Advantages of electro-Fenton over electrocoagulation for disinfection of dairy wastewater

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Abstract

This study is focused on the disinfection of raw dairy wastewater by means of a sequential treatment including an electrocoagulation (EC) step with an Fe|Fe cell followed by electro-Fenton (EF) or UVA-assisted photoelectro-Fenton (PEF). The two latter methods were run with an air-diffusion cathode for H_2O_2 generation and either a boron-doped diamond (BDD) or a RuO_2-based anode. The inactivation of heterotrophic and lactic acid bacteria, *Escherichia coli* and enterococci was assessed. Low removal of organic load was found in all cases, whereas the bacteria were poorly removed by the flocs formed in EC but largely inactivated in EF and PEF. EF was also advantageous because it prevented the formation of harmful sludge containing active bacteria, in contrast to EC. Heterotrophs were the most stable bacteria, whereas the others were totally inactivated in most cases. In the sequential EC/EF process involving a BDD anode in the latter step, the inactivation rate for the lactic acid bacteria was higher at circumneutral pH, due to the great ability of produced active chlorine to oxidize the molecules of the cell walls. The use of a RuO_2-based anode also led to a quick inactivation at pH 3.0. A better performance was achieved when PEF replaced EF, regardless of the anode, owing to the enhanced bacterial inactivation by UVA radiation. The raw dairy wastewater at natural pH 5.7 treated by single EF step with a RuO_2-anode also yielded a faster removal of lactic acid bacteria, *Escherichia coli* and enterococci as compared to BDD, always remaining small contents of active heterotrophs in solution.

Keywords: Dairy wastewater; Electrocoagulation; Electro-Fenton; Heterotrophic bacteria; Lactic acid bacteria; Photoelectro-Fenton

1. Introduction

Milk processing in caseiculture consumes large quantities of water, producing about 10 L of wastewater per liter of processed milk [1]. Dairy wastewater is composed of high concentrations of organic matter, salts and bacteria, and its management is difficult because of its variable composition. In general, it contains different proportions of process water, non-valorized cheese whey and cleaning water [2]. As a result, it contains milk and whey proteins, along with other components such as sodium, calcium, chloride or lactic acid [3]. Before its discharge into the sewer system, it is necessary to reduce both, bacterial content and organic matter load. Lactose (0.18-45 g L^{-1}), proteins (1.8-34 g L^{-1}) and fat (0.08-6 g L^{-1}) account for the largest part of chemical oxygen demand (COD) and biological oxygen demand (BOD) [4,5]. The whey proteins are globular and are composed of 60% β-lactoglobulin, 22% α-lactalbumin, 9% immunoglobulins and 5.5% bovine serum albumin.

Electrocoagulation (EC) and Fenton-based treatments seem the most promising technologies to remove the bacteria and organic matter from dairy wastewater [5,6]. EC is an efficient, environmentally friendly phase-separation method based on the release of Fe^{2+} or Al^{3+} ions from sacrificial Fe and Al anodes [7-10]. Reaction (1) causes the dissolution of the Fe anode. The released Fe^{2+} can then be converted into $Fe(OH)_3$ in the presence of O_2 by reaction (2). At the cathode, OH^- ion and H_2 gas is formed from reaction (3).

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

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

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

Iron hydroxides ($Fe(OH)_2$ and $Fe(OH)_3$) are relatively non-toxic and form flocs that allow pollutant removal, yielding a sludge that may precipitate [11]. The flocs entrap colloidal particles by surface complexation or electrostatic attraction and by sweep flocculation [12].

Additionally, the H_2 gas bubbles generated at the cathode cause the flotation of some pollutants and, consequently, the separation process is facilitated [13]. As a conventional electrochemical method, EC requires simple equipment and is easy to operate. The periodic replacement of the sacrificial anodes, their passivation and the electricity cost have been reported as the main drawbacks of this technology.

Several authors used EC for disinfection in urban wastewater treatment facilities (WWTFs), describing total inactivation (> 99.99%) of *Escherichia coli* [14-16], total coliforms [17,18] or *Staphylococcus aureus* [19]. EC has also been applied to minimize the organic load of dye and textile wastewater [13,20-23], urban wastewater [24], olive oil mill wastewater [25] and cheese whey or dairy wastewater [3,26-29]. For a synthetic whey solution, Un et al. [3] described a maximum COD removal of 86.4% using a reactor in continuous with Fe electrodes and proposed a mathematic model to explain the abatement based on response surface methodology. Similarly, for a deproteinated whey wastewater, Guven et al. [26] found a maximum COD decay of 53.3% after 8 h of EC with Fe electrodes at a cell voltage of 11.3 V. Fayad et al. [28] obtained total removal of whey proteins from wastewater of pH 4 using Al electrodes in batch mode at 4.5 A. However, no previous studies about bacterial removal from whey and dairy wastewater have been reported in the literature.

Electrochemical advanced oxidation processes (EAOPs) based on Fenton's reaction chemistry like electro-Fenton (EF) and photoelectro-Fenton (PEF) are also becoming interesting approaches for the removal of organic pollutants from wastewater [30-33]. In EF, the strong oxidant hydroxyl radical ($^{\bullet}OH$) is generated in the bulk solution from Fenton's reaction (4). The most characteristic feature is the cathodic H_2O_2 electrogeneration from the two-electron reduction of injected O_2 at Fenton's optimum pH ≈ 3. Suitable cathodes for H_2O_2 production are carbon felt [34-37] and carbon-polytetrafluoroethylene (PTFE) coated on air-diffusion substrates [38-41]. The PEF process involves additional illumination of the solution

with UVA light (λ = 365 nm), producing $^{\bullet}OH$ from the photoreduction of $Fe(OH)^{2+}$, the photoactive species of aqueous Fe(III) ion, by reaction (5). Moreover, the incident photons can also photolyze oxidation products, like Fe(III)-carboxylate complexes by reaction (6) [38,39]. Note that UVA radiation does not photolyze H_2O_2 to $^{\bullet}OH$, a reaction that requires a more powerful radiation like UVC (λ = 254 nm).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (4)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (5)$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \quad (6)$$

