An Efficient Simultaneous Degradation of Sulfamethoxazole and Trimethoprim by Photoelectro-Fenton Process Under Non-Modified pH Using a Natural Citric Acid Source: Study of Biodegradability, Ecotoxicity and Antibacterial Activity

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Abstract

In this work, the photoelectro-Fenton system was evaluated as an alternative for the degradation of sulfamethoxazole and trimethoprim at unmodified pH by using citric acid present in extracts from a natural source as organic residues (orange and lemon peels). The addition of natural citric acid showed an efficient degradation of the antibiotics similarly to the efficiency by adding commercial reagent citric acid. The observed high efficiencies and rate constants are attributed to the increment of ferrous ion in the solution due to the fast conversion of iron form its ferric to ferrous state leading to the Fenton reaction and so increasing the hydroxyl radicals production. Although the addition of citric acid present in the extracts slightly increases the organic matter of the solutions, the degradation of the antibiotics was achieved simultaneously and efficiently, converting the photoelectro-Fenton process with the addition of natural citric acid into an alternative ecological system and sustainable for water contaminated with pharmaceutics. Additionally, the high biodegradable character and low ecotoxicity of the treated solutions were determined by a modified Zahn Wellens test and a bioassay with *D. magna*, respectively. Finally, simultaneous degradation of sulfamethoxazole and trimethoprim was reached after only 45 min of treatment in which the antibacterial activity was completely eliminated, suggesting that degradation products do not represent any environmental risk nor human health.

Highlights

- SMX and TMP were simultaneously degraded with the PEF process by citric acid addition.
- Efficiency in the degradation was maintained with lemon and orange peels extract.
- Complete degradation of SMX and TMP increased the biodegradability of the treated solutions.
- The treated SMX-TMP solutions showed lower ecotoxicity.
- Degradations of 100% of SMX and 71% of TMP leads to a complete elimination of antibacterial activity.

1. Introduction

Antibiotics are powerful medications used to treat or prevent bacterial infections. In the correct way, antibiotics consumption can save human and animal lives, but in an incorrect way (unnecessary situations, incorrect doses, premature interruption of the treatment and the use of bad quality drugs), causes the failure of the antibiotic. This is a frequent and harmful practice for individual health and the environment. According to the World Health Organization (WHO), this is a factor that contributes to the development of bacterial resistance, as well as the creation of multidrug-resistant bacteria also called superbugs (Estrategia mundial de la OMS para contener la resistencia a los antimicrobianos 2001; Bai et al. 2018).

In the specific case of sulfamethoxazole and trimethoprim (SMX - TMP), they are the main prescribed antibiotics for patients with bronchitis and infections symptoms caused by *Staphylococcus* and

Streptococcus bacteria, since they inhibit the synthesis of tetrahydrofolate and subsequently the DNA acting as bactericidal and bacteriostatic compounds (Suárez Olivares 2011; Página de créditos 2015; Daza et al. 2017). This high consumption increases their appearance in wastewaters, such as those of Bogotá D.C treatment plant (WWTP-Salitre), in which concentrations of 0.63 µg/L for SMX and 0.32 µg/L for TMP where quantified in the influent, while the effluent showed concentrations of 0.64 µg/L for SMX and 0.34 µg/L for TMP (Botero-Coy et al. 2018). Due to the constant presence of antibiotics in wastewater in which bacterial diversity is high, bacterial resistance has increased; for example, in 2013 in Bogotá approximately 74% resistance to SMX and TMP was found by 1769 strains of *E.coli (Pallares and Martínez 2013; López and Garay 2016;* Daza et al. 2017; Bello Fernández et al. 2018). Moreover, these commercial drugs are found in combination with a 1: 5 ratio (TMP: SMX) to carry out their mechanism of action (Arredondo García et al. 2019). This because both drugs act synergistically blocking successive steps of folate metabolism in bacteria, which is necessary for the production of cell wall proteins, puric and pyrimidine bases of DNA, thereby acquiring maximum antibacterial activity, which is usually bactericidal and bacteriostatic (Sass 2017; Montiel A. 2018).

These antibiotics are considered contaminants of emerging concern (CECs) recalcitrant to conventional water treatments. Therefore, an application of complementary processes such as advanced oxidation processes (AOPs), effective systems in the elimination of mixtures of CECs from water is an urgent need (Qiu et al. 2015). Among the AOPs, the photoelectro - Fenton (PEF) can be highlighted, which is mainly based on the Fenton reaction, where ferrous ion reacts with hydrogen peroxide producing •OH radicals (Eq. 1) (Barbosa et al. 2016; Boczkaj and Fernandes 2017).

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH$ (1)

The PEF system involves light irradiation with different light sources, such as LEDs, which allows to the formation of extra •OH through the aqua complexes $[Fe(OH)]^{+2}$ photolysis (Eq. 2) (Eskandarian et al. 2016; Davididou et al. 2017; Matafonova and Batoev 2018), and favors the ferrous ions regeneration from ferric ion (as a Fenton reaction product) complexes. Ferrous ion has much higher water solubility than ferric ion and it could promote the Fenton reaction (Eq. 1), then to promote the formation of soluble ferrous ion from low or insoluble ferric ion by light interaction, becomes an enhancement of the Fenton process. Many organic acids are known as excellent ligands of photo active ferric complexes, which undergo photolysis under irradiation reducing Fe^{+3} to Fe^{+2} (Eq. 3) facilitating the PEF system (Casado 2019; Brillas 2020). Moreover, organic radicals are produced that could contribute to the degradation of the organic matter according to the ligand nature. Furthermore, organo-ferric complexes present an extra advantage to the Fenton-based process related to the pH, since the formation of these leads to the solubilization of the highly insoluble ferric ion at near neutral pH, which represents a limitation of the classic Fenton reaction (in the absence of organic ligands, ferric ion precipitates under pH above 3 and the reaction is restricted) (I. N. Dias et al. 2014; Ruales-Lonfat et al. 2016).

$[Fe(OH)]^{+2} + h\nu \rightarrow Fe^{2+} + \bullet OH$ (2)

$[Fe(OOCR)]^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R\bullet$ (3)

Among the organic acids, citric acid stands out given its proven high photoactive capacity to produce reactive species and to increase soluble iron in the system (Clarizia et al. 2017; Villegas-Guzman et al. 2017; Casado 2019). Additionally, citric acid could be easily extracted from diverse organic wastes, especially from the citrus food industries, since despite being organic waste they contain significant amounts of the acid (Villegas- Guzman et al. 2017; Amanollahi et al. 2019). Hence, it becomes an interesting organic acid to be tested during a Fenton-based water treatment and turning organic wastes into citric acids source.

