).

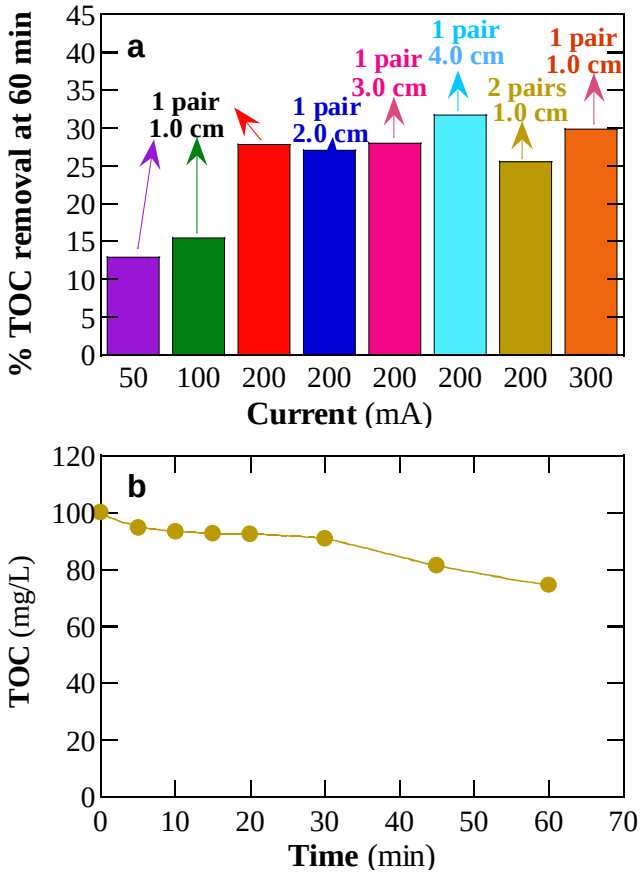
a
% TOC removal at 60 min
45
40
35
30
25
20
15
10
5
0
1 pair
1.0 cm
1 pair
2.0 cm
1 pair
3.0 cm
1 pair
4.0 cm
2 pairs
1.0 cm
1 pair
1.0 cm
50
100
200
200
200
200
200
300
Current (mA)
b
TOC (mg/L)
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
Time (min)