Apart from homogeneous $^{\bullet}OH$, other oxidizing agents can be generated in an undivided cell, depending on the electrolyte and anode nature [30-32]. In non-chlorinated medium, the heterogeneous $M(^{\bullet}OH)$ is formed as main species at the anode M from water discharge via reaction (7). Boron-doped diamond (BDD) thin-films are the most convenient anodes for this, since they produce great amounts of oxidant $BDD(^{\bullet}OH)$ [31,40]. In chloride medium, active chlorine species (Cl_2/HClO/ClO^-) are also formed, thus competing with $M(^{\bullet}OH)$ and $^{\bullet}OH$ to destroy the organics or microorganisms. Chloride is anodically oxidized to Cl_2 via reaction (8), which is hydrolyzed to hypochlorous acid (HClO) via reaction (9) [8]. Cl_2 predominates at pH < 3 and has lower oxidation power than HClO, the most abundant species from pH 3 to 8. At higher pH, HClO is dissociated to ClO^-. The oxidation of Cl^- is enhanced at dimensionally stable anodes (DSA®) like RuO_2, but with low ability to produce adsorbed hydroxyl radicals ($RuO_2(^{\bullet}OH)$) [33,40].

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (7)$$

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

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

A limited number of papers has been devoted to explore the disinfection power of EF in real wastewater matrices [42,43]. For example, Durán Moreno et al. [42] found that this process allowed the overall inactivation of total coliforms, *Escherichia coli*, *Shigella* and *Salmonella sp*. from municipal wastewater. In earlier work [24], we reported that a sequential EC/EF treatment of primary and secondary WWTF effluents allowed the complete removal of all the active microbiota, namely *E. coli*, enterococci, *C. perfringens* spores, somatic coliphages and eukaryotes, with partial inactivation of the heterotrophic (HT) bacteria. Worth mentioning, the PEF process has not been tested for disinfection.

This work aims to compare the ability of single EC with Fe|Fe cell with that of EF and sequential EC/EF and EC/PEF processes to inactivate the microorganisms contained in a real dairy wastewater sample. EF and PEF were comparatively performed with a BDD/air-diffusion or RuO_2-based/air-diffusion cell to assess the role of generated oxidants. Considering the microbiological complexity of this wastewater, HT and lactic acid (LA) bacteria, *E.coli* and enterococci were selected as indicators to monitor the disinfection.

2. Materials and methods

2.1. Chemicals

Analytical grade heptahydrate Fe(II) sulfate was purchased from Sigma-Aldrich. The EF and PEF assays after the EC-pre-treated wastewater were made after adjusting the pH at 3.0 with analytical grade H_2SO_4 or $HClO_4$ supplied by Merck. Analytical solutions were prepared with ultrapure water (Millipore Milli-Q, resistivity >18.2 MΩ cm), whereas reagents and organic solvents were of HPLC or analytical grade supplied by Merck, Panreac and Sigma-Aldrich.

2.*2. Sample of dairy wastewater*

Fresh dairy wastewater was treated in all the assays. The raw wastewater was obtained from a small dairy industry located in Lliçà d'Amunt (northeastern Spain). Samples were collected in polyethylene bottles and stored at 4 ºC before usage in 24-48 h. The main average physicochemical characteristics were: pH 5.7±0.2, conductivity 2.95±0.12 mS cm^{-1}, 1416±24 mg C L^{-1} of total organic carbon (TOC), 850±17 mg L^{-1} of K^+, 115±9 mg L^{-1} of Na^+, 1345±28 mg L^{-1} of Cl^-, 98±5 mg L^{-1} of SO_4^{2-} and 0.045±0.002 mg L^{-1} of Fe^{2+}.

2.3. Microbial enumeration

LA and HT bacteria were quantified after 10-fold dilution with ¼-strength Ringer's solution and culture, respectively, by duplicate on Plate Count Agar (PCA) and Man, Rogosa and Sharpe Agar (MRS), purchased from Scharlab. The incubation for HT was made at 30 ºC for 48 h and that of LA, at 30ºC for 4 d, according to ISO 9308-2:2012. The theoretical detection limit was 1 colony-forming units per mL (CFU mL^{-1}). *E. coli* and enterococci were quantified by most probably number (MPN) using MUG/EC and MUD/SF Kit 96-well microplates supplied by Bio-Rad Laboratories. Both bacteria were incubated at 42 ºC for 48 h, following ISO 9308-2:2012, with detection limit of 0.35-1.35 CFU mL^{-1}.

2.4. Electrolytic systems

All the electrolytic assays were performed with an open, undivided, jacketed, cylindrical cell. The temperature of the treated wastewater was kept at 25 ºC by thermostated water and it was always vigorously stirred at 800 rpm with a magnetic PTFE bar. After each trial and before the next, the cell was cleaned with a H_2O_2/H_2SO_4 mixture for 10 min, rinsed with ultrapure water and dried in an oven at 80 ºC.

In EC, 175 mL of raw dairy wastewater were electrolyzed with two 10-cm^2 Fe (mild carbon steel) plates as the anode and cathode, separated about 1 cm. A constant current was applied provided by an Amel 2053 potentiostat-galvanostat. Before each EC run, the surface of both Fe

electrodes was mechanically abraded with SiC paper, chemically cleaned with 0.1 M H_2SO_4 and ultrasonically cleaned in ultrapure water, followed by drying with an air stream.

The subsequent EF and PEF assays were carried out at constant current provided by the above potentiostat-galvanostat with 120 mL of the supernatant liquid, which already contained soluble iron ions formed in the EC treatment of the wastewater. In some cases, the pH was adjusted to 3.0 with $HClO_4$ in order to maintain the same SO_4^{2-} and Cl^- ions content in the sample. The EF runs of the raw dairy wastewater at natural pH were conducted with 150 mL of sample after addition of 0.25 mM Fe^{2+}. The anode was either a BDD thin-film electrode over Si substrate purchased from NeoCoat or a RuO_2-based plate supplied by NMT Electrodes. The cathode was a carbon-PTFE air-diffusion electrode purchased from Sainergy Fuel Cell. The immersed area of all electrodes was 3 cm^2 and the interelectrode gap of about 1 cm. The cathode produced H_2O_2 upon injecting compressed air at 1 L min^{-1}, as described elsewhere [39]. In the PEF treatments, the wastewater was illuminated with UVA light (300-420 nm, λ_{max}= 360 nm) emitted by a Philips TL/6W/08 fluorescent black light blue tube that was placed at 6 cm above the solution. The UVA irradiance of this tube was 5 W m^{-2}. Prior to the initial EF run, the surface of the BDD and RuO_2-based anodes were cleaned in 0.050 M Na_2SO_4 at 300 mA for 180 min. Under these conditions, the air-diffusion cathode was activated as well. Before each further EF or PEF experiment, the BDD and RuO_2-based anodes were immersed in ultrapure water at 100 ºC for 10 min and dried under an air stream, whereas the air-diffusion cathode was cleaned with a 1:3 (v/v) H_2O/HCl mixture and rinsed with ultrapure water, followed by air-drying.