Therefore, in this work, the simultaneous degradation of antibiotics SMX and TMP in aqueous medium is evaluated by the PEF process with the addition of citric acid present in the extract of organic citrus residues (lemon and orange peels) under circumneutral pH. The efficiency of the process was evaluated in terms of the initial degradation rates of the pollutants (Cf/Co*100) and variations on important parameters such as biodegradability, toxicity and antibacterial activity (AA) of the treated solutions.

2. Materials And Methods

2.1 Reagents

Standard HPLC grade sulfamethoxazole and trimethoprim (98% purity) was purchased from Sigma Aldrich. Iron (II) sulfate heptahydrate, dibasic potassium phosphate, orthophosphoric acid, potassium hydrogen phosphate, potassium bicarbonate, potassium carbonate, sodium chloride and citric acid were Merck analytical quality. The HPLC grade acetonitrile was obtained from Panreac. All solutions were prepared with ultrapure water from a Millipore Milli-Q system with resistivity > 18 MΩ cm at 25°C.

For biodegradability analysis: glucose, calcium chloride, iron chloride, copper sulfate, manganese sulfate, zinc sulfate, magnesium chloride, ammonium chloride and sodium sulfate were used with Panreac analytical quality. The solutions were prepared with deionized water.

2.2 Electrochemical system

The degradations assays were carried out in a 250 mL undivided glass cell. 200 mL of a solution with $2.96x10^{-4}$ mol/L of SMX and $2.58x10^{-4}$ mol/L of TMP, 0.050 mol/L sodium chloride was used as the support electrolyte and $3.0x10^{-5}$ mol/L of Fe^{2+} was treated. For the electrochemical cell, a 2 cm^2 carbon felt air diffusion cathode (GDE) and a 2.89 cm^2 Ti/IrO_2 anode doped with SnO_2 (DSA) were used and was operated at a constant current mode of 5.19 mA/cm^2. The solution was irradiated with a white light LED radiation source wrapped around the cell (United Kingdom; 3.8 W) with 60 LEDs (1.0 m). The PEF system was previously described (Martínez-Pachón et al. 2018; Martínez-Pachón et al. 2019). The experiments were carried out at neutral pH and a $3.0x10^{-5}$ mol/L of citric acid was added from either the analytical grade reagent or the extraction of the natural source.

2.3 Extraction of citric acid from natural products

The extraction procedure was based on an already registered protocol with modifications (Villegas-Guzman et al. 2017). Commercial fruits such as orange (*Navel orange*) and lemon (*Subtle lemon*) were used. Infusions of the husks as natural sources of citric acid for the PEF system were tested. The peels were dried at 60°C for 24 h and ground, 2 g of the dry material was weighed and mixed with 40 mL of boiling water for 5 min to help the extraction of soluble organic acids (M. I. Dias et al. 2015; Ozkan 2019). The mixture was then centrifuged for 5 min at 5000 rpm. Extractions were prepared just before the experiments and immediately used.

2.4 HPLC degradation analysis

A Shimadzu LC-20AT HPLC equipped with an SPD-M20A photodiode array detector and a C18 column (Waters Spherisil ODS2, 250 mm x 4.6 mm ID with particle sizes of 5 µm) was used. The mobile phase was composed of a phosphate buffer (pH 3.5, 0.01 mol/L)/acetonitrile (50/50 v/v) at 25°C, under isocratic conditions. The mixture was pumped with a flow rate of 1.0 mL/min, resulting in a maximum system pressure of 98 bar, detection was set at 270 nm for SMX and 204 nm for TMP. Twenty microliters of sample were injected by full loop injection. Under these conditions, SMX and TMP were eluted at 3.61 min and 5.57 min respectively.

2.5 Biodegradability analysis with activated sludge

The biodegradability analysis was carried out over a period of 12 days, using aerobic microorganisms from the purge of a plastic processing plant in Bogotá D.C. 100 mg/L of biomass was added to the SMX and TMP solutions to obtain a biomass ratio of 5:1 in 230 mL of total volume. The tested solutions were: **1.** $[SMX]_o$: $2.96x10^{-4}$ mol/L, $[TMP]_o$: $2.58x10^{-4}$ mol/L, **2.** After 45 min of treatment, **3.** After 90 min of treatment, **4.** $[Glucose]_o$: $1.11x10^{-4}$ mol/L as a positive control. Each solution contained micronutrients (calcium chloride, iron chloride, copper sulfate, manganese sulfate and zinc sulfate), and macronutrients (magnesium chloride, ammonium chloride, sodium sulfate, dipotassium phosphate and monopotassium phosphate).

The process was slowly aerated with an aquarium pump (AP-005 XILONG), constantly stirred and the temperature was maintained at 37°C in a Shaker (Wise Shake SHO-1D Digital Orbital Shaker). Before undergoing the activated sludge treatment, residual hydrogen peroxide and active chlorine species were inactivated by mixing with enough sodium disulfite (0.1 mol/L). Samples were monitored on days 2, 4, 6, 8 and 12 by analyzing the total organic carbon (TOC) in the Shimadzu TOC-LCSH equipment. Dissolved oxygen concentration to evaluate respirometry was measured using a HI 9829 multiparameter meter (HANNA Instruments), equipped with the HI 76x9829 series probes.

2.6 Toxicity analysis with *Daphnia magna* bioassay

The described standard methodology in ISO 6341 and other studies was used (Biological methods 2012; Khan et al. 2017; Espinosa-Barrera et al. 2021). The *D. magna* media with reconstituted water was applied

and fed with *Scenedesmus subspicatus* algae (Vidal et al. 2016). The reconstituted water was prepared with deionized distilled water (Álvarez-Manzaneda et al. 2017; Barrera Herrera et al. 2019). Before placing the *D. magna* in the solutions, the pH of the samples was adjusted to 7.0 using sodium hydroxide (1.0 mol/L). The solution was slowly aerated with an aquarium pump (AP-005 XILONG) and temperature was maintained at 20°C on a stirrer (Wise Shake SHO-1D digital orbital shaker). The bioassay was carried out for 48 h following the mobility of 10 *D. magna* in different solutions (described in point 3.9. Biodegradability analysis with activated sludge). Potassium dichromate was used as the positive control and reconstituted water as the negative control.

