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Inactivation of microbiota from urban wastewater by single and sequential electrocoagulation and electro-Fenton treatments

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ABSTRACT

This work aims at comparing the ability of two kinds of electrochemical technologies, namely electrocoagulation (EC) and electro-Fenton (EF), to disinfect primary and secondary effluents from municipal wastewater treatment plants. Heterotrophic bacteria, *Escherichia coli*, enterococci, *Clostridium perfringens* spores, somatic coliphages and eukaryotes (amoebae, flagellates, ciliates and metazoa) were tested as indicator microorganisms. EC with an Fe/Fe cell at 200 A m^{-2} and natural pH allowed >5 log unit removal of *E. coli* and final concentration below 1 bacteria mL^{-1} of coliphages and eukaryotes from both effluents in ca. 60 min, whereas heterotrophic bacteria, enterococci and spores were more resistant. A larger removal was obtained for the primary effluent, probably because the flocs remove higher amount of total organic carbon (TOC), entrapping more easily the microbiota. EF with a boron-doped diamond (BDD) anode and an air-diffusion cathode that produces H_2O_2 on site was first performed at pH 3.0, with large or even total inactivation of microorganisms within 30 min. A more effective microorganism removal was attained as compared to EC thanks to $^{\bullet}OH$ formed from Fenton's reaction. A quicker disinfection was observed for the secondary effluent owing to its lower TOC content, allowing the attack of greater quantities of electrogenerated oxidants on microorganisms. Wastewater disinfection by EF was also feasible at natural pH (~7), showing similar abatement of active microorganisms as a result of the synergistic action of generated oxidants like active chlorine and coagulation with iron hydroxides. A sequential EC/EF treatment (30 min each) was more effective for a combined decontamination and disinfection of urban wastewater.

1. Introduction

Wastewater disposal through direct discharge into the aquatic environment entails potential risks for humans, animals and ecosystems due to the presence of chemical and microbiological contaminants. Among the challenges and priorities to 2030, the Sustainable Development Goals of United Nations (2015) include the improvement of water quality by eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and considerably increasing safe reuse globally. Nowadays, municipal wastewater treatment plants (WWTPs) substantially reduce the contaminants from influents, yielding effluents that are discharged to rivers or seas. However, water scarcity along with increasing population and intensification of agricultural and industrial activities have triggered the development of efficient methods to obtain safe reclaimed water for crop irrigation, aquifer recharge and drinking water production (Fernandez-Cassi et al., 2016).

Bacteria, viruses, protozoa and metazoa have been detected in urban wastewater and many of them are pathogens that cause diseases to living beings. These microorganisms are biologically and structurally different and hence, their inactivation depends on the applied treatment (Hijnen et al., 2006; Cervero-Aragó et al., 2015). The microbiological quality of treated water is normally assessed with indicators like fecal coliforms, but its validity to ensure the effectiveness of water treatment over viruses, protozoa or non-fecal bacteria is rather arguable (Ashbolt et al., 2001; Figueras and Borrego, 2010; Payment and Locas, 2011). Other indicators such as heterotrophic bacteria, enterococci, bacteriophages and adenovirus have been also considered. For example, Agulló-Barceló et al. (2013) proposed the spores of sulfite-reducing clostridia as indicators of *Cryptosporidium* total oocysts. Quality requirements of reclaimed water are usually regulated by national environmental protection agencies. In Spain, for example, 100 colony-forming unit (CFU) per 100 mL is the maximal content of *Escherichia coli* permitted for reuse in food crops, whereas

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200 CFU per 100 mL is the limit for urban unrestricted reuse (Real Decreto 1620, 7 December 2007).

Urban effluents reaching WWTPs are typically conveyed through a multistep process comprising: (i) a primary treatment to remove solid material, (ii) a secondary treatment to minimize the content of organic matter (OM) and microorganisms and (iii) a tertiary process for disinfection and destruction of trace organics. Often, the secondary treatment consists of a biological method that requires large areas and long residence times, whereas the tertiary treatment involves chlorination or UV irradiation (Martínez-Huitle and Brillas, 2008; Montemayor et al., 2008; Souza et al., 2013). Electrochemical disinfection can be an interesting alternative because it is more eco-friendly and cost-effective (Ghernaout and Ghernaout, 2010), being electrocoagulation (EC) and electro-Fenton (EF) two of the most promising technologies for this purpose.

EC involves the *in situ* generation of coagulants by electrochemical oxidation of a sacrificial anode (iron or aluminum) in an undivided cell. The released metal ions are further transformed into hydroxides that neutralize charges or act as sweep flocs with large surface areas and hence, they foster their aggregation or precipitate as a sludge, adsorbing the dissolved pollutants (Ghernaout and Ghernaout, 2012; Ghernaout, 2013). Using Fe as the anode, for example, Fe^{2+} is formed from Reaction (1) and in the presence of dissolved O_2 gas is converted into Fe(III) from the global Reaction (2) (Barrera-Díaz et al., 2014; Brillas and Martínez-Huitle, 2015). H_2 is formed at the cathode from water reduction by Reaction (3). $Fe(OH)_2(s)$ at pH > 5.5 and $Fe(OH)_3(s)$ from pH > 1.0 act as: (1) coagulants that remove particles by surface complexation or electrostatic attraction and (2) flocculants that eliminate particles by sweep flocculation (Ghernaout and Ghernaout, 2012**).**

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$4Fe + 10H_2O + O_2(g) \rightarrow 4Fe(OH)_3(s) + 4H_2(g) \quad (2)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \quad (3)$$

The EF process is based on the electrogeneration of H_2O_2 by two-electron reduction of O_2 gas at a carbonaceous cathode like a carbon-polytetrafluoroethylene (PTFE) air-diffusion electrode (Sirés et al., 2014; Moreira et al., 2017), via Reaction (4). This method is very effective when a small quantity of Fe^{2+} (<1 mM) is added to the effluent to react with H_2O_2 yielding Fe^{3+} and $^{\bullet}OH$ from Fenton's Reaction (5) at optimum pH ca. 3 (El-Ghenymy et al., 2015; Thiam et al., 2015, 2016). $^{\bullet}OH$ is a very strong oxidant with ability to mineralize most organics (Sirés et al., 2014). Additionally, in an undivided cell at high current, organics and microorganisms are also destroyed by physisorbed hydroxyl radical M($^{\bullet}OH$) produced from water oxidation at the surface of a large O_2-overvoltage anode M such as boron-doped diamond (BDD) by Reaction (6). BDD thin-film electrodes are the best anodes for EF due to the high activity of BDD($^{\bullet}OH$) (El-Ghenymy et al., 2015; Bruguera-Casamada et al., 2016, 2017).