2.5. Analytical methods

The pH was measured with a Crison GLP 22 pH-meter. The conductivity was determined on a Metrohm 644 conductometer. TOC analysis was carried out with a Shimadzu TOC-VCNS analyzer, with an accuracy of ±1% by injecting 50 μL aliquots previously filtered with 0.45 μm

177 filters purchased from Whatman. The concentrations of cations and anions was determined
178 following the procedures above reported [25].
179 The inactivation profiles for all the microorganisms were monitored from the decay of the
180 logarithm of their concentration *N* (in CFU mL^{-1}). For each experimental condition, at least two
181 independent tests were made, and the average log *N* value is given in the graphs along with the
182 standard deviation (95% confidence interval).

183 **3. Results and discussion**

184 *3.1. Microbiological characterization of the dairy wastewater*

185 The samples of the dairy wastewater showed certain variability of pH with time and for
186 this reason, they were processed within 24 h and treated before 48 h as maximal. The
187 microscopic vision evidenced the presence of filamentous fungi, fat, yeasts and bacteria.
188 Protozoa were not observed, at least in detectable quantity. The initial microbiological analysis
189 of the samples gave, in average, the following results: $(4.3\pm0.3)\times10^{6}$ CFU mL^{-1} of HT,
190 $(3.4\pm0.1)\times10^{5}$ CFU mL^{-1} of LA, $(2.6\pm0.2)\times10^{5}$ CFU mL^{-1} of *E. coli*, $(1.2\pm0.1)\times10^{6}$ CFU mL^{-1}
191 of total coliforms, $(2.5\pm0.1)\times10^{2}$ CFU mL^{-1} of *Staphylococcus* and $(1.8\pm0.1)\times10^{5}$ CFU mL^{-1} of
192 yeast and fungi.

193 *3.2. Electrocoagulation with Fe|Fe cell*

194 The EC of the dairy wastewater was performed with a Fe anode since its dissolution
195 provided the amount of iron ions required for EF and PEF post-treatments [22,25]. First assays
196 were made with 175 mL of the wastewater at natural pH 5.7 using a stirred Fe|Fe tank reactor
197 and by applying 100 and 200 mA (current density of 10 and 20 mA cm^{-2}, respectively) for 60
198 min to assess the effect of increasing amounts of generated coagulants over disinfection. Under
199 these conditions, a consumption of 1.93 electrons per Fe atom was determined from the anode
200 weight loss [25], in good agreement with the expected two-electron Fe oxidation (reaction (1)).

Fig. 1 depicts the low drop of log *N* for HA and LA bacteria in the above trials. HA was poorly inactivated at 100 mA, only in the order of 0.6 log units, whereas a slightly superior inactivation close to 1.0 log units was found at 200 mA. It is then apparent that the increase of current yielded a quicker disappearance of both bacteria that remained entrapped in the major amounts of $Fe(OH)_n$ flocs and sludge formed. In the EC process, a gradual clarification of the wastewater samples was observed, changing from initial white to final dark-green color. This transition can be mainly related to the presence of iron ions and iron hydroxide flocs in suspension that give such dark-greenish coloration. The accumulation of released iron ions was also confirmed from the increase of the conductivity from 2.95 to 4.4 mS cm^{-1} at the end of the run at 200 mA. It is noticeable that the wastewater was alkalinized during the EC treatment because of the continuous uncompensated production of OH^- ion from reaction (3), since the Fe anode was dissolved according to reaction (1) without significant H^+ generation from H_2O oxidation. This is in contrast to that occurring when using insoluble anodes like BDD and RuO_2 [8,30-33]. For example, after 60 min at 200 mA, the pH rose from 5.7 to 7.8.

A poor loss of TOC of 185 and 255 mg C L^{-1} (13% and 18% of initial value) after 60 min of EC at 100 and 200 mA, respectively, was found as well. This reveals a low ability of the $Fe(OH)_n$ flocs to coagulate the high amounts of pollutant molecules contained in the dairy wastewater, except whey proteins. Since the isoelectric point of these proteins is of 5.2 for β-lactoglobulin, 4.2-4.5 for α-lactalbumin, 5.5-6.8 for immunoglobulins and 4.7-4.9 for bovine serum albumin, it is expected that they were rather removed by the flocs due to its low solubility under our experimental conditions [44]. In contrast, it has been shown that soluble molecules such as lactose, glucose and fatty acids cannot be removed by EC with Fe anode [20,21,27]. The large presence of the latter molecules in the organic load of dairy wastewater could explain its very low TOC removal achieved by this treatment. Also worth highlighting, a low specific

energy consumption of 2.3 and 8.2 kWh m^{-3} was obtained for the EC treatment at 100 and 200 mA, respectively.

To corroborate that the microorganisms were retained on the dark-reddish sludge formed by the $Fe(OH)_n$ flocs, the remaining wastewater from a 200 mA trial was decanted to be separated from the sludge and its flocs were subsequently collected by filtration. Analysis of these wastes showed the existence of a higher content of heterotrophs still actives in the flocs (3.2×10^5 CFU mL^{-1}) than in the sediment (8.3×10^2 CFU mL^{-1}). For a whey wastewater, Un and Kandemir [29] reported the presence of hematite (Fe_2O_3) and magnetite (Fe_3O_4) phases in the dried sludge obtained through EC with Fe anode. They proposed that part of this sludge could be used as an iron source in other applications and its excess could be used as a fertilizer or incinerated if it is very toxic. Our results for the sludge produced from dairy wastewater reveal the retention of an important content of active bacteria, meaning that it should be incinerated to avoid their infection in living beings.