2.7 Analysis of antibacterial activity

It was determined by analyzing the inhibition zone during the agar diffusion test, using *Escherichia coli* ATCC 25922 as microorganism indicator. Following the Kirby-Bauer method described by (Efraim A Serna-Galvis et al. 2016), 30 µL of the solutions were added (samples along the degradation treatment) on white filters. Subsequently, they were placed in Petri dishes containing 25 mL of Müller-Hinton agar inoculated with an *E. coli* solution (with an optical density of 0.500 to 580 nm). After 24 hours of incubation at 37°C, bacterial growth was observed and the diameter of the inhibitory halo was measured with a vernier. The analyses were performed in duplicate to ensure the reproducibility of the methodology.

3. Results And Discussion

3.1 Effect of the citric acid on the degradation of SMX and TMP by PEF system

3.1.1 Effect of citric acid source (comparison of natural and commercial sources)

Several studies have shown the positive effect of using organic acids in the degradation of CECs (I. N. Dias et al. 2014; Moreira et al. 2015; Villegas- Guzman et al. 2017; Giannakis 2018; Y. Zhang et al. 2019). Considering pH 3.0 as the recommended condition to performed Fenton-based process since the Fenton reaction is most favorable at acidic media (Gozzi et al. 2017; Nogueira et al. 2017; Brillas 2020), the addition of citric acid for the degradation of SMX and TMP can be analyzed during the PEF treatment. Several natural products have organic acids as main constituents in their juices, peels and pulps (Pliego et al. 2016; Ruales-Lonfat et al. 2016; Kowalski et al. 2019). Therefore, the evaluation of natural products as possible sources of organic acids becomes an interesting alternative, especially for Colombia, where orange or lemon juices are part of the agro-industrial economic sector, and consequently a large amount of orange and lemon peel waste have been reported (Domingos et al. 2019). In the specific case of the orange, it occupies the second place in the Colombian national production with 456.301 tons (DANE 2019). Additionally, during the production of industrial orange juice only half of the fresh weight of orange is transformed into juice and the 50% remaining (228.150 tons) consists of pulp, peel and seeds (Rezzadori et al. 2012). Approximately 95% of these agro-industrial wastes are made from peels (orange

and lemon peel residues) generating a serious disposal problem which implies the use of extensive economic and energy resources, in addition to risk increase of air, water and soil pollution because of the pollution (Ortiz et al. 2020). In this work, two different types of citric acid source were tested, performing an aqueous extraction of lemon and orange peel, due to the high amount of fruit peel in organic waste, generated by the domestic sector (Villegas- Guzman et al. 2017). The addition of natural products was set taking into account the amount of citric acid that was obtained in the extraction, maintaining in the system the molar ratio 1: 1 (Citric acid: Iron) (Moreira et al. 2017; Efraim A Serna-Galvis et al. 2020).

Significant differences were observed among the citric acid sources regarding the degradation rates and the after 30 min of treatment efficiency (Table 1), which both parameters show to be larger for the commercial reagent compared to the natural extractions (orange and lemon peels).

However, Fig. 1 shows the effect of the citric acid source (commercial reagent, lemon peel extract and orange peel extract) along the process on the simultaneous degradation of SMX and TMP (Fig. 1A and 1B respectively) by the PEF system at pH 4.8, pH obtained by adding citric acid (without modifying the pH). In particular, the degradation showed similar efficiency when citric acid present in the natural products extract is added to the system compared to the analytical grade reagent, since SMX was completely degraded at 45 min and TMP at the 90 min in the three evaluated cases. These results show that the presence of possible presence of organic matter in the extractions do not represent a significant competition for the produced oxidant species responsible of promoting the target molecules (antibiotics) degradation (Ouiriemmi et al. 2017; Villegas-Guzman et al. 2017; Villegas- Guzman et al. 2017).

Citric acid reduces the amount precipitated ferric ions as insoluble hydroxides due to the formation of the iron-citrate complex (Eq. 4) which presents a photocatalytic activity even under visible light (SM2) (Davididou et al. 2017; Oturan et al. 2018). As seen in Fig. 1, similar degradation profiles were obtained for the commercial reagent and extracts (orange and lemon peels) as a natural source suggesting that iron-citrate complexes can absorb photons from the light emitted by diodes (LEDs) (Eq. 5) producing ferrous ion in solution (Ruales-Lonfat et al. 2016). Furthermore, the photoactivity of the formed organo-ferric complexes promotes the formation of extra oxidative species (O_2•$^-$/HO_2•, •OH and R•) by the ligand-to-metal charge transfer (LMCT) (Feng et al. 2012; Jho et al. 2012) allowing the degradation of both SMX and TMP without the pH adjustment requirement before and after the treatment.

$$Fe^{3+} + C_6H_8O_7 \rightarrow Fe^{3+}[C_6H_5O_7]^{3-} + 3H^+ \quad (4)$$

$$Fe[C_6H_5O_7]^{3-} + h\nu \rightarrow Fe^{2+} + C_6H_5O_7{}^{2-} \quad (5)$$

In order to provide deeper information about the citric acid source, additional experiments were performed in which pH was tested (Figure SM1). Similar results were observed for SMX degradation for the case of the acidic system (pH 3.0) and for the addition of citric acid case reaching 100% of SMX elimination after 45 min showing the positive effect of the citric acid as additive (Figure SM1A).

In the case of TMP, at pH 3.0 it was completely degraded after 45 min but for the citric acid present in the orange extract addition case, its degradation was obtained after 90 min (Figure SM1B), twice the time than SMX. Furthermore, this results for SMX and TMP show a positive effect on degradation in the experiments with the addition of citric acid (green line), when compared with the corresponding controls of pH 7.0 (yellow line) and pH 4.8 acidified with HCl (pH similar to that obtained by adding citric acid; red line), due to the fact that high pH and without having an iron complexing agent, iron (III) aqua complexes are formed (Eq. 6), decreasing the generation of hydroxyl radicals from Fenton reaction and, in turn, decrease the degradation efficiency of SMX and TMP (Boczkaj and Fernandes 2017; Clarizia et al. 2017).