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (5)$$

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (6)$$

Urban wastewater contains a large amount of SO_4^{2-} and Cl^- (Thiam et al., 2016). These ions can be oxidized at the BDD anode to yield other oxidants like peroxodisulfate ($S_2O_8^{2-}$) from Reaction (7) and active chlorine (Cl_2/HClO/ClO^-) from Reactions (8)–(10) (Thiam et al., 2015; Steter et al., 2016). Recent work has shown that active chlorine can be formed during EC treatments (Ghernaout et al., 2011; Bocos et al., 2016), which may cause the formation of toxic disinfection by-products (DBPs).

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (7)$$

$$2Cl^- \rightarrow Cl_2(aq) + 2e^- \quad (8)$$

$$Cl_2(aq) + H_2O \rightarrow HClO + Cl^- + H^+ \quad (9)$$

$$HClO \leftrightarrows ClO^- + H^+ \; pK_a = 7.56 \quad (10)$$

Several authors have applied EC with Fe or Al anodes to disinfect urban effluents from WWTPs, finding a total removal (>99.99%) of *E. coli* (Ghernaout et al., 2008; Cotillas et al., 2013; Llanos et al., 2017), total coliforms (Elazzouzi et al., 2017; Makwana and Ahammed, 2017) or *S. aureus* (Valero et al., 2017). Durán Moreno et al. (2004) also found an overall removal of total coliforms, *E. coli*, *Shigella* and *Salmonella* sp. from municipal wastewater at the end of EC with H_2O_2 addition, so-called EF by these authors. However, an exhaustive study on the evolution of urban wastewater microbiota during EC or EF has not been reported so far. Furthermore, the feasibility of a sequential EC/EF treatment has only been explored to remove organic matter, turbidity and total suspended solids from synthetic and urban wastewater (Daghrir and Drogui, 2013; Thiam et al., 2014).

This paper aims to assess the ability of EC with an Fe/Fe cell, EF with a BDD/air-diffusion cell and a sequential EC/EF process to inactivate microorganisms contained in real urban wastewater collected from primary and secondary WWTP clarifiers. Considering the microbiological complexity of both effluents, heterotrophic bacteria, *E. coli*, enterococci, *C. perfringens* spores, somatic coliphages and eukaryotes were selected as indicators. The decay of microorganism content over electrolysis time was determined at constant current density (*j*) to clarify if the sequential EC/EF treatment is potentially beneficial to disinfect urban wastewater.

2. Materials and methods

2.1. Urban wastewater

Urban effluents were obtained from a WWTP located in Reus (Spain). Several sets of fresh samples were collected on different days from the primary treatment effluent as well as from the secondary treatment (i.e., activated sludge) effluent. These effluents were selected to assess the influence of different OM content on microorganism abatement in the EC, EF and sequential EC/EF processes tested. They were introduced in sterile containers, transported to the laboratory in larger isothermal containers at 4 °C, microbiologically characterized within 24–48 h after collection and stored at 4° C. Tests revealed the presence of bacteria, bacteriophages, spores and protozoa. To ensure the detection of protozoa, the secondary effluent sample was doped with 5% of the treatment plant

sludge, which did not alter substantially the number of bacteria and bacteriophages.

2.2. Microbial enumeration

In EC, microbiota concentrations were determined after separation of the sludge formed, whereas no filtration was required in EF. Heterotrophic bacteria were quantified upon 10-fold dilution with ¼-strength Ringer's solution and culture by duplicate on Plate Count Agar (PCA) from Scharlab (Spain) at 37 °C for 48 h (Serrano-Suárez et al., 2013), according to ISO 9308-2:2012. The theoretical detection limit was 1 CFU mL^{-1}. *E. coli* and enterococci were quantified by most probably number (MPN) using 4-methylumbelliferyl-beta-*d*-glucuronide (MUG)/EC and 4-methylumbelliferyl-β-D-glucopyranoside (MUD)/SF Kit 96-well microplates from Bio-Rad Laboratories, respectively, both incubated at 42 °C for 48 h, following ISO 9308-2:2012. The theoretical detection limit was 0.35–1.35 bacteria mL^{-1}. Spores of *Clostridium perfringens* (sulfite-reducing clostridia) were quantified after heating the sample at 80 °C for 10 min, followed by mixing with liquefied sulphite polymyxin sulphadiazine (SPS) Agar from Scharlab. Samples were incubated at 44 °C for 24 h, following ISO 7939. The theoretical detection limit was 1 spore mL^{-1}. Somatic coliphages were quantified by cell lysis using a double-layer counting method with *E. coli* WG5, according to ISO 10705-2. The theoretical detection limit was 1 lysis calve per mL.

Eukaryotes were analyzed by microscopy using a Leitz Dialux20 microscope. Two Eppendorf tubes with 1 mL sample were centrifuged at 1500 rpm for 10 min. Supernatants were discharged and the pellets (about 200 μL each) were analyzed by microscopy. Abundance of active protozoa (such as amoebae, flagellates and ciliates) and metazoa was counted from 100 μL samples by successive 25 μL replicates in vivo at 100 × magnification. When small flagellates (<20 μm) and amoebae (<20 μm) were abundant enough, they were counted at 400 × magnification and, for each replicate, 30 microscopic fields on the coverslip (20 mm × 20 mm) were taken. The counts were carried out using well-homogenized samples. Protozoan species were identified at different levels: ciliates were determined as species level (Foissner et al., 1994; Curds et al., 2008), whereas flagellates (Lee et al., 2000) and amoebae (Page, 1988) were grouped according to their size and morphology. Note that the groups of amoebae cannot be considered as taxa since they might be composed of several amoebae belonging to diverse lineages (Page, 1988).