3.3. Sequential EC/EF with BDD at pH 3.0 and circumneutral pH

Next, the sequential assays were carried out for 60 min in EC and 120 min in EF. The EC step was firstly performed as explained in section 3.2, i.e., 175 mL of sample at natural pH with Fe|Fe cell at 200 mA. Once ended, the wastewater was filtered and 120 mL of the transparent and greenish supernatant liquid were introduced in a rinsed and cleaned cell to be post-treated by EF. The pH of this liquid was adjusted to pH 3.0 with H_2SO_4 (optimum acidity for EF) and it already contained enough soluble iron ions from the previous EC process (about 3 mg L^{-1} [22]), to generate homogeneous $^{\bullet}OH$ upon optimum conditions of Fenton's reaction (4). The EF process was then run after introducing a BDD anode and an air-diffusion cathode in the stirred cell and by applying a current of 100 mA (current density of 33.3 mA cm^{-2}) for 120 min. No significant change in pH was found during this post-treatment.

Fig. 2 shows the evolution of log *N* for HT and LA bacteria in the above sequential EC/EF treatment. Worth mentioning, after filtration of the resulting wastewater from EC and adjustment to pH 3.0 before EF, the initial concentration of both microorganism was reduced by about 2 log units, resulting average values of 8.75×10^{2} CFU mL^{-1} for HT bacteria and 4.76×10^{3} CFU mL^{-1} for LA bacteria. The decay of the former bacteria could be related to two effects: (i) the retention of the microorganisms onto the flocs that remain in the filter and (ii) their larger inactivation at the acidic pH of the wastewater. However, the latter explanation seems not valid for the LA bacteria, which are acid tolerant and can survive between pH 3.2 to 9.6, with optimum growth in the pH range 4.0-4.5 [45]. This bacterial group is composed of a large variety of microorganisms, cocci or rods, with common Gram-positive, anaerobic, microaerophilic or aerotolerant, non-espore-forming, non-pathogens, non-toxigenic, and negative oxidase, catalase and benzidine characteristics, and lactic acid production as the major end by-product of the fermentation of carbohydrates [46,47].

Fig. 2 shows that in the EF step, the HT bacteria underwent a loss of 2.3 log units, which remained invariable between 60 and 120 min of electrolysis, whereas the LA bacteria were inactivated gradually to larger extent up to 3.3 log units. The greater LA reduction would be related to its higher initial concentration in the wastewater. It seems unreasonable to explain the decay on the basis of the toxicity produced by the electrogenerated H_2O_2, because this bacteria group, especially the rod-shaped lactobacilli, in presence of O_2 already produces certain amount of H_2O_2 that is chemically and enzymatically transformed into oxygen radicals with more potent antimicrobial activity than H_2O_2 itself [48,49]. The inactivation of HT and LA bacteria in EF can then be associated to the action of strong oxidizing agents generated, including $^{\bullet}OH$ from Fenton's reaction (4), BDD($^{\bullet}OH$) from reaction (7) and active chlorine (Cl_2/HClO) from reactions (8) and (9), as established elsewhere [50,51]. These strong oxidants are expected to attack the molecules of the cell walls causing the lysis and death of bacteria [24,52]. In contrast,

the weaker oxidant H_2O_2 is expected to contribute to the disinfection to a much smaller extent [48,49], being rather inactive for LA bacteria, as stated above.

Unlike the EC step where the pH and conductivity of the treated dairy wastewater underwent large variations, the subsequent EF process at pH 3.0 showed a good stability of both parameters. After 120 min of EF, the pH decayed slightly to 2.6, suggesting the formation of acidic by-products, and the initial conductivity of 6.4 mS cm^{-1} (due to H_2SO_4 addition for pH adjustment) rose up to 7.0 mS cm^{-1}. Moreover, the sequential EC/EF treatment only yielded a small TOC reduction of 385 mg C L^{-1} (27% of the initial 1416 mg C L^{-1}), indicating not only the low ability of the Fe(OH)n flocs for organic coagulation in EC, as stated above, but also the low oxidizing power of $^{\bullet}OH$, BDD($^{\bullet}OH$) and active chlorine to mineralize them in EF. It is also noticeable that the dark-green wastewater obtained after EC was clarified upon acid addition before EF and at the end of this treatment, it reached a clear yellow-brown color due to the removal of suspended solids and the presence of iron ions.

To assess the disinfection power of the generated oxidizing agents under non-optimum conditions of Fenton's reaction (4), another sequential EC/EF treatment of the raw dairy wastewater was made, but without varying the pH of the filtered supernatant liquid obtained by EC to be treated by EF. Thus, the EC step with Fe|Fe cell was carried out by applying 200 mA for 30 min, where the pH increased from 5.7 to 7.5. The subsequent EF with BDD at 100 mA was carried out for 60 min, showing a pH decay from 7.5 to 6.8. The conductivity also rose up to 4 mS cm^{-1} in the former case, remaining practically unchanged in the second one. Moreover, about 20% of the initial TOC was removed in this sequential EC/EF process, corroborating again the low ability of the species formed in each step to coagulate/mineralize the organic matter of the wastewater.

For the aforementioned experiment, Fig. 3 reveals a little drop of 0.8 log units in the concentration of both HT and LA bacteria after 30 min of EC. After filtration of the liquid

supernatant, the content of these groups of bacteria were reduced by 2.3 log and 2.8 log units, respectively. It should be noteworthy the large inactivation achieved after 60 min of EF, where 15 CFU mL^{-1} were only detected for HT, whereas the LA bacteria disappeared completely. Compared with the results of Fig. 2, one can infer that the oxidizing agents formed at circumneutral pH were more effective to disinfect the wastewater than those produced at pH 3.0, although with a slightly lower inactivation power over the HT bacteria. This indicates that the disinfection of the sequential EC/EF process over dairy wastewater is so good operating at circumneutral pH that it is not necessary to regulate the optimum pH 3.0 for the EF post-treatment. At circumneutral pH, active chlorine is mainly in the form of HClO, which is more powerful than Cl_2 that is also present at pH 3.0 [31-33]. The specific energy consumption for this assay was 19.5 kWh m^{-3}, arising from 4.1 kWh m^{-3} (21%) of EC plus 15.4 kWh m^{-3} (79%) of EF. Although the EF post-treatment was much more efficient for disinfection, it demanded greater energy consumption than the EC step.