$Fe^{2+} + OH^{2+} \rightarrow [Fe^{3+}(OH)]^{2+}$ (6)

Considering that experiments were carried out to promote the simultaneous degradation SMX and TMP, the addition of citric acid seems to be a promising alternative instead of acidifying the solution since after 45 min of treatment when SMX is completely eliminated, biodegradability of the treated solutions should be increased with less toxic character and antibacterial activity (properties discussed in the subsequent points) (Cai and Hu 2017; Martínez-Costa et al. 2018; Alharbi et al. 2019). Based on the results, the use of extract from lemon and orange peel is a great alternative to implement it in PEF processes, with high efficiency in the degradation of contaminants of emerging concern (CECs) and less contamination by part of organic waste (Ruales-Lonfat et al. 2016; Gyuri Sági et al. 2018).

3.1.2 Comparative analysis of SMX and TMP degradation using the PEF system

Degradation rate constants (*k*, mol/min) and elimination efficiencies percentages (Efc, %) for both antibiotics through the PEF system in the presence of different sources of citric acid (commercial reagent, lemon peel extract and orange peel extract) are presented in Table 1. Results show that both *k* and Efc of SMX were higher than those of TMP. In fact, the *k* values for TMP degradations are four times lower than the *k* values for SMX. In addition, after 30 min of treatment Efc was at 54–65% for TMP being significantly lower compared to SMX (77 to 95%). Differences between the antibiotics degradations are due to the chemical properties of the molecules represented by the pKa which is closely related to the molecules reactivity (Table 2) and so, the medium pH affect the reactive sites by modifying the hydration of the target molecule. Consequently, an important impact on the apparent mass transfer coefficient of the SMX is promoted by the oxidants action favoring SMX degradation in a wide range of pH (Lin et al. 2013; R. Zhang et al. 2016).

Table 2
Chemical information of SMX and TMP.

Name		Sulfamethoxazole	Trimethoprim
Chemical formula		$C_{10}H_{11}N_3O_3S$	$C_{14}H_{18}N_4O_3$
Structure (Potential cleavage sites)			
pKa	pKa_1	1.71	3.24
	pKa_2	5.65	7.87

The addition of citric acid lead to a solution of pH 4.8 (without modifying the pH), in which SMX molecule is protonated, maintaining an aniline in the structure (benzene ring with an amine) (I. N. Dias et al. 2014; Martínez-Costa et al. 2018), this structure is susceptible to nucleophilic attacks by hydroxyl radicals, cleaving nitrogen to release nitrogen in volatile forms such as N_2 and NxOy (Thiam et al. 2015).

On the other hand, a similar break in the benzene ring takes place for the SMX molecule leading to the generation of typical by-products in the degradation of organic molecules such as short-chain organic acids (oxalic, oxamic, maleic and fumaric acids have been recorded), which in turn could have similar actions to the citric acid during in the PEF system, favoring the formation of organo-ferric complexes and so an improve degradation efficiency could take place (Gimeno et al. 2016; Peng et al. 2017; Y. Liu et al. 2018). In parallel, the used of DSA anode in the PEF system produces active chlorine species (ACS) which lead to the breakdown of the benzene ring of the SMX causing the total oxidation of the amine group, directly producing gaseous nitrogen (N_2), nitrates (NO_3^-) and/or chlorides (Cl^-) (García-Espinoza et al. 2018; H. Liu et al. 2020).

On the contrary, based on the TMP pKa (Table 2), the addition of citric acid did not affect the molecular hydration of the TMP (I. N. Dias et al. 2014; Moreira et al. 2015; Moreira et al. 2017). Hence TMP degradation could be mainly attributed to the production of the ACS regarding the pH and so at $pH \leq 3.0$ Cl_2 would be predominant (Eq. 7) which has a standard oxidation potential of 1.36 V, while at a pH close to neutral ($3.0 < pH < 7.0$), degradation would be promoted by hypochlorous acid ($E° = 1.49$ V), and at $pH > 7.0$, the production of hypochlorite ions is favored ($E° = 0.89$ V) (Eq. 8–9) (Brillas and Martínez-Huitle 2015; Martínez-Pachón et al. 2019; Zhao et al. 2019).

$$Cl^- \rightarrow Cl_2 + 2e^- \quad (7)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (8)$$

$$HOCl \rightarrow H^+ + ClO^- \quad (9)$$

Additionally, SMX and TMP have potential cleavage sites according to their structures consistent with the identified degradation products (DPs) promoted by oxidative species (•OH and ACS) (Andrade et al. 2009; de Amorim et al. 2013). Four potential cleavage points for SMX have been highlighted, which are located around the functional groups with nitrogen (primary amine of aniline and secondary amine) and aromatic rings (benzene ring of aniline and 3-methylisoxazole), but only one potential cleavage site for TMP in the middle of the two aromatic rings (Table 2) (Formation and Characterization of Sulfamethoxazole-Trimethoprim Cocrystal by Milling Process 2017; Murillo-Sierra et al. 2018). Therefore, there is a higher probability of the SMX to undergo a breakdown instead of TMP which represents a higher degradation speed. Nevertheless, the addition of citric acid into the PEF system leads to the complete degradation of both SMX and TMP (after 90 min of treatment) which would end up in the elimination of the non-biodegradable effect, toxic character and the antibacterial activity of these antibiotics (after 30 to 45 min of treatment) as discussed in the following sections.

The biodegradability, ecotoxicity and antibacterial activity tests (following sections) were carried out with citric acid present in the orange extract. The orange extract was chosen, due to the enormous production of organic waste from this citrus fruit, mainly due to its high consumption and production in Colombia, to such a degree that it belongs to the group of the 10 most preferred fruits by consumers colombians, where 50% of the population consume between 93 to 196 g/d (the highest consumption in grams of fruits) (Rezzadori et al. 2012; Rodríguez Leyton 2019). Additionally, the rates constants (*k*) in the degradations of SMX and TMP were higher with the extract from the orange peel compared to the one extract from the lemon peel, showing less competition for oxidants despite the organic matter extra present in orange peel extract (Villegas-Guzman et al. 2017; Villegas- Guzman et al. 2017; Ortiz et al. 2020).