2.3. Electrochemical systems

The EC assays were carried out in an undivided cylindrical tank reactor containing 200 mL of primary or secondary effluent kept at 25 °C thanks to a thermostatically-controlled water bath. The anode and cathode were 10 cm^2 Fe plates separated 1 cm. In these trials, a $j = 200$ A m^{-2} was always applied. The EF experiments were conducted in a similar undivided cell with 100 mL of each wastewater after addition of 0.25 mM $FeSO_4{\cdot}7H_2O$ (>99% purity, Sigma-Aldrich), except in EC/EF runs. The cell was equipped with a 3 cm^2 BDD thin-film electrode over Si substrate from NeoCoat (Le-Chaux-de-Fonds, Switzerland) and a 3 cm^2 carbon-PTFE air-diffusion electrode from Sainergy Fuel Cell (Chenai, India), separated about 1 cm. The cathode was mounted as described elsewhere (El-Ghenymy et al., 2015) and was fed with air flowing at 1 L min^{-1} to produce H_2O_2. A $j = 333$ A m^{-2} was employed for all the EF runs. The wastewater was always vigorously stirred at 800 rpm with a magnetic PTFE bar. The constant current in all the electrolyses was provided by an Amel 2053 potentiostat-galvanostat, using a Demestres 601BR digital multimeter for the direct measurement of the cell voltage. Before the EC assays, the Fe surfaces were mechanically abraded using SiC paper, followed by cleaning with 0.1 M H_2SO_4 solution and final ultrasonic cleaning in Milli-Q water. Before the EF runs, the BDD surface was cleaned and the air-diffusion cathode was activated by polarization in 0.050 M Na_2SO_4 at $j = 1000$ A m^{-2} for 180 min.

After each trial, the cell was cleaned with a H_2O_2:H_2SO_4 mixture for 10 min, rinsed with Milli-Q water and dried in an oven at 80 °C. The Fe and BDD electrodes were immersed in Milli-Q water at 100 °C for 10 min and dried under an air stream. The air-diffusion cathode was cleaned with a 1:3 (v/v) H_2O:HCl mixture and rinsed with Milli-Q water followed by air-drying. For EF at pH 3.0, $HClO_4$ was used to adjust the pH in order to maintain the content of reactive SO_4^{2-} and Cl^- ions in the urban effluents. Samples withdrawn from the treated effluents were adjusted to pH near 7 by adding 1 M NaOH solution to minimize the effect of low pH during microorganism culture. The pH was adjusted to about 7 with 1 M H_2SO_4 after the EC step prior to the sequential treatment with EF.

2.4. Analytical methods

The solution pH was measured with a Crison GLP 22 pH-meter and the electrical conductance was determined with a Metrohm 644 conductometer. Total organic carbon (TOC) analysis of samples was carried out with a Shimadzu TOC-VCNS analyzer. Reproducible values with an accuracy of ±1% were found by injecting 50 μL aliquots, which were previously filtered with 0.45 μm filters from Whatman, into the analyzer.

The inactivation profiles for all microorganisms were determined from the decay of their log (N_t/N_0), where N_t and N_0 denote their concentration at time t and 0, respectively. The microorganism content is given as the mean value from two independent trials, and the graphs also show the error bars that account for a 95% confidence interval.

3. Results and discussion

3.1. Electrocoagulation

The EC assays were performed with 200 mL of the primary and secondary effluents using a stirred Fe/Fe tank reactor at $j = 200$ A m^{-2} for 90 min. The initial pH of 7.54 ± 0.16 rose continuously up to a final value of 9.08 ± 0.27, whereas the conductivity remained practically unchanged, varying between 2.50 and 2.04 mS cm^{-1}.

Fig. 1a and b highlights an uneven disappearance of the different microorganisms during the treatment of both wastewater samples. Somatic coliphages were the less persistent organisms, being undetectable after 20 min in both matrices, followed by the eukaryotes, whose content decreased substantially at that time with total disappearance at 60 min. In contrast, the concentration of heterotrophic bacteria decayed to ~10^3 CFU mL^{-1} in 90 min, corresponding to a reduction of 3.66 and 2.81 log units for the primary and secondary effluents, respectively. Fig. S1 reveals a quick removal of such bacteria in both matrices during the first 10 min of EC, followed by a slower concentration decay until the end of the electrolysis. A similar trend was found for all the other bacteria analyzed. In all cases, a larger content reduction was obtained for the primary effluent compared to the second one, probably because of its higher amount of microbiota and the presence of a larger amount of organic matter with ability to be coagulated and adsorb microorganisms. The removal process was usually stabilized after 30–40 min of electrolysis, whereupon no further microorganism abatement was achieved.