3.4. Comparative sequential EC/EF and EC/PEF with BDD and RuO_2-based at pH 3.0

A series of comparative trials was made to check the influence of the anode, BDD or RuO_2-based, over the disinfection power of the EF post-treatment, as well as considering that of the incident UVA light using the PEF one. The EC step was performed again with 175 mL of a sample of dairy wastewater in a stirred Fe|Fe cell at 200 mA for 45 min. The EF or PEF steps were carried out with 120 mL of the filtered supernatant liquid once adjusted at pH 3.0 with $HClO_4$ (to no alter the Cl^- and SO_4^{2-} content of the samples) and by applying 100 mA, for 120 min as maximal.

As expected, the initial pH of 5.7 and conductivity of 2.9 mS cm^{-1} of the raw wastewater rose up to 7.8 and 4.4 mS cm^{-1}, respectively, after the EC pretreatment. In contrast, no significant change of pH close to 3 and conductivity of about 6.4 mS cm^{-1} was observed after the EF and PEF post-treatments. For the latter steps, the use of a BDD anode always caused a

higher TOC abatement than that of RuO_2-based. The initial TOC was reduced by 25% and 28% for EC/EF and EC/PEF with BDD, respectively, and to lesser extent of 21% and 24% for the analogous runs with RuO_2-based. In all cases, the EC step yielded the higher TOC removal of about 17%-18%. These findings agree with the superior ability of BDD($^{\bullet}$OH) compared to RuO_2($^{\bullet}$OH) to destroy the organic matter [31-33], thereby confirming the important oxidative role of the former radical. The enhancement of TOC removal by PEF can be accounted for by the oxidation action of UVA light that can photolyze photoactive intermediates, e.g. from reaction (6), and originate more amounts of $^{\bullet}$OH from reaction (5) and photo-excitation of active chlorine [53].

A different trend can be observed in Fig. 4a and b for the inactivation of HT and LA bacteria by the above trials. An important and similar loss of bacterial concentration of 3-4 log units always occurred after conditioning the supernatant liquid of EC at pH 3.0 with $HClO_4$ (probably more toxic than H_2SO_4), whereas both groups of bacteria disappeared rapidly after 60 min of EF and 30 min of PEF, regardless the anode used. This means that the disinfection process in EF takes place thanks to $^{\bullet}$OH and active chlorine as the most efficient oxidants for lysing the cells. The quicker inactivation attained by PEF is due to the additional excess of $^{\bullet}$OH produced under the 6 W UVA radiation that facilitates their lysing, along with its photolytic action over the nucleic acids (DNA and RNA) of the cells [54]. Despite the PEF post-treatment produces faster disinfection and larger TOC abatement of the dairy wastewaters, the high energy spent by the UVA lamp prevents their use in practice and the alternative EF step seems more useful for such purposes.

3.5. EF treatment at natural pH

Last experiments were made to assess the disinfection performance of EF over the dairy wastewater. To do this, 0.25 mM Fe^{2+} were added to 150 mL of sample at natural pH for further electrolysis in stirred BDD/air-diffusion and RuO_2-based/air-diffusion cells at 100 mA for 120

min. No substantial change of the initial conductivity of 2.8 mS cm^{-1} was found for these trials, whereas the initial pH of 5.8 rose slightly up to 6.6 at the end of electrolysis, regardless the anode used. A slight decay of the initial TOC of 10% for BDD and 13% for RuO_2-based was determined as well, corroborating the very low ability of the oxidizing agents generated to mineralize the complex organic molecules of the dairy wastewater.

Fig. 5a and b depict the change of log *N* of HT and LA bacteria, *E.coli* and enterococci with time for EF with BDD and RuO_2-based anodes, respectively. As can be seen, the complex group of heterotrophs were the most resistant at inactivation. Its concentration profile showed a quicker removal within the first 30 min of electrolysis, with reductions of 2.7 log units for BDD and greater of 5.7 log units for RuO_2-based. The loss of efficiency at longer time was due to the lower bacterial concentration. After 120 min of EF treatment, 131 and 9.5 CFU mL^{-1} of these bacteria using BDD and RuO_2-based still survived. The faster inactivation achieved by RuO_2-based suggests that active chlorine, formed to greater extent from this anode than from BDD, plays a more relevant role to remove the bacteria than hydroxyl radicals. However, the contribution of $^{\bullet}OH$ formed from Fenton's reaction (4) was confirmed by performing electro-oxidation trials where the air-diffusion cathode was replaced by a stainless steel plate, leading to a slower removal by 1 log unit.

A similar disinfection trend for both anodes can be observed in Fig. 5a and b for the other bacteria, which were more quickly inactivated. In the case of LA bacteria, the concentration diminished 2.14 log units for BDD and 5.5 log units for RuO_2-based at 30 min, disappearing after 120 and 60 min of electrolysis, respectively. The inactivation of *E. coli* and enterococci was even much faster, since they were completely removed at 60 and 30 min using BDD and RuO_2-based, respectively.

The above results are similar to the large disinfection reported in earlier work for the EF treatment with BDD anode of primary and secondary effluents at neutral pH [24]. They are also

consistent with the removal of 99.95% coliform bacteria from landfill leachate achieved using this technology [43]. Although EF is optimal at pH near 3 where more $^{\bullet}OH$ is generated from Fenton's reaction (4), the combined oxidation ability of this radical and active chlorine to inactivate the microorganisms not only makes feasible its application at natural pH, but also favors the use of a RuO_2-based anode, much cheaper than the BDD. The EF with RuO_2-based can then be envisaged as more useful in practice than any sequential EC/EF process to largely disinfect dairy wastewater since it avoids the sludge produced in the EC step, which needs further treatment to prevent infections from the active bacteria retained in it.