Figure 1

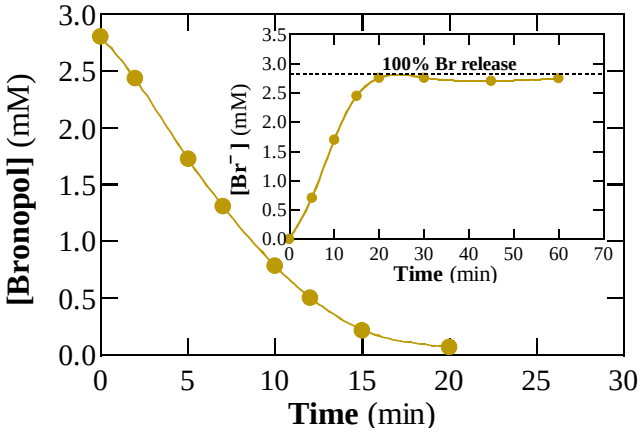

Figure 2

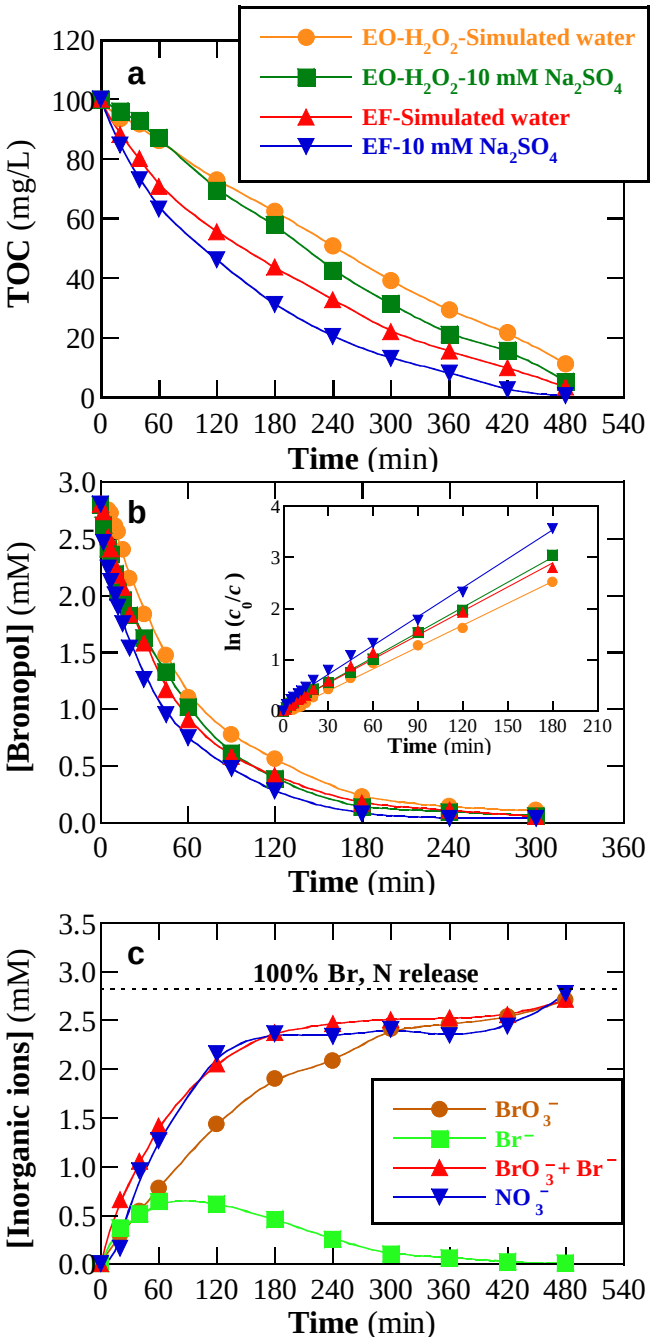
a
EO-H2O2-Simulated water
EO-H2O2-10 mM Na2SO4
EF-Simulated water
EF-10 mM Na2SO4
TOC (mg/L)
Time (min)
b
[Bronopol] (mM)
ln (c0/c)
Time (min)
c
100% Br, N release
BrO3−
Br−
BrO3− + Br−
NO3−
[Inorganic ions] (mM)
Time (min)

Figure 3

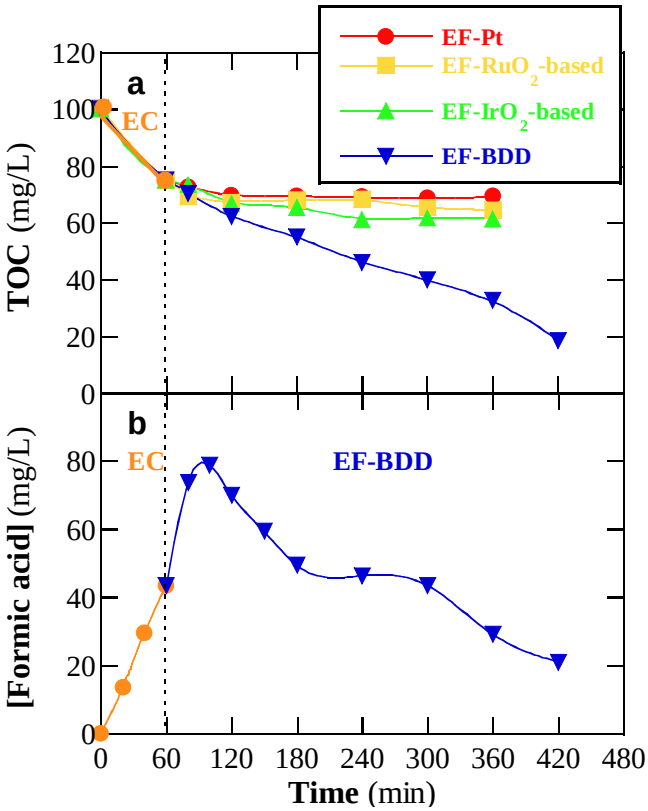
EF-Pt
EF-RuO2-based
EF-IrO2-based
EF-BDD
a
EC
TOC (mg/L)
120
100
80
60
40
20
0
b
EC
EF-BDD
[Formic acid] (mg/L)
80
60
40
20
0
0
60
120
180
240
300
360
420
480
Time (min)