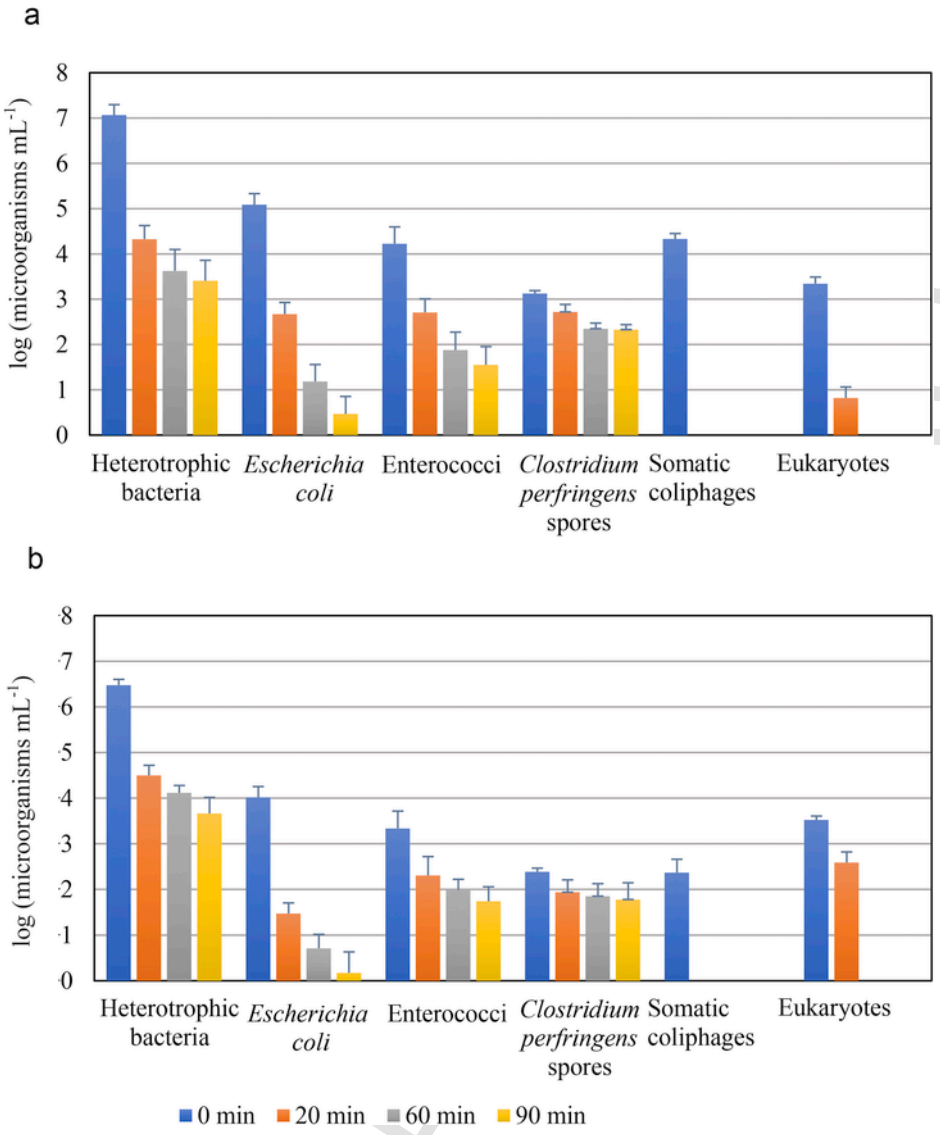

Fig. 1. Variation of the logarithm of concentration of heterotrophic bacteria, *Escherichia coli*, enterococci, *Clostridium perfringens* spores, somatic coliphages and eukaryotes with electrolysis time upon electrocoagulation (EC) of 200 mL of (a) primary and (b) secondary effluents using an undivided Fe/Fe cell (electrodes with 10 cm^2 area) at current density (*j*) of 200 A m^{-2} and 25 °C.

On the other hand, almost complete abatement of *E. coli* was attained, with a strong reduction of 4.62 log units in the primary effluent and 3.84 log units in the secondary effluent. It was the less persistent bacterium to EC among those tested. Much poorer decay of 2.68 and 1.60 log units in such media was found for enterococci. Worth noting, *C. perfringens* spores became the most resistant target, with a decay as low as 0.80 and 0.61 log units in the primary and secondary effluents, respectively. Finally, the large influence of EC on the eukaryotic community, as depicted in Table 1, is also noticeable, with no apparent activity of all these microorganisms after 60 min of electrolysis. The presence of eukaryotes was somewhat longer when treating the secondary effluents. At 5 min, only some flagellated volvocales could not be removed from the primary effluent, whereas all kinds of eukaryotes still remained in the second one despite their strong content drop. At 20 min, only amoebae could not be abated substantially in the latter effluent.

Despite the large disappearance of all the microbiota under study, TOC content underwent a rather discrete removal for both kinds of wastewater upon EC treatment. Fig. 2 shows that TOC decayed 17.6 mg L^{-1} (24.6% of the initial 71.4 mg L^{-1}) for the primary effluent and 5.5 mg L^{-1} (35.2% of the initial 15.6 mg L^{-1}) for the secondary one. The relatively larger decontamination of the latter wastewater can be related to its smaller organic load, which is pre-eminently removed by precipitation over the $Fe(OH)_n$ flocs originated during the treatment at the same *j* value.

Additional analyses were made with the sludge collected during the EC treatments, confirming that a small proportion of coagulated microorganisms were still active. This suggests their adhesion with encapsulation on the flocs formed, as recently reported by Delaire et al. (2016). The successful disinfection of sewage water samples is in accordance with the results obtained by other authors using EC with different anodes at other applied currents. For example, Ghernaout et al. (2008) described a large abatement of *E. coli* and algae from surface water with aluminum, stainless steel and common steel anodes. Bacteria removal in surface water (Ricordel et al., 2010) and in model solutions (Ricordel et al., 2014) using aluminum anode has

Table 1
Time course of eukaryotic community (in microorganisms mL^{-1}) during the treatment of primary and secondary effluents by electrocoagulation (EC) and electro-Fenton (EF). EC was carried out in an undivided Fe/Fe cell with electrodes of 10 cm^2 area at j = 200 A m^{-2}, whereas EF was performmed at pH 3.0 or close to 7 (natural pH) using an undivided BDD/air-diffusion cell with electrodes of 3 cm^2 area at j = 333 A m^{-2}. Temperature was kept at 25 °C in all trials.

Eukaryote	Primary effluent				Secondary effluent			
EC	0 min	5 min	20 min	60 min	0 min	5 min	20 min	60 mi
Amoebae	70	<1	<1	<1	597	296	101	<1
Flagellates	2190	362	4	<1	1540	48	<1	<1
Ciliates	34	<1	<1	<1	798	467	1	<1
Metazoa	2	<1	<1	<1	29	10	5	<1
EF pH *3.0*	Raw	0 min	10 min	30 min	Raw	0 min	10 min	30 mi
Amoebae	3	1	<1	<1	3540	20	<1	<1
Flagellates	100	<1	<1	<1	13,800	3480	<1	<1
Ciliates	17	3	3	<1	476	131	<1	<1
Metazoa	2	1	<1	<1	12	4	<1	<1
EF natural pH	0 min	5 min	10 min	30 min	0 min	5 min	10 min	30 mi
Amoebae	3	3	<1	<1	30	<1	<1	<1
Flagellates	640	620	<1	<1	220	<1	<1	<1
Ciliates	8	<1	<1	<1	64	<1	<1	<1
Metazoa	40	40	30	<1	14	<1	<1	<1

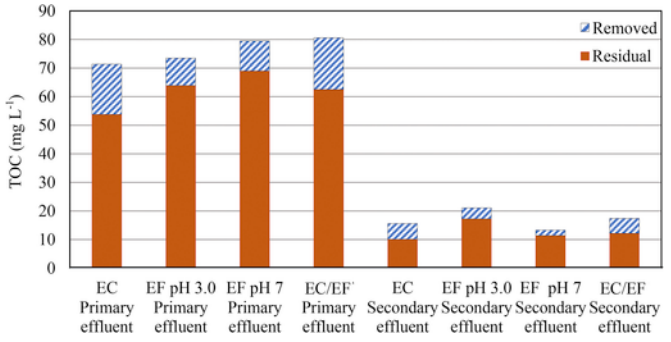

Fig. 2. TOC removed and residual upon different treatments: EC of 200 mL of primary and secondary effluents at j = 200 A m^{-2} for 90 min; electro-Fenton (EF) of 100 mL of the same wastewater samples at pH 3.0 and pH~7 using an undivided BDD/air-diffusion cell (electrodes with 3 cm^2 area) at j = 333 A m^{-2} and 25 °C for 30 min; two-step EC/EF processes for 30 min each.

been reported as well. The quick reduction for somatic coliphages agrees with the results of Zhu et al. (2005) for MS2, a kind of coliphage, spiked into simulated natural water and treated by EC and membrane microfiltration.

