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Improvement of solar photo-Fenton by extracts of amazonian fruits for the degradation of pharmaceuticals in municipal wastewater

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Abstract

Extracts of copoazu (*Theobroma gramdiflorum*), canangucha (*Maurita Flexuosa*), and coffee (*coffea arabica*) were explored as enhancers of the solar photo-Fenton process to eliminate acetaminophen, sulfamethoxazole, carbamazepine, and diclofenac. The process performance, at pH 6.2 and 5 mg L^{-1} of iron without the extracts, has a very limited action (~35% of the pollutants degradation at 90 min of treatment) due to the iron precipitation. Interestingly, the extracts addition increased the soluble iron forms but only copoazu extract improved the pollutants degradation (~95% of elimination at 90 min of the process action). The copoazu extract acted as a natural complexing agent, maintaining the soluble iron up to 2 mg L^{-1} even after 90 min, and consequently enhancing the pollutants degradation. The effect of copoazu extract dose on the process performance was also assessed, finding that an iron: copoazu extract molar ratio equal to 1:0.16 was the most favorable condition. Then, the process improved by copoazu extract was applied to municipal wastewater. Remarkably, the process led to ~90% of total pharmaceuticals degradation at 20 min of treatment. This work evidences the feasibility of amazonian fruits extracts to improve the solar photo-Fenton process to degrade pharmaceuticals in aqueous matrices at near-neutral pH.

Keywords: Advanced oxidation process improvement; Iron complexation; Microcontaminants elimination; Municipal wastewater treatment; Natural enhancers.

1. Introduction

Untreated municipal wastewater (MWW) is recognized as the most hazardous pollution source to environmental water due to the high presence of nutrients (e.g., N and P) and organic contaminants (Preisner 2020). Pharmaceuticals are among organic pollutants commonly found in MWW (Liu et al. 2017; Shraim et al. 2017; Botero-Coy et al. 2018). Although the discharge of pharmaceuticals into the environment is not yet regulated, there is a growing interest in their final disposal, thus they are considered as contaminants of emerging concern (CECs) (Küster and Adler 2014; Sánchez Pérez et al. 2020). Indeed, pharmaceuticals can induce toxicity, mortality, and developmental abnormalities in aquatic species (Bielen et al. 2017). Thus, their input into the environment should be limited/avoided. An option to eliminate pharmaceuticals in MWW is the application of advanced oxidation processes (AOP), which are based on the generation and utilization of short-lived, strong oxidant, and highly reactive radical species (mainly hydroxyl radical, HO•, E°: 2.80 V (Armstrong et al. 2013)). To produce the hydroxyl radical, catalytic AOPs such as photo-Fenton are widely used (Miklos et al. 2018).

Photo-Fenton comprises the reaction of ferrous ions with hydrogen peroxide initially (Eq. 1). Then, the ferric species can be reduced in the aqueous medium by the action of UV-Vis light, producing extra hydroxyl radicals (Eq. 2) and making the system a catalytic process (Pignatello et al. 2006). Photo-Fenton process has shown to be very efficient in the degradation of pollutants in MWW (Papoutsakis et al. 2016). This process has gained the attention of researchers due to its operational easiness and the possibility of solar irradiation utilization (Pouran et al. 2015; Clarizia et al. 2017).

However, the photo-Fenton process at pH higher than 3.0 is limited by Fe^{3+} precipitation (Eq. 3) (Villegas-Guzman et al. 2017b). Interestingly, some organic compounds can complex iron (III) keeping it in soluble forms, allowing it to work at near-neutral pH conditions (Clarizia et al. 2017). Furthermore, many Fe^{3+}-organic ligand complexes can absorb light in the near-UV and visible regions more efficiently than aqua-complexes and undergo photo-reduction through a ligand-to-metal charge transfer (LMCT). Then, the ferrous ion is regenerated (Eq. 4) and other radicals are produced (Eqs. 4-5, which could contribute to the oxidation of organic substances) (Miralles-Cuevas et al. 2014; Clarizia et al. 2017; Villegas-Guzman et al. 2017a).

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

$$Fe^{3+} + H_2O + h\nu_{(UV\text{-}vis)} \rightarrow Fe^{2+} + HO\bullet + H^{+} \qquad (2)$$

$$Fe^{3+} + HO^{-} \rightarrow Fe(OH)_{3\ \text{(insoluble solids)}} \qquad (3)$$

$$[Fe^{3+}\text{-}L]_{\text{complex}} + h\nu \rightarrow Fe^{2+} + L\bullet \qquad (4)$$

$$L\bullet + O_2 \rightarrow\rightarrow\rightarrow O_2\bullet^{-} \qquad (5)$$

Several poly-carboxylate acids that act as chelating agents of iron such as oxalic acid, citric acid, ethylenediamine-N,N-disuccinic acid (EDDS), ethylene-diamine-tetra-acetic acid (EDTA), and nitrile-acetic acid (NTA), have been successfully utilized to improve the solar photo-Fenton process performance at near-neutral pH (Arzate et al. 2020). Nonetheless, EDTA or NTA have high toxicity and low biodegradability. Meanwhile, chelation with citric or oxalic acid requires reduced pH for their best performance (for instance, the optimal behavior for the Fe^{3+}-citrate and

Fe^{3+}-oxalate complexes, occurs at pH 5.0 and 4.3, respectively) (Papoutsakis et al. 2015). In turn, iron complexation with EDDS represents additional costs to the process by the purchasing of such reagent. Thus, to overcome these issues, natural substances polyphenols-rich have been recently evaluated (Ruíz-Delgado et al. 2019; Prada-Vásquez et al. 2020). Also, current works are focused on the search for non-toxic and biodegradable chelating compounds, which must be environmentally sustainable and inexpensive to propose a large-scale photo-Fenton process at near-neutral pH (Klamerth et al. 2013). Indeed, juices of orange or lime and coffee extract (organic acid-rich compounds) have been evaluated as SPF enhancers with promising results for the elimination of CECs and bacteria (Villegas-Guzman et al. 2017b).

In this context, natural products rich in polyphenols and/or organic acids have interesting potential in the application of solar photo-Fenton (SPF) at natural pH. Thus, chelating compounds that are biodegradable, do not generate toxicity after carrying out the treatment, and inexpensive could lead to an SPF environmentally sustainable with the potential to propose a large-scale (Klamerth et al. 2013). Some of the abundant native products from Colombian Amazonia contain polyphenols (Genaro-Mattos et al. 2015; Mussatto 2015; Geremu et al. 2016; Heeger et al. 2017), such products have potential as iron complexing agents. Therefore, in our research, three typical products of the region: copoazu (also named cupuassu, *Theobroma gramdiflorum*), canangucha (*Maurita Flexuosa*), and husk coffee (*Coffea arabica*) were considered.