4. Conclusions

The iron hydroxide flocs formed during EC with an Fe|Fe cell were able to remove only small TOC contents (up to 18%) and HT and LA bacteria concentrations (< 1.0 log units) from raw dairy wastewater. Furthermore, it was shown that the sludge retained active bacteria. A poor abatement of the organic matter was also found in single EF and PEF with BDD or RuO_2-based anodes, as well as in sequential treatments, indicating the low oxidation ability of hydroxyl radicals and active chlorine to attack the complex molecules of such wastewater. In contrast, the application of these EAOPs yielded a large inactivation of all bacteria. Heterotrophs were the most hardly inactivated microorganisms, whereas LA bacteria, *E.coli* and enterococci were more rapidly removed and even completely inactivated. In the sequential process involving the EF step with BDD, a quick inactivation of LA bacteria was found at circumneutral pH, revealing the pre-eminent oxidation role of active chlorine over the molecules of the cell walls. This was corroborated by the quick inactivation of both bacteria using a RuO_2-based anode at pH 3.0, since this material promoted the active chlorine production. With PEF as post-treatment, total disinfection was rapidly achieved due to the additional bacterial inactivation induced by UVA light. Direct EF treatment of dairy wastewater

at natural pH also led to faster inactivation of all bacteria using the RuO_2-anode, which was complete for LA bacteria, *E. coli* and enterococci. This method is thus preferred for dairy wastewater disinfection because it avoids the need of sludge management from EC, although it is more energy-intensive than EC.

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Figure captions

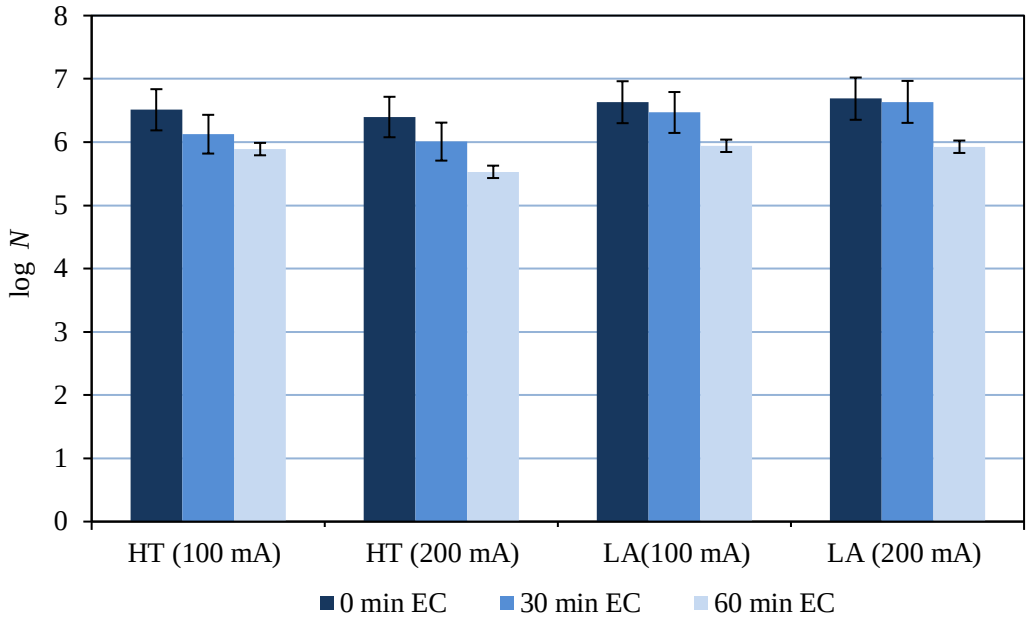
Fig. 1. Variation of logarithm of the concentration of heterotrophic (HT) and lactic acid (LA) bacteria with electrolysis time upon electrocoagulation (EC) of 175 mL of dairy wastewater at natural pH using an undivided Fe|Fe cell (10 cm^2 electrode area) at a current of 100 or 200 mA and 25 ºC.

Fig. 2. Change of the logarithm of the concentration of heterotrophic and lactic acid bacteria with time for a sequential EC/EF treatment performed for 60 and 120 min, respectively. In the EC step, 175 mL of dairy wastewater at natural pH were treated in an undivided Fe|Fe cell at 200 mA. The following EF step was carried out with 120 mL of the supernatant solution adjusted to pH 3.0 using a BDD/air-diffusion cell (3 cm^2 electrode area) at 100 mA. Temperature: 25 ºC.

Fig. 3. Variation of the logarithm of the concentration of heterotrophic and lactic acid bacteria in a sequential EC/EF treatment performed for 30 and 60 min, respectively. The EC and EF steps were made under the same conditions as in Fig. 2, but the initial pH of the supernatant liquid in EF was ca. 7.5, the value obtained at the end of EC.

Fig. 4. Change of the logarithm of the concentration of heterotrophic and lactic acid bacteria with time in sequential (a) EC/EF and (b) EC/PEF treatments. In both cases, the first process (EC) was performed with 175 mL of dairy wastewater at natural pH in an undivided Fe|Fe cell at 200 mA for 45 min. The subsequent EF or PEF treatment was made with 120 mL of the supernatant solution at pH 3.0 using a BDD/air-diffusion or RuO_2-based/air diffusion cell at 100 mA for 120 min. In PEF, the solution was irradiated with a 6 W UVA lamp. Temperature: 25 ºC.