3.2. Electro-Fenton at pH 3.0

Urban wastewater was then treated by a technology of transformation like EF, firstly at its theoretically optimum pH of 3.0, with addition of 0.25 mM Fe^{2+}. To do this, the pH of the primary and secondary effluents was adjusted with an inert acid like $HClO_4$ to preserve the content of reactive SO_4^{2-} and Cl^- ions. The assays were made with 100 mL of each effluent using a stirred BDD/air-diffusion cell at j = 333 A m^{-2} for 30 min. Microbial quantifications were carried out for the raw samples before acidification as well as for conditioned ones (pH = 3.0 and Fe^{2+} addition) to discard any substantial effect of pre-electrolysis steps. In these trials, the pH of both kinds of wastewater dropped up to 2.79 ± 0.13, suggesting the formation of acidic products from organic matter (Sirés et al., 2014). However, Fig. 2 illustrates the occurrence of a very low TOC abatement of 9.6 mg L^{-1} (13.1% of the initial 73.5 mg L^{-1}) for the primary effluent and 3.8 mg L^{-1} (18.0% of the initial 21.1 mg L^{-1}). A lower decontamination was then achieved by EF compared to EC, where the organic matter was separated from the effluent by entrapment on iron hydroxides. This means that urban wastewater contained very recalcitrant organic pollutants that were very slowly destroyed and mineralized by oxidants like H_2O_2, BDD($^{\bullet}OH$), $^{\bullet}OH$, $S_2O_8^{2-}$ and active chlorine formed from Reactions (4)–(9).

Fig. 3a and b shows the decrease of microbiota concentration by EF at pH 3.0 in both aqueous matrices, which became much more effective than the corresponding EC treatments (see Fig. 1a and b). This can be related to the different inactivation mechanisms in both processes, involving the lysis of the cell walls caused by the attack of the generated oxidizing species in EF (Bruguera-Casamada et al., 2016, 2017) instead of the entrapment of cells onto the flocs produced in the previous EC cell. Note that direct killing of cells by the electrical field applied is also feasible (Ghernaout, 2017). Note also that under EF conditions at pH 3.0, no flocs of iron hydroxides are formed and no microbiota coagulation takes place. After 30 min of EF, for example, the concentration of heterotrophic bacteria was below 10 CFU mL^{-1}, with decays of 3.62 and 3.97 log units for the primary and secondary effluent, respectively. Fig. S2 highlights certain effect of acidic conditions (pH 3.0) on heterotrophic bacteria since control tests without current supply showed an inactivation of about 1.20 ± 0.06 log units for both samples. This value was much lower than the one reached in EF process, thus corroborating the important role of inactivation with generated oxidants. In contrast to the apparently analogous behavior of microorganisms in both water matrices found in EC (see Fig. S1), Fig. S2 shows a quicker disappearance of heterotrophic bacteria in the secondary effluent. This trend can be accounted for by the smaller organic load of that wastewater, which therefore enhances the attack of oxidizing species over the microbiota since they are produced at similar rate in both samples operating at the same j = 333 A m^{-2}.

Fig. 3a and b depicts the total inactivation of enterococci and somatic coliphages, always in less than 10 min. Similarly, *E. coli* was completely inactivated in the secondary effluent, whereas it persisted longer time in the primary one although it was already inactive at 30 min. As in the case of EC, the most resistant microorganisms were the *C. perfringens* spores in both EF trials. Worth noting, greater decays of 2.10 and 1.60 log units were obtained for the treatment of primary and secondary effluents, respectively.

The above trends agree with those described by Durán Moreno et al. (2004) for the inactivation of *E. coli* by EF using sewage water. Nevertheless, our results are better to those reported by Aziz et al. (2013), who only found a 3-log units drop of coliform content from landfill leachate by EF.

On the other hand, a look at Table 1 allows inferring a very substantial effect of acidic pH on the eukaryotic community. A comparison between the two raw effluents and the two conditioned ones informs about a survival <50% in all cases. Among ciliates, only *Peritrichia* belonging to the genera *Opercularia* and *Vorticellides* survived, whereas persistent metazoa were rotifers belonging to different groups present in the control with *Philodinidae* in the primary effluent and some *Lecanidae* in the secondary one. Finally, a drastic inactivation of all eukaryotes after 10 min of EF can be observed in Table 1, with the exception of the ciliate *Opercularia microdiscum*. Note that this microorganism belongs to a genus of ciliates with high resistance to stress conditions caused by toxics in activated sludge processes (Madoni, 1994).

3.3. Electro-Fenton at natural pH

The EF process is expected to be optimal at pH 3.0 because it produces the highest quantity of the strong oxidant $^{\bullet}OH$ from Fenton's