Copoazu and canangucha are typical fruits of the Amazon region (Rogez et al. 2004; Contreras-Calderón et al. 2011; Galeano 2011; Koolen et al. 2013; Nobre et al. 2018), these have been used in the food industry in Brazil and Peru. In the Colombian Amazon region, copoazu and canangucha are part of the nascent agro-industry, specifically the production of candies where just a part of pulp is used as raw material and the rest is a waste. Likewise, coffee is an emblem of the national economy of Colombia, and it is also cultivated in its Amazonian region.

This study aimed to evaluate the feasibility of extracts of three amazonian fruits to enhance the SPF process at near-neutral pH to simultaneously degrade four representative pharmaceuticals (acetaminophen, diclofenac, sulfamethoxazole, and carbamazepine) in municipal wastewater. Under authors' knowledge, this work is the first study about the use of amazonian fruits for enhancing the degradation of the pharmaceuticals in MWW, which pretends to provide a starting point about the utilization of amazonian agro-industrial products and wastes as iron complexing agents in the photo-Fenton process. In our work is covered the following topics: i) limitation of conventional SPF at near-neutral pH to eliminate the target pollutants, ii) performance of the SPF system in the presence of extracts of the amazonian fruits, iii) influence of the iron: extract ratio on the pollutants degradation and iron availability, and iv) enhancement of the pharmaceuticals degradation in raw MWW by the best extract.

2. Materials and methods

2.1. Reagents

Iron (III) sulfate heptahydrate and hydrogen peroxide were purchased from Panreac®. Sulfuric acid, acetonitrile (HPLC grade), sodium bisulfite, and sodium hydroxide were supplied by Merck®. All solutions were prepared using deionized water or municipal wastewater from Florencia-Colombia (which characterization is provided in Table 1).

2.2. Analytical measurements

The concentration of the four pharmaceuticals was analyzed using a Shimadzu HPLC with a UV detector at 254 and 267 nm with a C18 column (5 µm, 4.6 x 150 mm), with a flow of 0.5 mL min^{-1}. The injection volume was 100 µL. The method consisted of a gradient flow with phase A: 25 mmol L^{-1} formic acid and phase B: acetonitrile, as follows, at 0 min 90%A, 3 min 90%A, and 13 min 20%A, 13.1 min 0%A, 20 min 0%A, 20.1 min 90%A, and 25 min 90%A.

The removal percentage of each pharmaceutical was calculated using Eq. 6

$$x_i = (C_{initial} - C_{final} / C_{initial}) * 100 \tag{6}$$

Where $C_{initial}$ is the initial concentration and C_{final} means the final concentration of the pharmaceutical (in µmol L^{-1}).

The pondered removal percentage (X) was determined by Eq. 7.

$$X = \frac{\sum_{i=1}^{n} C_{initial,i} * x_i}{\sum_{i=1}^{n} C_{initial,\,i}} \tag{7}$$

Where the subscript i refers to each pharmaceutical (i.e., $1 \leq i \leq n$; $n = 4$) and x_i represents the removal percentage of each pharmaceutical.

The organic matter as total organic carbon (TOC) was monitored by the combustion catalytic oxidation method using a Shimadzu TOC-L instrument. Dissolved iron was determined by complexation with 1,10-phenanthroline with filtered and unfiltered samples according to Standard Methods for the Examination of Water and Wastewater (3500-Fe B) (APHA et al. 2012). The hydrogen peroxide concentration was followed by the meta-vanadate method based on the reaction of H_2O_2 with ammonium metavanadate in an acidic medium, which results in the formation of a red-orange color from peroxovanadium cation, with maximum absorbance at 450 nm (Nogueira et al. 2005).

The concentration of total polyphenols in fruit extracts was quantified using the Folin-Ciocalteu (Horszwald and Andlauer 2011) with some modifications. The result is given as mg of gallic acid equivalent per L (mg GAE L^{-1}) (Heeger et al. 2017). Municipal wastewater (MWW) from Florencia-Caquetá Colombia was used. Physical and chemical characterization of MWW was determined by analytical standardized methods (Table 1) (APHA et al. 2012).

Table 1. Physicochemical characteristics of the MWW from Florencia-Caquetá Colombia

Parameter	Method	Minimum Value	Maximum Value
Nitrates (NO_3^-) (mg L^{-1})	HCl-UV 4500 –NO_3^-	4.62	14.38

Ammonia Nitrogen ($NH_4^{\mp}$), (mg L^{-1})	4500-NH_3	17.73	43.34
Total Nitrogen (TN), (mg L^{-1})	Persulfate oxidation (4500 –N)	124	210.3
Orto-phosphates (PO_4^{-3}), (mg L^{-1})	Ascorbic acid (4500-P)	1.46	3.21
Sulfates (SO_4^{-2}), (mg L^{-1})	Titrimetric (4500-SO_4^{-2})	45.60	188.3
Chlorides (Cl^-), (mg L^{-1})	Argentometric (4500-Cl^--B)	62.05	103.34
Alkalinity (mg L^{-1})	Titrimetric (2320-B)	53.49	146.76
Hardness, (mg L^{-1})	Titrimetric (2340-C)	57.1	119
pH	Potentiometric (4500-pH)	6.45	6.75
Total organic carbon (TOC, mg C L^{-1})	Combustion-IR (5310-B)	28	89.32
Chemical oxygen demand (COD, mg O_2 L^{-1})	Closed reflux (5220 C)	256	580
Biochemical oxygen demand (BOD_5, mg O_2 L^{-1})	Respirometry-Method (5210 B)	126	302

Total suspended solids (TSS, mg L^{-1})	Gravimetric (2540 D)	54.12	147.67
Total solids (TS, mg L^{-1})	Gravimetric (2540 B)	128.56	258.78

*All methods were taken from Standard Methods for examination of water and wastewater (APHA et al. 2012).

2.3. Reaction system for the solar photo-Fenton process

SPF experiments were carried out at near-neutral pH (6.2) using 0.0066 mM of each pharmaceutical (SMX, DCF, CBZ, and ACT) spiked simultaneously in 1 L of deionized water or actual raw municipal wastewater (MWW) in a 1L beaker. 5 mg L^{-1} of Fe (III) and 68 to 120 mg L^{-1} of H_2O_2 were added to the reactor. The degradation was done with a solar simulator (Suntest CPS+, Atlas) equipped with an air-cooled xenon lamp with an illumination surface of 560 cm^2 and 250 - 750 W m^{-2} of solar intensity (global irradiance).