Figure 4

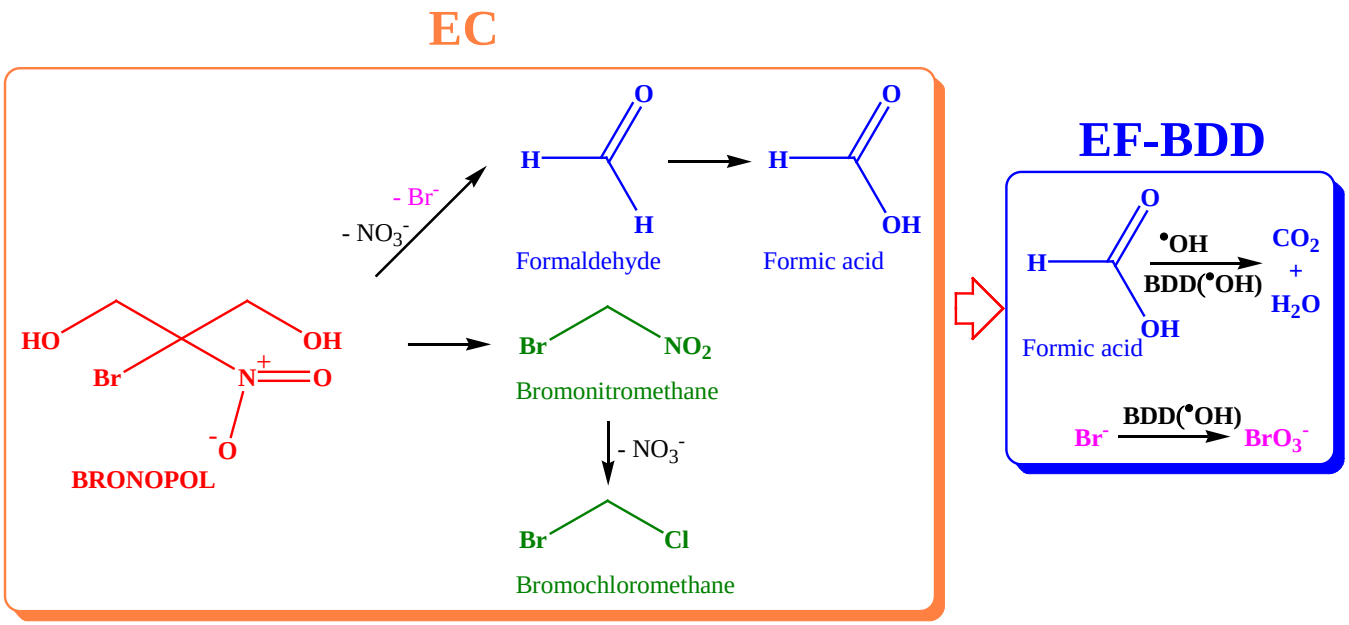
EC
HO
OH
Br
N
O
O
BRONOPOL
- Br-
- NO3-
H
O
H
Formaldehyde
H
O
OH
Formic acid
Br
NO2
Bromonitromethane
- NO3-
Br
Cl
Bromochloromethane
EF-BDD
H
O
OH
Formic acid
•OH
BDD(•OH)
CO2
+
H2O
Br-
BDD(•OH)
BrO3-

Figure 5