3.2 Degradation extent of the PEF system adding orange peel extract to SMX and TMP elimination.

3.2.1 Biodegradability test of SMX and TMP solutions submitted the PEF system

Previous degradation results show the ability of the PEF system to eliminate both antibiotics, SMX and TMP, in a simultaneous process. However, a degradation extent analysis showed that mineralization of the treated samples did not occur (Figure SM3) indicating the formation of stable DPs during the treatment, which may require more time to induce their degradation, or they could be recalcitrant to the treatment. Consequently, additional experiments should be performed to establish the possible environmental and human risk of these DPs. The biodegradability tests of the treated solutions it's a well indicator of the possible generation of bioaccumulative DPS that could be even more toxic than the initial molecule (Jojoa-Sierra et al. 2017; Rosseti 2017; Maurício et al. 2018). Therefore, a modified Zahn Wellens test was carried out to evaluate biodegradability to the treated solutions at different times along the PEF process (0, 45 and 90 min of treatment).

Figure 2 shows that for the untreated SMX and TMP solutions, the TOC did not varied even after 12 days of biological treatment. This data is in correspondence to the the null biodegradability of both SMX and TMP and so the antibiotics can be bioaccumulates and toxic affecting the activated sludge biomass ending up into a decrease in the microbiological population and an increase of dissolved oxygen is observed in respirometry results (Figure SM4). Consequently, antibiotics inhibit the microorganisms action and the TOC remains constant (Alvarino et al. 2015; Gyuri Sági et al. 2018; Mendes Barros et al. 2020).

However, after 45 min of the PEF treatment, ~ 55% TOC removal was observed at the end of the biological analysis. This increment in the elimination of organic matter (TOC%) by the activated sludge indicates a higher biodegradability character of the residual organic matter presented in the treated solution. Moreover, treated solutions after 90 min were easily mineralized by the biological system showing total elimination of the initial TOC after 12 days confirmed by the respirometry assay where the dissolved oxygen was 3.4 mg/L, the closest value to the positive control (~ 2.1 mg/L O_2) (Figure SM4). In fact, the final TOC removal for this solution was over 100% (after 90 min of treatment using the PEF system), meaning that the microorganisms within the active sludge live and consume oxygen even after the TOC removal suggesting that microorganisms within the active sludge were not affected by the compounds of the residual organic matter (varied DPs from SMX and TMP) and continue to consume the dissolved oxygen, confirming the biodegradable character of the treated solutions (Vasiliadou et al. 2018; Karlikanovaite-Balikci and Yagci 2019). Therefore, the addition of orange peel extract to the PEF system under non-modified pH has the ability to transform recalcitrant compounds such as SMX and TMP into biodegradable compounds that could be released into the environment without apparent consequences (Efraím A Serna-Galvis et al. 2015; Efraím A Serna-Galvis et al. 2019).

3.2.2 Ecotoxicity analysis of treated solutions by the *D. magna* bioassay

A high biodegradability character is commonly related with a low toxicity; however, these are different parameters and so a biodegradable compound does not imply null toxicity. Therefore, the toxicity of the treated solutions was evaluated with a *D. magna* bioassay, which is widely used as an environmental bioindicator (Libralato et al. 2018; Galhano et al. 2020). The sensitivity of *D. magna* to potassium dichromate was evaluated following the ISO 6341 standard (Biological methods 2012; Espinosa-Barrera et al. 2021), obtaining 100% of inhibition with potassium dichromate $6.8x10^{-9}$ mol/L after 48 h (Fig. 3). An acute ecotoxicological test was performed using *D. magna* against the treated (45 and 90 min) and untreated SMX - TMP solutions.

Figure 3 shows the inhibition level of *D. magna* by direct contact with the untreated solution and those treated with the PEF system in which 40% of inhibition after 48 h was observed for the untreated SMX-TMP solution indicating the high toxicity of the tested solution, representing the risk of waters contaminated with these antibiotics.

On the other hand, a remarkable effect was observed for both treated solutions based on the survival of the organisms (0% of inhibition after 48 h) attributed to the fact that for both cases, 45 min sample and 90 min sample, SMX and TMP were completely degraded, respectively, by the process. This fact indicates the low ecotoxicological character of the treated solutions by the PEF process when orange peel extract is added into the system.

Additionally, the use of orange peel extract in the PEF process does not imply an ecological risk, since the average lethal dose (LD50) of citric acid is registered between 5–11.7 g/kg (for animals), which is equivalent to 0.026–0.061 mol/L of citric acid, values a thousand times higher than those used in the experiments ($3.0x10^{-5}$ mol/L) (Usui et al. 2016; Oyebadejo and Solomon 2019). Furthermore, citric acid participates as a crucial component in various metabolic pathways, such as energy production and amino acid synthesis. This facilitates its degradation in the environment by vegetation, algae and bacterial biomass (Kaur et al. 2017; Nasser et al. 2020).

Respirometry assay can be used as a standard measure of a possible inhibition respiratory process of the activated sludge, providing valuable information of the activated sludge activity and the toxicity of the subjected solutions (Copp and Spanjers 2002; Tobajas et al. 2016; Vasiliadou et al. 2018). The respiration rate of an activated sludge can be reduced in the presence of CECs as a consequence of its toxicity against the sludge microorganisms (such as heterotrophic and nitrifying bacteria). According to the results, the SMX-TMP solution causes an inhibition of 75.13%, presuming a toxic character (Figure SM4) in accordance to previous reports (Chen et al. 2019; Mendes Barros et al. 2020). On the contrary, treated solutions showed 70.37% of inhibition for the 45 min sample and 31.67% for 90 min sample after 25 h of the modified Zahn Wellens test. Results suggest that the produced DPs presented in the treated solutions are less toxic than their precursor molecules (SMX - TMP). Therefore, the application of the PEF system in the presence of orange peel extract eliminates these type of CECs allowing to DPs more biodegradable and non-ecotoxic, which favors the possible releasing of the treated solutions into the environment without a serious consequence to aquifer ecosystem organisms, consistent data with previous studies based on other CECs (Oropesa et al. 2017; Kovacevic et al. 2018; Libralato et al. 2018).

3.2.3 Antibacterial activity (AA) evolution during SMX and TMP degradation by the PEF system adding orange peel extract

In the case of antibiotics treatment, in addition to the biodegradability and ecotoxicity evaluation as degradation extent, it is important to determine the residual antibacterial activity (AA) since previous report indicates that even if the initial molecule is degraded degradation products keep an AA (Efraím A Serna-Galvis et al. 2017), representing still a major concern even more for cases as SMX and TMP which are commercially found together. Therefore, the evolution of AA was determined for the mixture of the two antibiotics (SMX-TMP) (Fig. 4).