2.4. Extracts characterization

Three amazonian fruits (canangucha “*Maurita Flexuosa*”, coffee “*Coffea arábica*” and copoazu “*Theobroma gramdiflorum*”) were considered. Copoazu fruits were collected in a medium green state, and 10 mL of the liquid extract was obtained by squeezing 5 g of the pulp from inside the fruits. The ripe fruit of canangucha was taken from a palm, 30 g of the pulp fruit were squeezed, obtaining 8 mL of the liquid extract. For the coffee extract, the ripe fruits of coffee trees were taken, the seed was extracted and the external shell (30 g) was used to obtain its aqueous extract by maceration using 20 mL of distilled water. The content of total phenols (by Folin-Ciocalteu methodology) and total organic carbon in the extracts were assessed (Table 2). Extracts of the amazonian fruit were added to the aqueous samples to be treated by the SPF systems considering the molar ratio between the iron and total polyphenols (i.e., Fe: total polyphenols in the extract).

3. Results and discussion

3.1. Treatment of the representative pharmaceuticals by solar photo-Fenton

The capability of the SPF process to degrade a mix of the four representative pharmaceuticals in deionized water (at pH 6.2) was initially tested, the results are presented in Fig. 1A. It was found that the SPF process exhibited a low degrading action on three of the considered pharmaceuticals. After 90 min of treatment, it was obtained removals of 18% for both CBZ and ACT, 35% for SMX, and 68% for DCF. In addition to the pollutants elimination, the evolution of iron and the consumption of hydrogen peroxide were also followed during the SPF process (Fig. 1A). The analysis of dissolved iron in the SPF system indicated that iron is not available in solution, at 20 min of treatment there was no soluble iron, and at this time only ~5 mg L^{-1} of H_2O_2 were consumed. These results suggest that the production of hydroxyl radicals by the reaction between the iron and the hydrogen peroxide (Eq. 1) is limited due to the iron is not in soluble forms (Pignatello et al. 2006; Serna-Galvis et al. 2020). Consequently, the elimination of pollutants is low.

To understand the observed degradation by the process, some sub-systems/components were also tested. It was considered the direct action of the solar irradiation on the pharmaceuticals (i.e., photolysis) and the combination of light with hydrogen peroxide (i.e., H_2O_2/light). Fig. 1B shows the results for such control experiments. The sunlight alone induced a high degradation of DFC (~ 75% of elimination at 90 min of irradiation), whereas SMX and CBZ experimented moderate photolysis (removals between 10 and 15% after 90 min of treatment). In contrast, ACT showed no elimination by the sole action of the solar light.

The differences among the photolysis of the four pollutants can be understood considering the UV-Vis spectra of them (see Fig. S1 in the Supplementary material). From the spectra can be noted that DCF, SMX, and CBZ have light absorption above 300 nm, while ACE only absorbs wavelengths below 300 nm. In turn, the used solar simulator emits light from 300 to 800 nm. Thus, there are intersections of the absorption and emission spectra more significant for DCF, SMX, and CBZ than for ACT, which can explain the behavior observed in Fig. 1B.

According to the literature, photolysis of DCF promoted by solar light yields carbazole structures from the elimination of a chlorine-substituent with the subsequent cyclization (Salaeh et al. 2016; Leydy Katherine Ardila et al. 2019). Meanwhile, SMX begins its photolytic degradation with the breaking of the sulfonamide bond and rearranging the isoxazole ring (Alharbi et al. 2017; Martínez-costa et al. 2018). In the case of CBZ, the solar light can induce transformations, such as hydration of central double bond, ring expansions, and complementary hydroxylation to yield acridone and acridine (Yazdanbakhsh et al. 2019).

On the other hand, it can be noted that for CBZ and ACT, which were more resistant to the photolysis, their degradations are improved by the hydrogen peroxide addition (i.e., the H_2O_2/light subsystem, Fig. 1B). H_2O_2 enhances the pharmaceuticals elimination probably due to its direct oxidant effect (Eq. 8, (Alharbi et al. 2017)) and the formation of some radicals by its homolysis by the UVB component of the solar light (Eq. 9, (Mohapatra et al. 2014; Alharbi et al. 2017)).

$$H_2O_2 + \text{pharmaceutical} \rightarrow \text{degradation products} \quad (8)$$

$$H_2O_2 + h\nu_{UVB} \rightarrow 2HO\bullet \quad (9)$$

The results from the subsystems (control experiments) suggest that, under the tested experimental conditions, the main routes of the SPF action on the pharmaceuticals are photolysis and attack of some radicals generated by both the Fenton reaction and the hydrogen peroxide homolysis by the solar light. Consequently, under work conditions (pH 6.2), iron precipitation was probably responsible for the poor pharmaceutical degradation by the SPF system (Eq. 3, (Pignatello et al. 2006; Serna-Galvis et al. 2020)). In fact, the pondered degradation of pharmaceuticals was ~ 35%. Particles as insoluble iron can avoid light penetration (Christensen and Linden 2003; Mamane et al. 2006), then, this decrease the efficiency of direct (photolysis) and indirect (H_2O_2/light) irradiation action on the pharmaceuticals. Therefore, to obtain a higher removal of the target pollutants, strategies to maintain the iron as soluble species and increase the hydroxyl radical production should be applied. Such topic is developed in the next section.