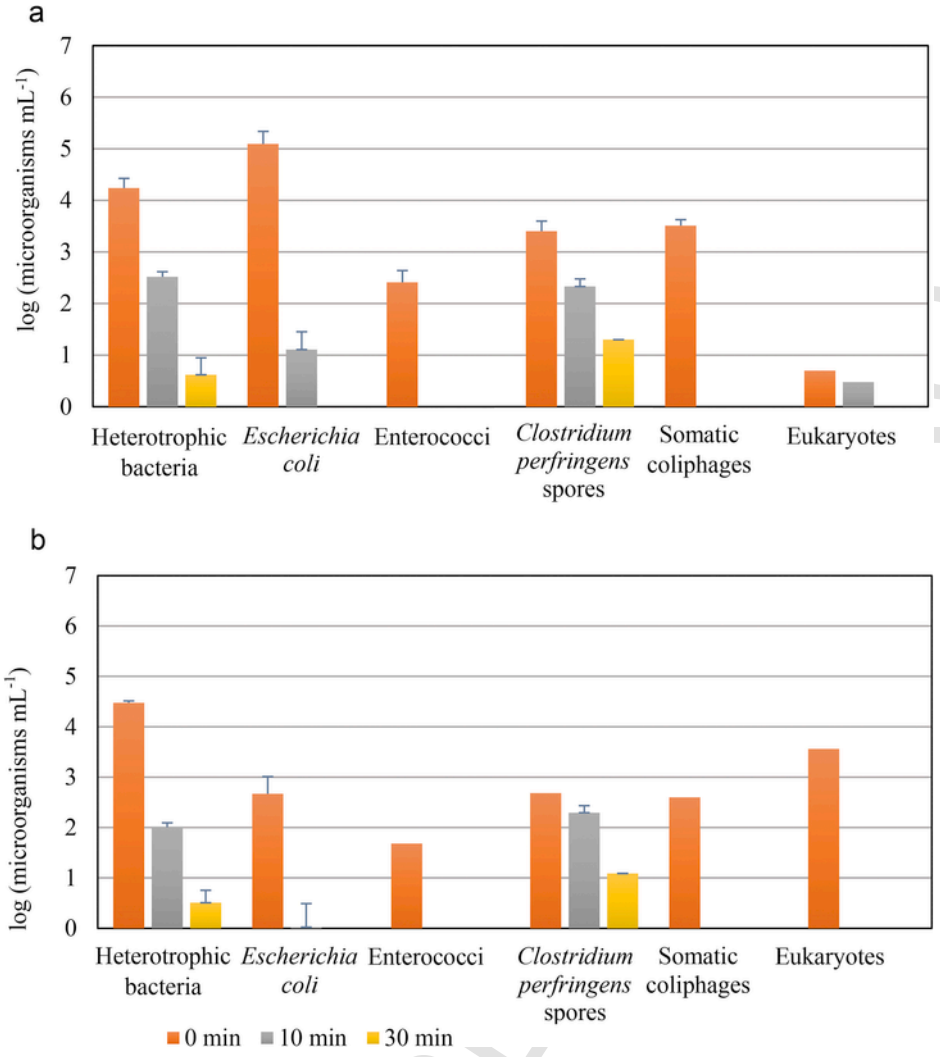

Fig. 3. Change of the logarithm of the concentration of the same microorganisms of Fig. 1 along 30 min of EF treatment of 100 mL of (a) primary and (b) secondary effluents at pH 3.0 and $j = 333$ A m^{-2}.

Reaction (5) (Sirés et al., 2014; Brillas and Martínez-Huitle, 2015). Nevertheless, although a lower amount of $^{\bullet}$OH is generated at eco-friendly near-neutral pH, the disinfection role of the other oxidants like H_2O_2, BDD($^{\bullet}$OH), $S_2O_8^{2-}$ and active chlorine, along with iron hydroxides formed at pH~7, may be sufficient. The main aim of this approach was to draw conclusions for further use of the process in a two-step treatment of urban wastewater, as will be discussed in section 3.4.

The EF treatments of 100 mL of the primary and secondary effluents were carried out at natural pH under the same conditions described at pH 3.0, i.e., after addition of 0.25 mM Fe^{2+} in a stirred BDD/air-diffusion cell operated at $j = 333$ A m^{-2} for 30 min. In these cases, the Fe^{2+} content was hardly soluble at the initial pH of 7.18 ± 0.07, which slightly increased up to 7.39 ± 0.19. No substantial variation in conductivity of 2.70 ± 0.25 mS cm^{-1} was observed. The data of Fig. 2 corroborate the decontamination ability of EF at near-neutral pH, with final TOC removal of 10.5 mg L^{-1} (13.2% of the initial 79.5 mg L^{-1}) for the primary effluent and 1.9 mg L^{-1} (14.2% of the initial 13.3 mg L^{-1}) for the secondary one. Similar TOC abatement was then achieved at pH 3.0 and neutral pH, suggesting that oxidants like active chlorine can play an important role in EF regardless of the solution pH (Thiam et al., 2015; Steter et al., 2016).

Fig. 4a and b depicts the excellent disinfection power of EF at neutral pH, giving rise to a remarkable decrease of the content of all microorganisms contained in the two wastewater samples. After 30 min of treatment, the heterotrophic bacteria concentration diminished 4.12 log units in the primary effluent and 3.20 log units in the secondary one. Note that in the former case, the decay was even superior to that obtained by EC and EF at pH 3.0. The decay profile of these bacteria shown in Fig. S3 demonstrates the large effect of the electrolysis during the first 10 min, whereupon the disappearance was strongly decelerated. The enhanced abatement found in the primary wastewater matrix is noteworthy since it is contrary to the behavior obtained in EF at pH 3.0 (see Fig. S2). This behavior suggests that, apart from the important oxidative action of active chlorine that accounts for a large inactivation, as pointed out above, the formation of iron hydroxides at neutral pH has a key role as well. As mentioned in section 3.1, coagulation with such hydroxides is more effective for the primary wastewater due to the larger TOC content, with ability to be precipitated and entrap the microorganisms. The formation of such precipitate counteracts the lower generation of $^{\bullet}$OH, leading to a superior performance of EF at pH~7 compared to that at pH 3.0.