Figure 4 shows the antibacterial activity (AA) evolution, which was completely eliminated after 45 min of treatment, at the same time in which 100% of SMX and 77% of TMP were degraded when adding citric acid reagent grade, and 100% of SMX and 71% of TMP when adding the orange peel extract, with similar degradation percentages for SMX and TMP in both experiments, which demonstrates that citric acid performs its iron complexing function efficiently regardless of the extraction source, enhancing the simultaneous degradation of antibiotics. On the other hand, the possible additional organic matter obtained in the extract does not affect the degradation or loss of AA, highlighting the great efficiency of the application of orange peel extract as source natural the citric acid in the PEF system for the treatment of water contaminated with CECs (Villegas- Guzman et al. 2017; Martínez-Pachón et al. 2019).

The AA observed by the Kirby Bauer test was clearly attributed to the synergistic combination of antibiotics (SMX - TMP), because the orange peel extract used during the degradation (with a citric acid concentration of $3.0x10^{-5}$ mol/L) did not show an antibacterial character (No obvious halo was detected) as other authors have shown (Fernández-López et al. 2005; El-Shawaf et al. 2012; Guo et al. 2020).

Considering that the evolution of AA could be related to the antibiotics transformations, the rapid elimination of antibacterial activity suggests that the synergistic effect of the antibiotics combination has been disrupted. The minimum inhibitory concentration (MIC) of the SMX and TMP mixture has been reported at 2:38 µg/mL of TMP:SMX against the ATCC 25922 strain (Smanthong et al. 2015; Suhartono et al. 2016; G Sági et al. 2018) where the two successive steps of folic acid metabolism become completely blocked due to the loss of the synergistic effect (due to the total degradation of SMX and therefore the loss of its 1: 5 (TMP: SMX) ratio) (Smanthong et al. 2015; Suhartono et al. 2016; Castillo et al. 2018; G Sági et al. 2018; Thiebault 2020). Therefore, results suggest that after only 45 min of treatment neighed the powerful mixture of the antibiotic or possible antibiotic by-products are not concentrated enough to show an antibiotic activity. Hence, by submitting the synergistic mixture of SMX and TMP to the PEF system in the presence of citric acid (independently of extraction source) turns the proposed system into a promising alternative to mitigate the increase in bacterial resistance, due to the formation of DPs without residual antibacterial activity.

Conclusions

This research demonstrated the efficiency of the PEF system with citric acid present in orange peel extract (as an iron complexing agent) in the simultaneous degradation of the antibiotics SMX and TMP. Additionally, using organic waste such as orange and lemon peels as citric acid sources can mitigate air, water and/or soil contamination due to the not well disposal of these agro-industrial wastes. Degradation efficiency was significantly improved by the formation of the photoactive iron-citrate complex, since a photoassisted LMCT is produced causing the rapid exchange of iron from its ferric to ferrous state, which immediately undergoes into the Fenton reaction favoring the hydroxyl radical’s production. Moreover, the use of citric acid allows an efficient degradation process comparatively to the classic Fenton reaction which required acidic media, instead in the presence of citric acid no pH modification is required before and after the process.

During the simultaneous degradation of SMX and TMP, a higher rate constant (*k*) and degradation efficiencies (Efc, at 30 min of treatment) were observed for SMX, attributed to the protonation form of the SMX at the working pH (pH 4.8 by adding citric acid, non-modified pH) favoring its breakdown at the four potential cleavage points. Additionally, treated solutions showed an increase in biodegradability character (elimination of 100% of TOC of the 90 min treated solution), a significant decrease of ecotoxicity (0% inhibition in the bioassay with *D. manga* after 45 min of treatment) and the loss of antibacterial activity (total loss of AA after 45 min of treatment). Results indicate the capacity of the PEF system under non-modified pH due to the addition of citric acid to promote a simultaneous degradation of SMX and TMP leading to the generation of less dangerous products than the initial antibiotics regarding the environment and possibly for human health. This way, this investigation proposes an ecological and efficient alternative for the elimination of CECs present in water, demonstrated with the tests of biodegradability, ecotoxicity and antibacterial activity on the treated SMX and TMP solutions, evaluations that in many investigations omit, despite being an important key for the future scaling up of AOPs treatments without generating a greater risk.

Declarations

Ethical Approval of Authors

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Consent to Participate

Not application

Consent to Publish

All authors agreed with the content and that all gave explicit consent to submit and that they obtained consent from the responsible authorities at the institute/organization where the work has been carried out, before the work is submitted.

All authors whose names appear on the submission

1) made substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data; or the creation of new software used in the work;

2) drafted the work or revised it critically for important intellectual content;

3) approved the version to be published; and

4) agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

Signature:

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Authors Contributions

In absence of specific instructions and in research fields where it is possible to describe discrete efforts, the Publisher recommends authors to include contribution statements in the work that specifies the contribution of every author in order to promote transparency. These contributions should be listed at the separate title page.

Carlos Delgado-Vargas: Methodology; Formal analysis, Writing- original draft. Writing-review & editing.

Paula Espinosa-Barrera: Conceptualization, Methodology, Formal analysis, Writing-original draft, Writing-review & editing.

Paola Villegas-Guzmán: Conceptualization, Writing-review & editing, Resources, Funding acquisition.

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Competing Interests

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or

kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Signature:

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Tables

Table 1
Degradation efficiency of the antibiotics SMX and TMP in terms of initial degradation rate and elimination percentage after 30 min of treatment.

Name		Sulfamethoxazole	Trimethoprim
Chemical formula		$C_{10}H_{11}N_3O_3S$	$C_{14}H_{18}N_4O_3$
Rate constant (mol/min)	Reagent	0.0440	0.0135
	Lemon peel extract	0.0209	0.0099
	Orange peel extract	0.0241	0.0129
Efficiency in 30 min (%)	Reagent	95.07	65.17
	Lemon peel extract	77.34	54.24
	Orange peel extract	82.74	56.44

Due to technical limitations, table 2 is only available as a download in the Supplemental Files section.