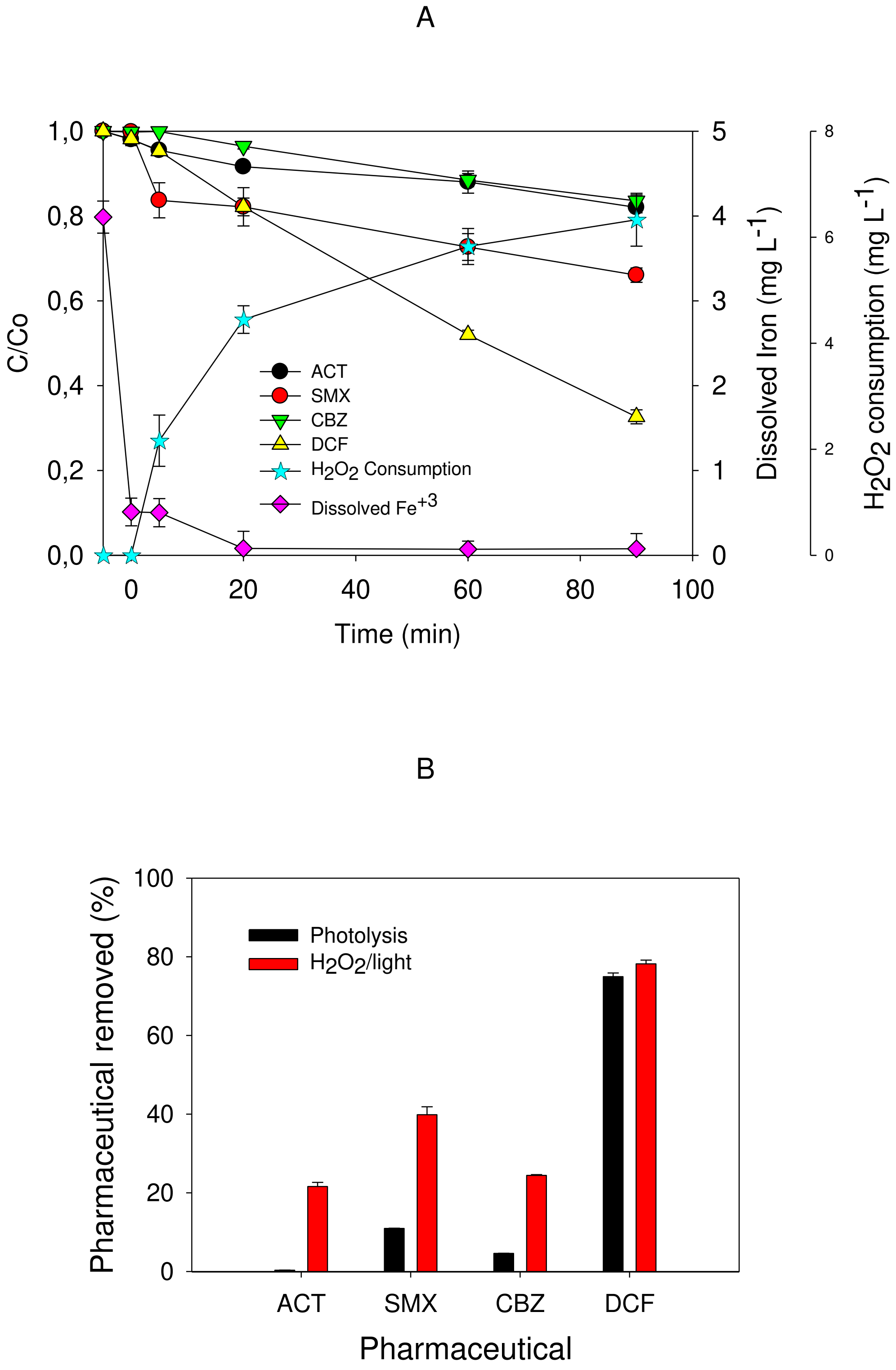


Fig. 1. A. Treatment of pharmaceuticals mixture in deionized water by SPF at near-neutral pH. **B**. removal of pharmaceuticals by control systems. Experimental

conditions $[Fe^{3+}]_o$ = 5 mg L^{-1} (90 µmol L^{-1}). $[Pharm]_o$ = 0.0066 mM. $[H_2O_2]_o$ = 120 mg L^{-1}, and $pH_{initial}$ = 6.2.

3.2. Performance of SPF in presence of COFE, CANE, and COPE

The effect of the addition of extracts of three amazonian fruits to the SPF system (at pH around 6) on both soluble iron keeping and degradation of ACT, CBZ, DCF, and SMX was evaluated. The considered extracts were CANE (canangucha extract), COFE (coffee extract), and COPE (copoazu extract). Fig. 2 shows the treatment of the mix of the target pharmaceuticals in the presence of COFE, CANE, or COPE.

Remarkably, in the presence of all extracts (Fig. 2A-C), the amount of dissolved iron was higher than in their absence (Fig. 1). Furthermore, the addition of COPE to the photo-Fenton system enhanced significantly the degradation of the four pharmaceuticals (Fig. 2D). From Fig. 2D, it can be also noted that despite COFE and CANE keep iron in soluble forms, these two extracts had a detrimental effect on the process performance for the pollutants elimination (with an exception for ACT in CANE presence).

Table 2 contains relevant characteristics of the tested extracts, which provide information to interpret the different results for CANE, COFE, and COPE. It must be mentioned that the COFE addition is able to provide a coloration more intense to the water (Fig. S2), this is probably due to the content of tannins and chlorogenic acid, (Genaro-Mattos et al. 2015)), which can affect the light penetration, avoiding the photolysis of pharmaceuticals and photo-regeneration of ferrous ions from iron-organic-complexes (Eq. 4). Also, the COFE has the highest content of TOC (this is twice that contributed by COPE and five times that of CANE, Table 2), such organic matter can also compete by the radicals, inhibiting the pharmaceuticals elimination.

In the case of CANE, a particular behavior was found. Only the elimination of ACT was improved concerning the conventional SPF. The results for the elimination of SMX, CBZ, and DFC with CANE can be rationalized analogously (competence by organic matter) to the indicated in the COFE case. Meanwhile, the selective elimination of ACT requires another view. The non-removal of ACT by CANE alone (Fig. S3) allowed us to discard a direct interaction between this pharmaceutical and polyphenols of CANE. Then, it could be suggested that ACT is transformed by a ferric-organic complex (or ferric ions under special complexing environments, Eq. 10), which favor redox reactions for hydroquinone-type or analogous structures as presented by ACT (Issa et al. 2013; Jiang et al. 2015; Peng et al. 2017). Although, such interaction allows to rationalize the elimination of ACT from the water by SPF in the CANE presence. This particular result should be studied in depth in future investigations.

$$\text{CANE-Fe}^{3+}_{\text{complex}} + \text{ACT} \rightarrow \text{Fe}^{2+} + \text{quinone-type products} \quad (10)$$

On the other hand, when COPE was added, an acceleration of the pharmaceuticals degradation and a significant increase in the H_2O_2 consumption was observed (Figs. 2C and 2D). To investigate the possible action of COPE as a photosensitizer, the treatment of the pharmaceuticals in presence of the fruit extract and solar light was carried out. When the sunlight is combined with COPE, after 90 min of treatment, the pharmaceutical removal was the same as the obtained by photolysis with sunlight alone. This suggests that COPE did not act as a photosensitizer for pharmaceuticals degradation (Porras et al. 2016).