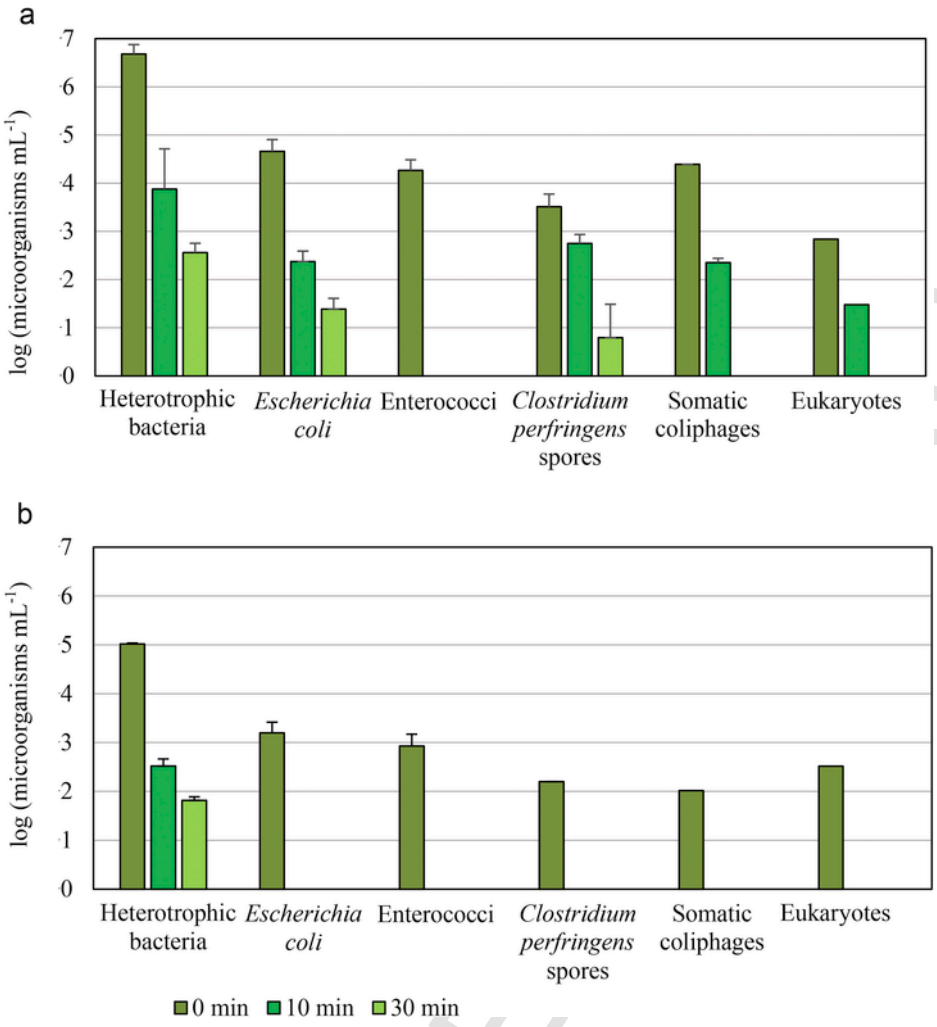

Fig. 4. Variation of the logarithm of the concentration of the same microorganisms shown in Fig. 1 upon EF treatment of 100 mL of (a) primary and (b) secondary effluents at neutral pH (~7) and $j = 333$ A m^{-2}.

Fig. 4a also shows the rapid and total disappearance of enterococci and somatic coliphages in the primary effluent, being the most sensitive microbiota as found in EC and EF at pH 3.0. In contrast, *E. coli* and the spores of sulfite-reducing bacteria persisted at the end of EF at near-neutral pH, as occurs with heterotrophic bacteria, with reductions of 3.27 and 2.72 log units, respectively. A different behavior can be observed in Fig. 4b for the secondary wastewater, where all the microbiota tested completely disappeared in less than 10 min, probably because of their much lower concentration compared to that in the primary effluent. These results were much better than those found by EC (see Fig. 1b) and EF at pH 3.0 (see Fig. 3b).

The data of Table 1 for EF at near-neutral pH reveal a total decay of the eukaryotic community in less of 5 min for the secondary effluent. In contrast, most of the eukaryote bacteria persisted until 5–10 min for the primary one. In particular, high contents of flagellates were detected at 5 min, which belonged to two groups of *Euglenozoa*, the *euglenidae bodonidae*. In the case of metazoa, the nematodes were the most resistant for 10 min, but they were undetectable at 30 min.

All the above findings indicate that EF at natural pH can be effective for the disinfection of urban wastewater, particularly for secondary effluents. From this, the performance of a sequential EC/EF process was investigated for both effluents, as discussed below.

3.4. Electrocoagulation/electro-Fenton without pH adjustment

As shown above, EC has greater ability than EF to remove organic matter, whereas EF is superior to disinfect both effluents. Since the maximum microbial removal observed in EC trials was already attained at 20–60 min, the sequential treatment was performed by selecting a duration of 30 min for the initial EC step, which was performed with 200 mL samples using a stirred Fe/Fe cell at $j = 200$ A m^{-2}. The subsequent EF treatment of 100 mL of the supernatant liquid, which already contained soluble iron ions formed in EC, usually <3 mg L^{-1} (Thiam et al., 2014), was performed for 30 min as well, using a stirred BDD/air-diffusion tank reactor at $j = 333$ A m^{-2}. In the former step, the pH of both wastewater samples increased from 7.37 ± 0.04 to 8.78 ± 0.09, which was adjusted to 7 with H_2SO_4 in order to apply EF, ending in a pH = 6.54 ± 0.17. The conductivity of both effluents changed slightly during the sequential treatment, from 2.55 ± 0.15 mS cm^{-1} to a final value of 2.72 ± 0.14 mS cm^{-1}. Somatic coliphages and eukaryotes were not analyzed in these assays because they were the most sensitive microbiota to EC, becoming undetectable at the end of such treatment (see Fig. 1a and b, and Table 1).

As expected from single treatments discussed above, Fig. 2 evidences a quite poor TOC removal for the sequential EC/EF, with an abatement of 18.1 mg L^{-1} (22.5% of the initial 80.6 mg L^{-1}) in the primary effluent and 5.2 mg L^{-1} (29.9% of the initial 17.4 mg L^{-1}) in the second one. These values differ from those reported by Lucena et al. (2004), who described a very high TOC abatement of about 90% for a secondary treatment of urban wastewater with conventional activated sludge, although they reached a very weak disappearance (1.5–2.4 log units) of bacterial indicators.

Fig. 5a and b illustrates the decay of bacteria concentration at different times of the sequential treatment in both wastewater samples. As can be seen, heterotrophic bacteria, *E. coli*, enterococci and *C. perfringens* spores still presented some activity at the end of the EC step, but the microorganisms were rapidly inactivated by EF demonstrating that the lysis of cell walls by generated oxidizing species (H_2O_2, BDD($^{\bullet}OH$), $^{\bullet}OH$, $S_2O_8^{2-}$ and active chlorine) became much more effective for bacterial removal than their adhesion to the iron hydroxides originated in EC. It can be noticed that when the pH of the EC supernatant was adjusted to 7, the content of all the microorganisms seemed to slightly increase, as shown in Fig. 5a and b, as well as in Fig. S4. This behavior confirms the survival of a certain number of bacteria adsorbed onto the sludge, as stated above, being resuspended in the solutions during the acidification process prior to the EF step. In the overall process for the primary and secondary wastewater, reductions of 5.17 and 4.37 log units for heterotrophic bacteria, 5.06 and 3.91 log units for *E. coli*, 4.61 and 3.60 log units for enterococci, and 3.33 and 2.79 log units for the spores of *C. perfringens* were obtained, respectively. The three latter were not detected at 30 min of EF, whereas a small content of ca. 100 CFU mL^{-1} of the former bacteria was determined as maximal after the treatment. Fig. S4 reveals a fast inactivation of heterotrophic bacteria during the 30 min of the EF step, despite the slight concentration increase upon pH adjustment to 7 after the EC step. These findings allow concluding that the sequential EC/EF process is more effective for disinfection of urban wastewater than single EC and EF at circumneutral pH, since almost complete inactivation of all the bacteria tested can be attained. The enhancement of the disinfection power of EF after EC suggests that during EC treatment the bacteria membranes are weakened by interaction with the $Fe(OH)_n$ flocs and the action of oxidants like active chlorine, further favoring the attack of oxidants in EF.