Figures

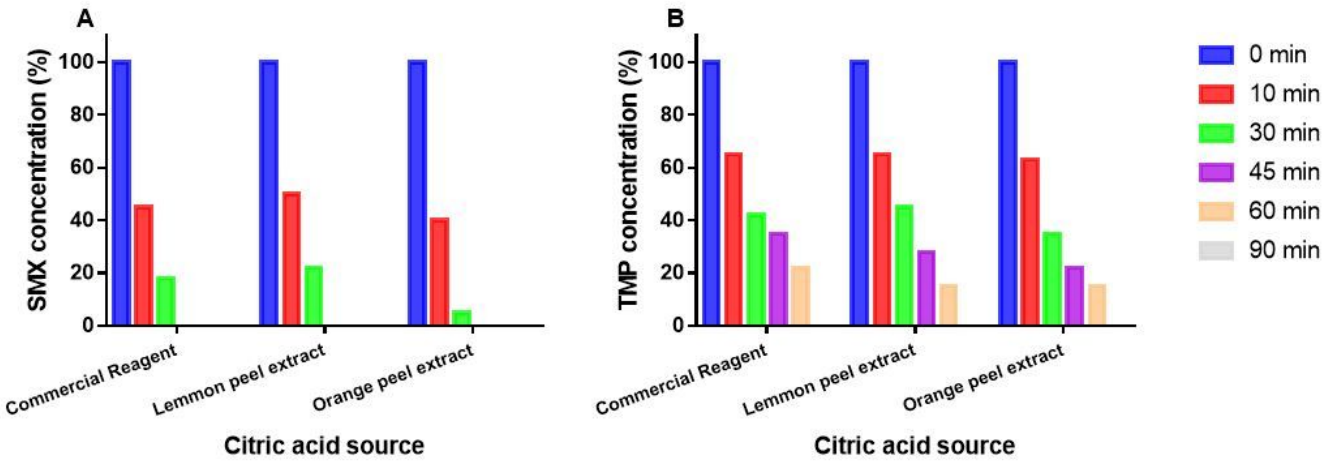

Figure 1

Simultaneous degradation of SMX and TMP using PEF system in the presence of citric acid from commercial reagent, lemon peel extract and orange peel extract. A. SMX degradation, [SMX]o: 3.94x10-4 mol/L, B. TMP degradation [TMP]o: 3.44x10-4 mol/L. Conditions: pHinicial: 4.8 by adding citric acid (without modifying the pH), [citric acid]: 3.0x10-5 mol/L, [Fe+2]: 3.0x10-5 mol/L, current density: 5.19 mA/cm2, radiation source: LED.

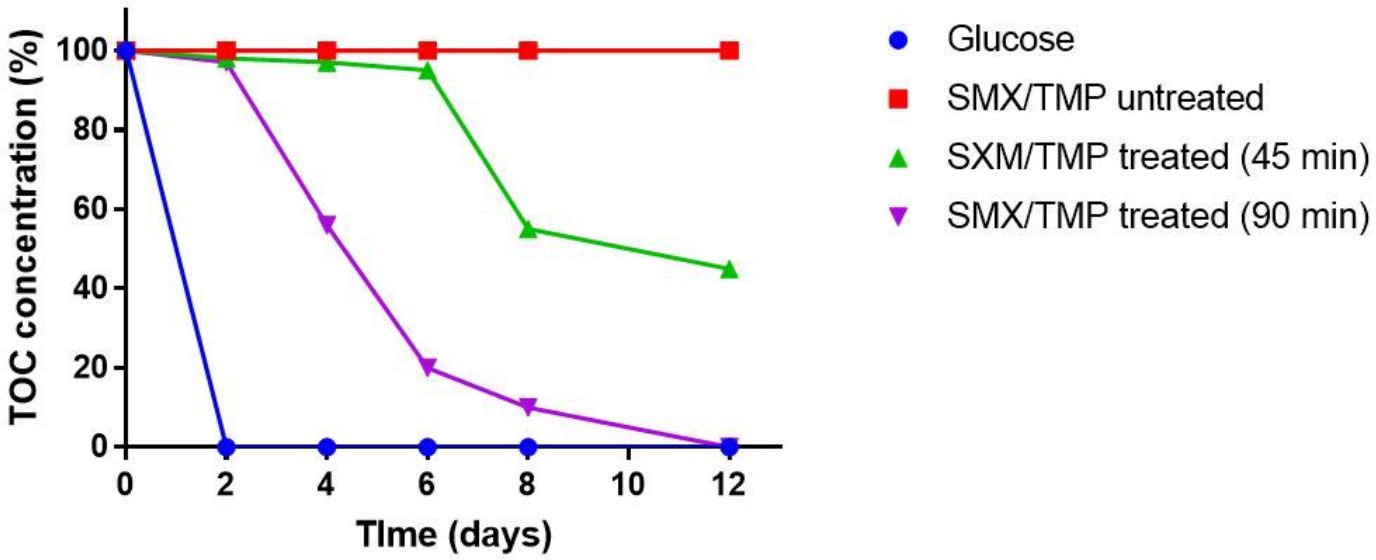

Figure 2

Biodegradability test of untreated and treated solutions by the PEF process adding orange peel extract. Biological process conditions: 54 mg/L of initial TOC, 230 mL of solution, pH 7.0, 37 °C. Conditions in the PEF process: [SMX]o: 3.94x10-4 mol/L, [TMP]o: 3.44x10-4 mol/L, pHinicial: 4.8 by adding citric acid present in orange peel extract (non-modified pH), [citric acid]: 3.0x10-5 mol/L, [Fe+2]: 3.0x10-5 mol/L, current density: 5.19 mA/cm2, radiation source: LED.