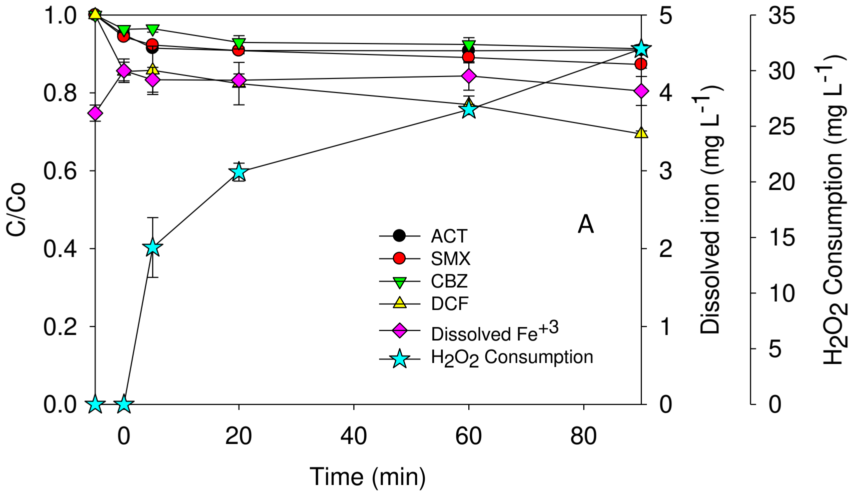
It can be mentioned that COPE is rich in polyphenols (Hernández Londoño 2010; Carlos Carmona-Hernandez et al. 2018; Pereira et al. 2018), as demonstrated in Table 2. The polyphenols complex the ferric ions easily (Eq. 11, (Ruíz-Delgado et al. 2019)), maintaining the iron in soluble forms as supported by Fig. 2C. Such complexes can interact with the hydrogen peroxide to produce other degrading species (e.g., hydroperoxyl radical, Eq. 12, (Ruíz-Delgado et al. 2019)). Besides, it is well-known that polyphenols can reduce ferric ions to ferrous ions (Fig. S4, (Oakes 2013)), which are required for the Fenton reaction (Eq. 1); thus, favoring the catalytic cycle of iron. Indeed, in COPE presence, there was a very high H_2O_2 consumption (Fig. 2C), which confirms the interactions indicated by Eqs. 1 and 12. Hence, the role of COPE as a complexing agent of iron and regenerator of ferrous ions favors the production of radicals in the system; then, an enhancement of the degradation of target pollutants occurs.

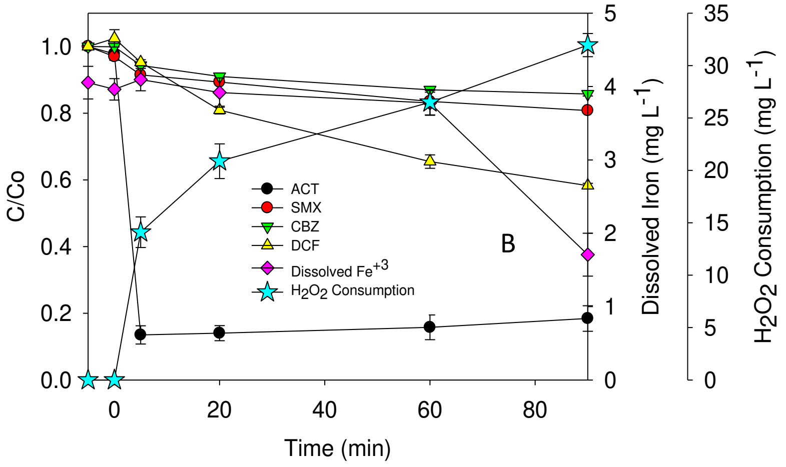
$$Fe^{3+} + \text{Polyphenols} \rightarrow (Fe^{3+}\text{-Polyphenols})_{\text{complex}} \quad (11)$$

$$(Fe^{3+}\text{-Polyphenols})_{\text{complex}} + H_2O_2 \rightarrow (Fe^{2+}\text{-Polyphenols})_{\text{complex}} + HOO\bullet + H^+ \quad (12)$$

It can be mentioned that the dissolved iron in the presence of COPE remained lower than in the cases of CANE and COFE (see Figs. 2A-C), suggesting that CANE and COFE exert an iron complexation stronger than COPE. Then, the complex of iron with COPE seems less stable, making the iron more available to interact with the hydrogen peroxide (Eqs. 1 and 12). Additionally, as HO• is non-selective, this can also react with the COPE components. As a consequence, the concentration of COPE decreases, and the soluble iron may diminish.

In the COPE presence, up to 95% of the pondered elimination of pharmaceuticals was reached, which highlights the high potential of COPE as an enhancer of the SPF process at near-neutral pH. To better understand its enhancing effect, experiments about variations of COPE: iron ratio were performed and their outcomes are presented and discussed in the next subsection.