Fig. 5. Variation of logarithm of the concentration of heterotrophic and lactic acid bacteria, *E. coli* and enterococci along 120 min of EF treatment of 150 mL of dairy wastewater at natural pH with 0.25 mM Fe^{2+} using (a) BDD/air-diffusion and (b) RuO_2-based/air-diffusion cells at 100 mA and 25 ºC.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LA (200 mA)
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30 min EC
60 min EC

Fig. 1

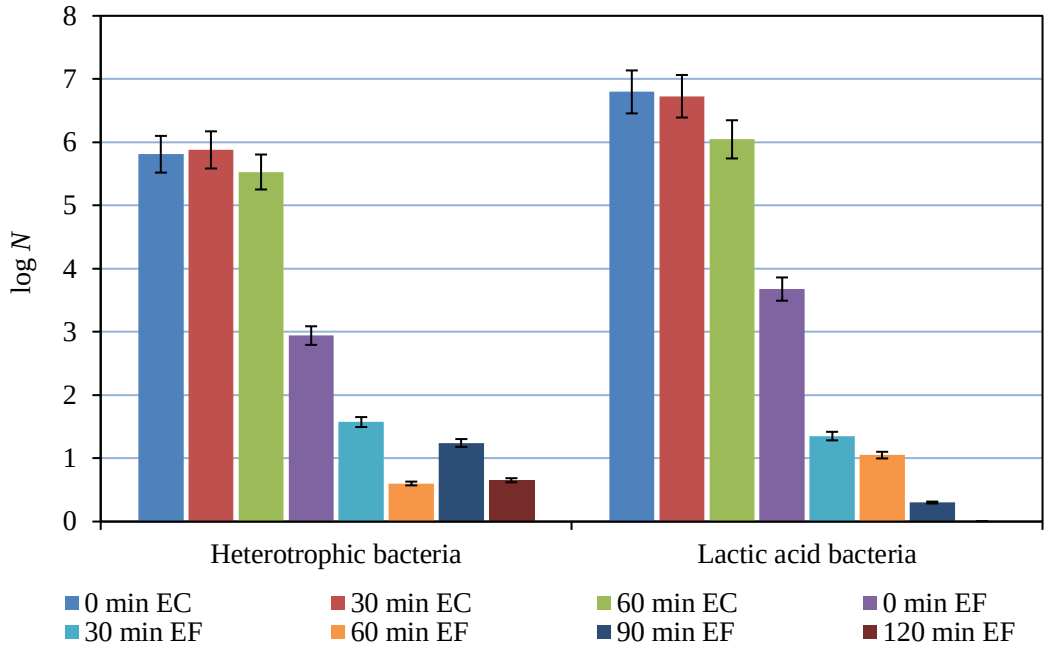
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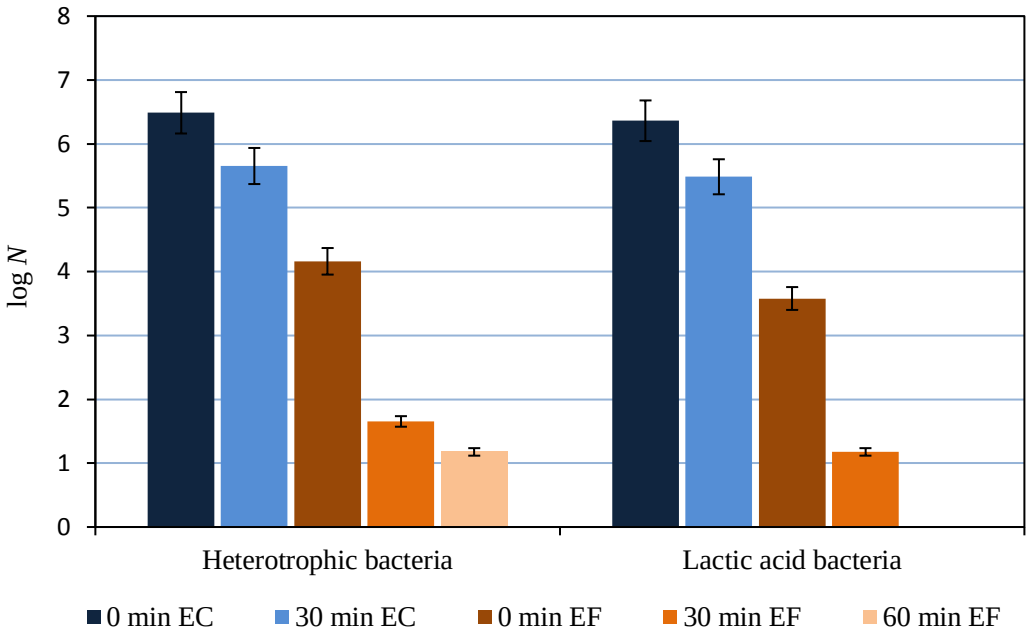
Fig. 2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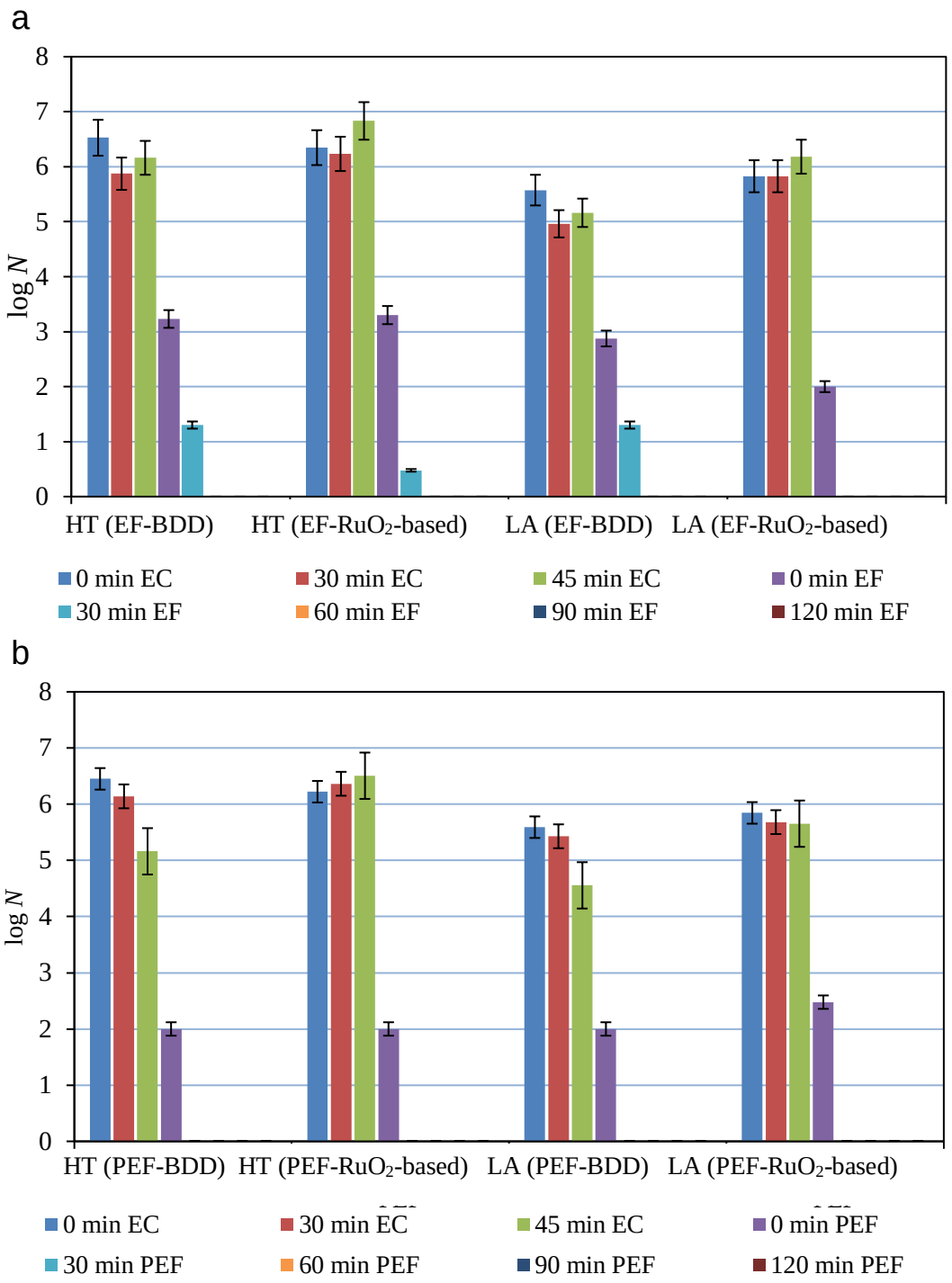
30 min EF
60 min EF