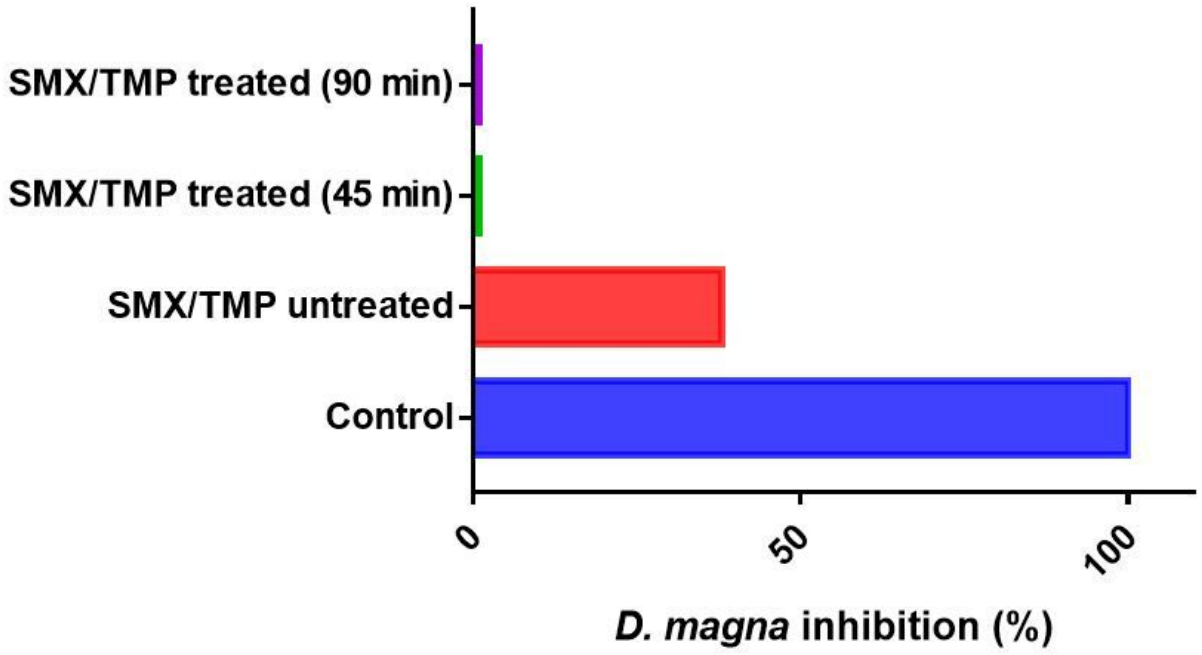

Figure 3

Toxicity test of the untreated and treated solutions by the PEF process adding orange peel extract: Potassium dichromate (positive control), SMX-TMP (untreated solution) and treated solutions after 45 min 90 min. Conditions: 10 organisms (D. magna) per test, 10 mL of reconstituted hard water, 20 mL of the solution to be evaluated, temperature: 20 °C, pH: 7.0. Conditions in the PEF process: [SMX]o: 3.94x10-4 mol/L, [TMP]o: 3.44x10-4 mol/L, pHinitial: 4.8 by adding citric acid present in orange peel extract (non-modified pH), [citric acid]: 3.0x10-5 mol/L, [Fe+2]: 3.0x10-5 mol/L, current density: 5.19 mA/cm2, radiation source: LED.

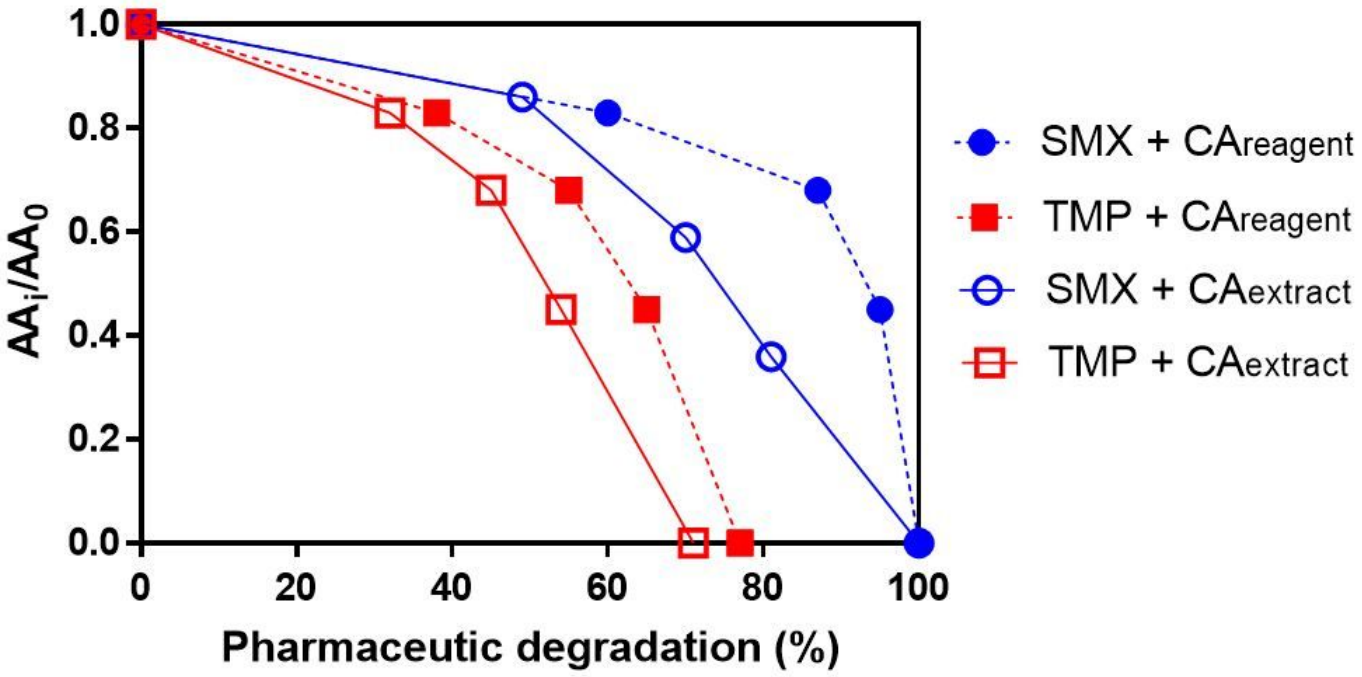

Figure 4

Evolution of antibacterial activity (AA) along 45 min of treatment with the PEF system in the presence of citric acid reagent commercial reagent (dashed line) and orange peel extract (solid line). Conditions: [SMX]o: 3.94x10-4 mol/L, [TMP]o: 3.44x10-4 mol/L, pHinicial: 4.8 by adding citric acid (non-modified pH), [citric acid]: 3.0x10-5 mol/L, [Fe+2]: 3.0x10-5 mol/L, current density: 5.19 mA/cm2, radiation source: LED.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Table2.jpg
- SupplementaryMaterial.docx