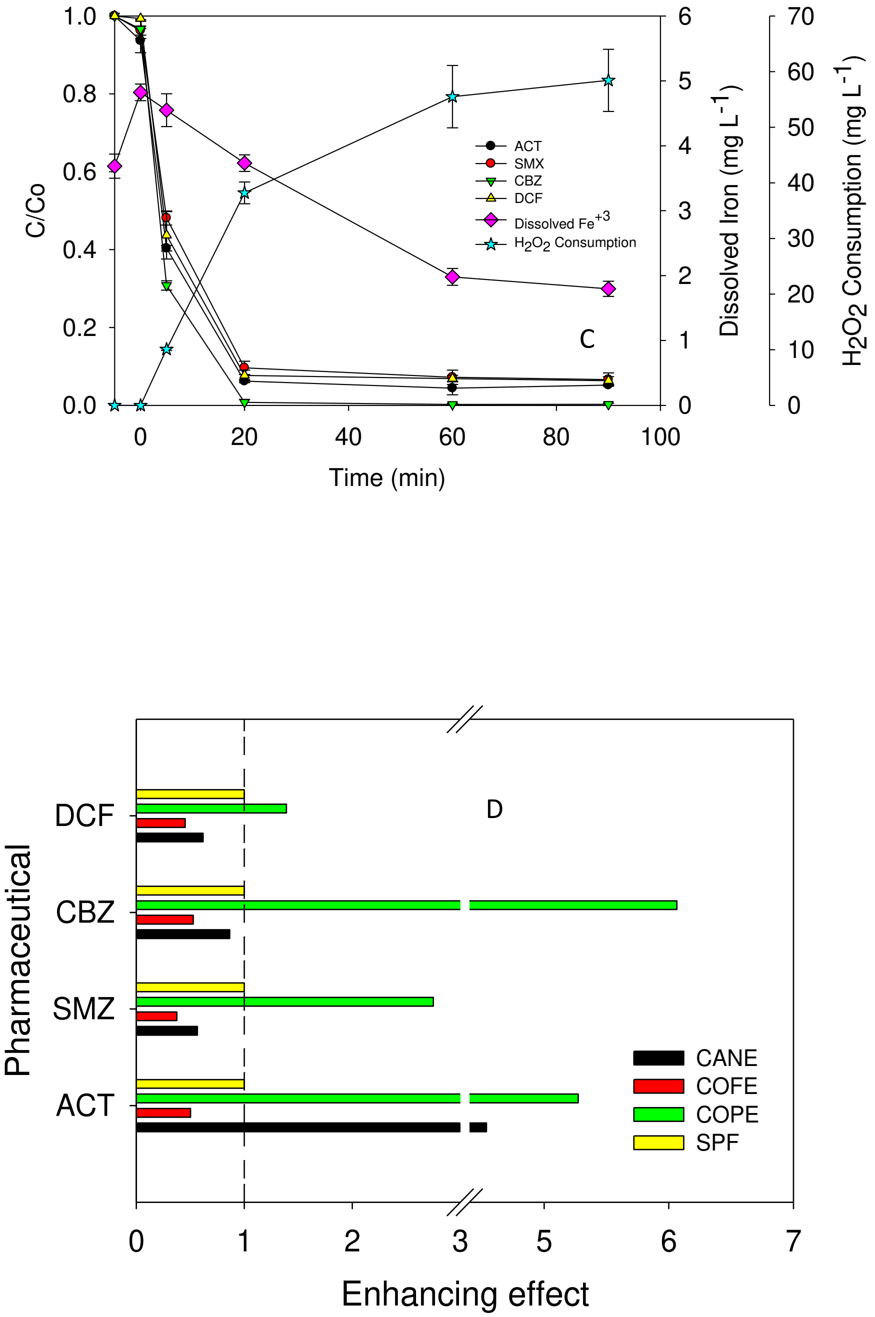


Fig. 2. Treatment of the pharmaceuticals mix in deionized water by SPF at natural pH in presence of extracts. **A.** COFE. **B.** CANE. **C.** COPE. **D**. Enhancing effect of three extracts. Molar ratio Fe:extract = 1:0.16. $[Fe^{3+}]_o$ = 5 mg L^{-1}. $[Pharm]_o$ = 0.0066 mM. $[H_2O_2]_o$ = 120 mg L^{-1}, and $pH_{initial}$ = 6.2.

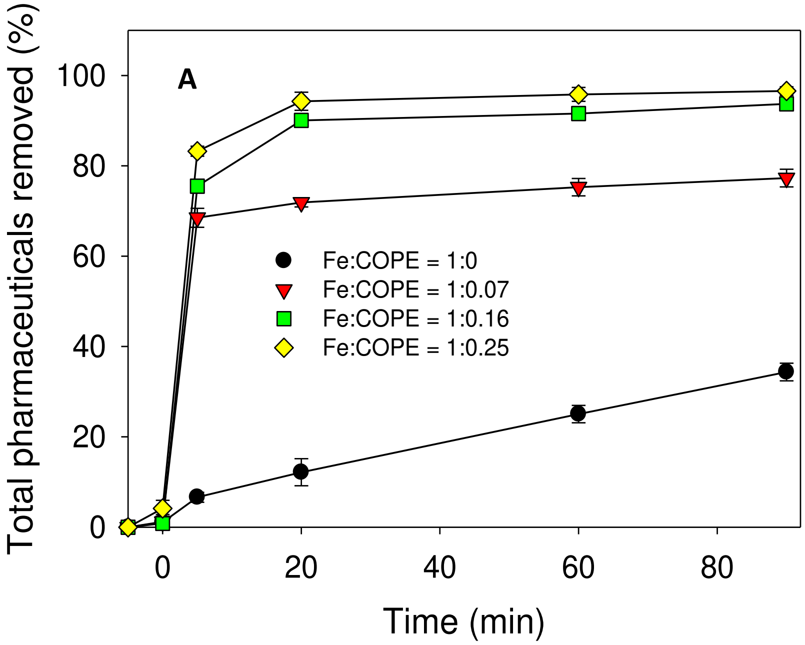
Table 2. Content of total phenols and TOC in the extracts from three amazonian fruits.

Extract	**Extraction technique**	**Total phenols (mg GAE L^{-1})**	**TOC content in the extract**
Canangucha extract (CANE)	Squeezed fruit pulp	297±10	32±3
Coffee extract (COFE)	Maceration of husk	454±32	162±11
Copoazu extract (COPE)	Squeezed fruit pulp	481±21	92±5

3.3. Influence of Fe:COPE ratio on the degradation of pollutants

After evaluation of the different amazonian fruits and considering the best performance of COPE, the pharmaceuticals mix in deionized water was treated by SPF at pH 6.2, using different amounts of the extract (Fig. 3a). It can be noted that the efficiency of SPF for the degradation of the pharmaceuticals significantly increased as the Fe:COPE ratio augmented from 1:0.07 to 1:0.16, and a slight improvement of the degradation was found for changes of the ratio from 1:0.16 to 1:0.25.

The positive effect on the degradation of the pollutants caused by the increment of COPE concentration was related to the ability of COPE to act as a complexing agent of iron. Hence, the dissolved iron and H_2O_2 consumption were measured during the SPF process at the different Fe:COPE ratios (Fig. 3b). These measurements showed that both the iron in solution and hydrogen peroxide consumption were higher as COPE amount increased. In fact, in presence of the highest COPE presence, 80% of the initial iron remained in the solution during the whole experiment (on the contrary, in absence of COPE more than 95% of iron was quickly precipitated).