Fig. 3


a
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HT (EF-RuO2-based)
LA (EF-BDD)
LA (EF-RuO2-based)
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45 min EC
0 min EF
30 min EF
60 min EF
90 min EF
120 min EF
b
log N
HT (PEF-BDD)
HT (PEF-RuO2-based)
LA (PEF-BDD)
LA (PEF-RuO2-based)
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30 min EC
45 min EC
0 min PEF
30 min PEF
60 min PEF
90 min PEF
120 min PEF

Fig. 4

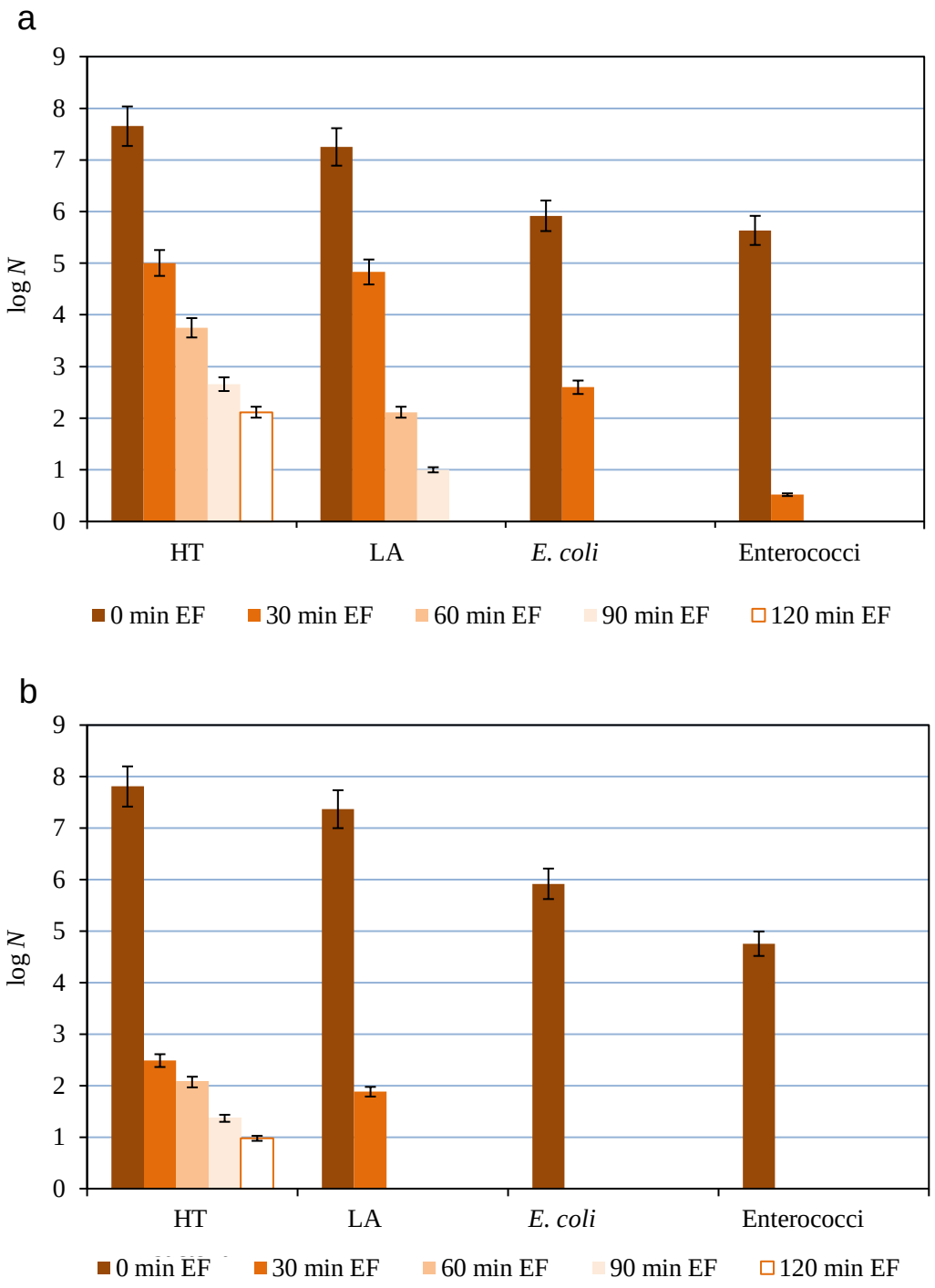
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Fig. 5