Comparison of the effectiveness of the sequential EC/EF treatment for urban wastewater disinfection with other coupled techniques is difficult due to the different systems and experimental conditions reported in the literature. Cotillas et al. (2013) described an integrated

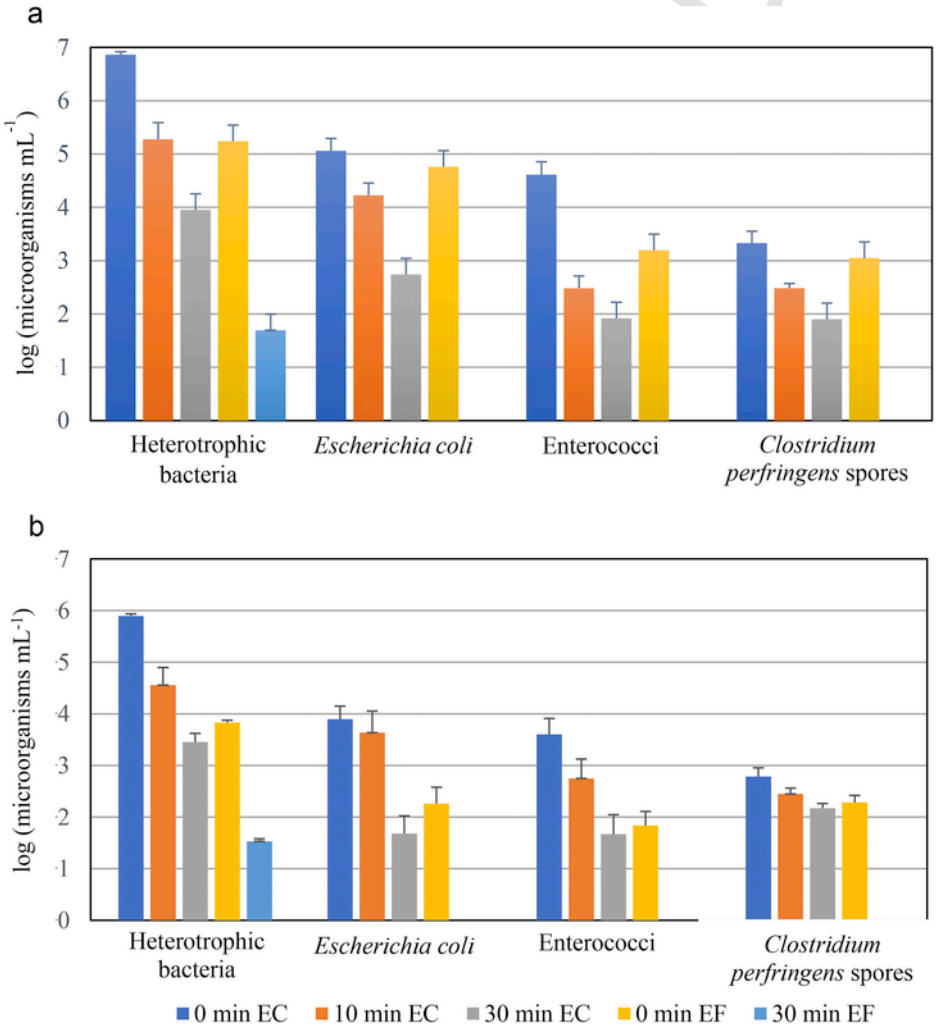

Fig. 5. Change of the logarithm of the concentration of the microorganisms upon sequential EC/EF treatment (30 min each). The EC step was applied to 200 mL of (a) primary and (b) secondary effluents at j = 200 A m^{-2} and 25 °C, being followed by the EF step with 100 mL of the resulting solution, at pH ~ 7 and j = 333 A m^{-2}.

electrodisinfection/EC cell with ability to reduce at least 4 log units of fecal coliforms from urban wastewater, similarly to our results. In contrast, Barrera-Díaz et al. (2015) integrated EC with Cu anode and electrochemically generated H_2O_2 processes to achieve a discrete reduction of 2 log units of heterotrophic bacteria and *E. coli*. For a single biological tertiary treatment, Fernandez-Cassi et al. (2016) showed removals of 0.49 log units of heterotrophic bacteria, 2.58 log units of *E. coli* and 1.65 log units of enterococci for a secondary effluent of a lagooning system, which are poorer results than those reported in our study. More contaminant and/or expensive treatments based on chlorine and/or UV irradiation also offer excellent inactivation rates for most microbiota contained in urban wastewater (Montemayor et al., 2008; Souza et al., 2013).

4. Conclusions

EC performed with a Fe/Fe cell at 200 A m^{-2} for 90 min caused a slow removal of organic load and abatement of microbiota from urban wastewater treatment plant effluents. The $Fe(OH)_n$ flocs adsorbed organics and microorganisms, being separated as a sludge where some of those organisms seemed to be still active. Heterotrophic bacteria, *E. coli*, enterococci and *C. perfringens* spores were the most persistent organisms. Higher decrease of microbial content was achieved by EF with a BDD/air-diffusion cell at pH 3.0 and j = 333 A m^{-2}, only yielding a very poor TOC abatement. The generated oxidants affected the bacteria walls, causing a large or even total inactivation of all the microbiota in both matrices. EF at circumneutral pH yielded similar results, with heterotrophic bacteria persisting at the end of electrolysis. The sequential application of EC and EF steps for 30 min each was the best treatment for the disinfection of urban wastewater. All the active microbiota (except the heterotrophic bacteria) were inactivated within 30 min of EF, including the spores. Bacteria membranes were weakened by interaction with $Fe(OH)_n$ flocs and oxidants in the EC step, further being rapidly affected by the generated oxidants in EF. As the next step, integration of electrochemical technology in current plant units should be made to demonstrate the techno-economic feasibility.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2017.09.056.

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