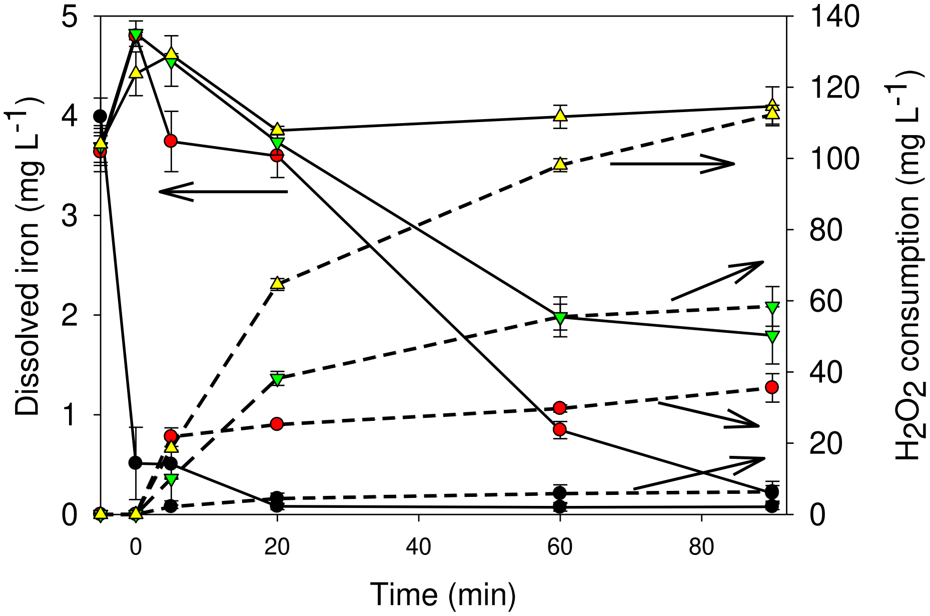


Fig. 3. A. SPF at near-neutral pH applied to the elimination of pharmaceuticals in deionized water. $[Fe^{3+}]_o$ = 5 mg L^{-1}. $[Pharm]_o$ = 0.0066 mM. $[H_2O_2]_o$ = 120 mg L^{-1}, and $pH_{initial}$ = 6.2. B. Behavior of dissolved iron and H_2O_2 consumption during SPF at near-neutral pH (6.2) with COPE in different molar relations Fe: COPE.

(–): Dissolved iron and (----): H_2O_2 consumption.

As the COPE amount was higher, more quantity of complexing agents (i.e., polyphenols) are available to keep the iron as soluble forms that can react with H_2O_2, thus favoring the radicals generation (Eqs. 1-5), and consequently, the elimination of the pharmaceuticals is enhanced. Nevertheless, at the Fe:COPE ratio 1:0.25, despite the iron remains in solution by interaction with the COPE (Fig. 3), there was only a little improvement of the pollutants removal concerning 1:0.16. The highest addition of the amazonian fruit extract may represent a very elevated load of organic matter. Thus, the organic matter in excess could compete by the radicals ((Klamerth et al. 2013; Papoutsakis et al. 2015; De la Obra et al. 2017), and therefore a significant increase in the process efficiency does not occur. Indeed, it would be expected that a Fe: COPE ratio higher than 1: 0.25 will induce a detrimental effect on the pharmaceuticals removal by the SPF process. Therefore, the above results indicated that 1:0.16 is the suitable Fe: COPE ratio for the subsequent experiments.

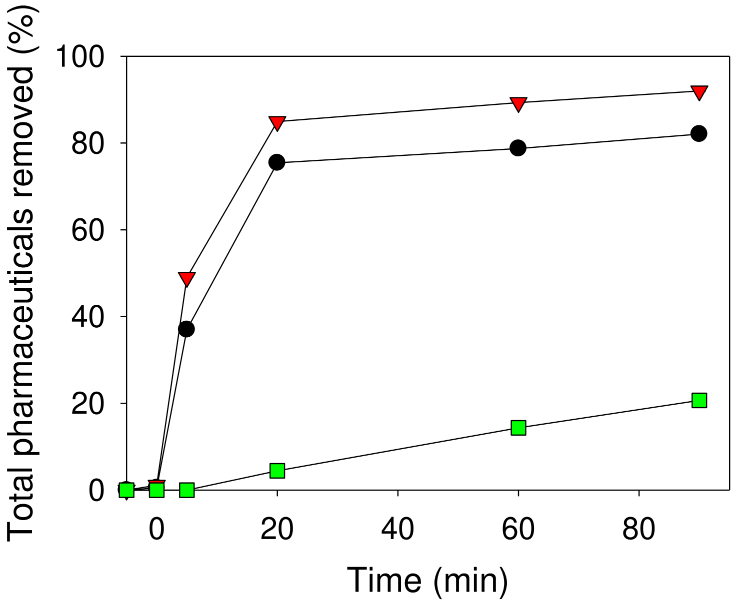
3.4. Pharmaceuticals degradation in raw municipal wastewater by SPF in COPE presence

After demonstrating the enhancing role of COPE on the SPF to degrade pollutants in deionized water, the process in presence of the copoazu extract was evaluated for the treatment of raw municipal wastewater (MWW) spiked with the target pharmaceuticals. The improving character of COPE in the complex matrix was also proven. Fig. 4A shows that similar to the observed in deionized water (Fig. 2), in the MWW, the presence of the extract led to a high pollutants degradation (~80% in 90 min of treatment). Again, the COPE maintains the iron in solution in the MWW matrix and increases the production of the radicals (evidenced indirectly by a higher H_2O_2 consumption) (Fig. 4B), which favors the pharmaceuticals removal.

Naturally, the presence of intrinsic organic and inorganic components in MWW competed by the radicals, decreasing a few pharmaceuticals elimination compared to the degradation in deionized water (Fig. S5). Organic matter from MWW (e.g., humic substances) can behave as radical scavengers or can induce a radiation attenuation, affecting the removal efficiencies (Mirzaei et al. 2017). Likewise, at the experimental pH (pH: 6.2), the HCO_3^- ion is the main inorganic carbon species in the MWW (alkalinity of the matrix under study ranges from 53.49 to 146.76 mg L^{-1}, Table 1). HCO_3^- has high reactivity with HO• (8.5×10^6 M^{-1} s^{-1}) (Klamerth et al. 2012; De la Obra et al. 2017) and consequently, also competes with the pollutants for the available radicals. Furthermore, in MWW, the presence of chloride, sulfate, and phosphate ions (see Table 1) may reduce the efficiency of the SPF process, since these anions react with hydroxyl radicals and generate other species that are lesser powerful and lesser reactive toward the pollutants. Besides, the presence of phosphate limits the pharmaceuticals degradation (see SPF without COPE in Fig. 4A) and decreases the soluble iron (see SPF without COPE in Fig. 4B) by precipitation as iron phosphate (Eq. 13) (Mirzaei et al. 2017).

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_{4(s)} \qquad (13)$$

In addition to the evaluation of COPE addition for treating MWW, the initial concentration of iron (III) was varied from 5 to 8 mg L^{-1} (consequently, the amount of added COPE was increased, keeping the Fe:COPE ratio in the 1: 0.16 proportion). Total removal of pharmaceuticals and consumption of hydrogen peroxide plus iron evolution were also followed (Fig. 4). As the initial concentration of iron increased, the pondered removal percentage of pharmaceuticals, as well as the peroxide consumption, increased. Remarkably, high pollutants removal (>90%) was achieved during 90 min of treatment, at 8 mg L^{-1} of iron. The increasing of the initial concentration of iron can promote the formation of more radicals, leading to a higher degradation of the pollutants (Eqs. 1-5), as indirectly evidenced by the highest H_2O_2 consumption at 8 mg L^{-1} of iron. Additionally, the presence of COPE favors the catalytic cycle of iron, and its maintenance in the solution (Fig. 4B). However, the SPF system using 8 mg L^{-1} of iron in the COPE presence, can generate a high amount of non-selective radicals as HO•, which can also attack the COPE, decreasing the extract availability. For this reason, at a long treatment time (e.g., 90 min) the soluble iron diminishes significantly (Fig. 4B).



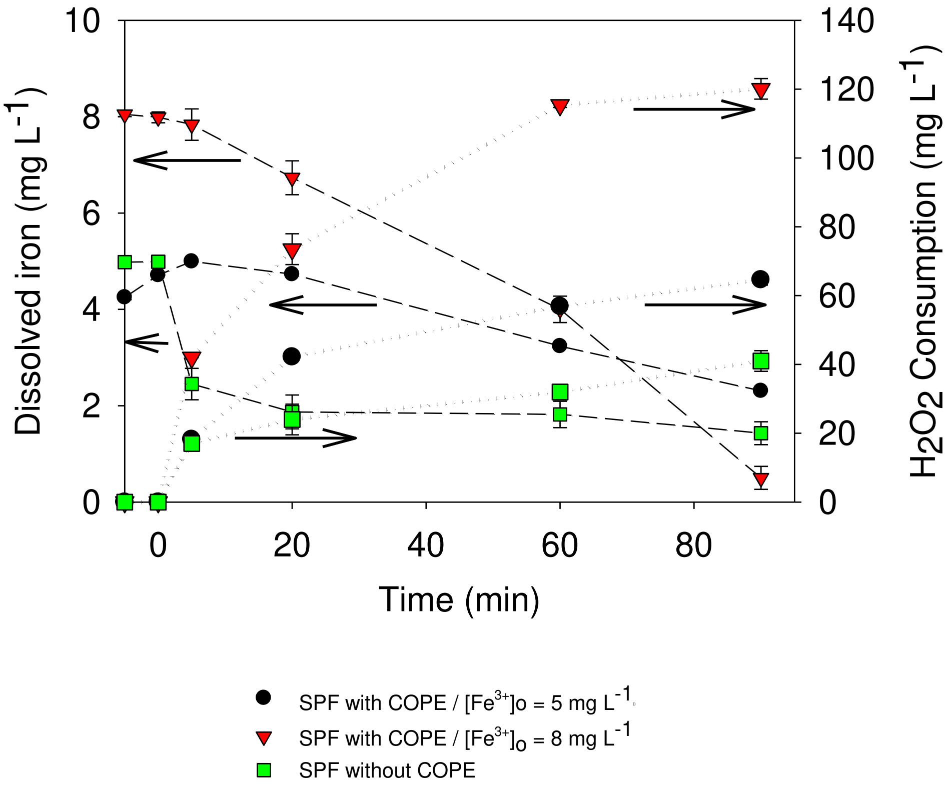


Fig. 4. Degradation of the four pharmaceuticals in MWW by SPF at near-neutral pH (6.2) without COPE and with COPE. (–) Total pharmaceuticals removal; (---) Dissolved iron, and (….) H_2O_2 consumption. [Pharm]o = 0.0066 mM. Fe:COPE = 1:0.16 and $[H_2O_2]_o$ = 120 mg L^{-1}, for the experiments of SPF without COPE the concentration of Fe^{3+} was 5 mg L^{-1}.

It should be mentioned that the high removal of the pollutants in the tested MWW by SPF in presence of amazonian fruit extracts, evidenced the great feasibility of this treatment to eliminate pharmaceuticals in actual complex matrices. This kind of AOP could receive special attention in developing countries in the amazonian region (e.g., Colombia, Peru, or Brazil), which have abundant solar light and agro-industrial wastes coming from the processing of fruits as copoazu. Nonetheless, additional tests on optimization (using a design of experiments) of operational parameters (such as COPE amount, concentrations of iron and hydrogen peroxide, and radiation intensity) to treat MWW can be developed in future work to obtain a deeper exploration of the intensification of the SPF system by COPE.

4. Conclusions

After the development of the present research, we can conclude that:

- The application of SPF without extracts induced a low removal of the four representative pharmaceuticals due to limitations in the iron availability in the solution.
- The addition of COFE, CANE, and COPE increased the dissolved iron but only COPE improved significantly the degradation of the target pollutants due to its ability to complex iron with the polyphenols present in this extract.
- The increment of Fe: COPE ratio from 1:0 to 1:0.16 augmented significantly the pollutants removal but an excess of COPE has little enhancer effect. Even a detrimental effect could be found at very high amounts of COPE due to competition by radicals and/or the increasing of water turbidity (light filtering).
- The treatment of MWW reached degradations > 75% after 90 min in the process improved with COPE. Furthermore, the increase of iron from 5 to 8 mg L^{-1} (maintaining the Fe: COPE molar ratio at 1: 0.16) augmented the pharmaceuticals elimination until 90% at only 20 min of treatment.

- This work showed the high feasibility of amazonian fruit extracts to improve the efficiency of photo-Fenton at near-neutral pH and high iron concentrations to remove pharmaceuticals in aqueous media. Additionally, our research also evidenced the viability of this process to be applied in developing countries, valorizing agro-industrial materials (considered mainly as raw matters or just as wastes) for the wastewater treatment.

Declarations

- Ethical approval and consent to participate

Not applicable.

- Consent to publish

Not applicable.

- Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

- Competing interests

The authors declare that they have no competing interests

- Funding

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- Authors' contributions

Lis Manrique-Losada: Investigation, Methodology; Formal analysis, Writing-original draft, Resources, Funding acquisition. ***Heidy L. Santanilla-Calderón***: Investigation, Methodology; Writing-original draft. ***Efraím A. Serna-Galvis***: Conceptualization, Formal analysis, Writing-review & editing. ***Ricardo A. Torres-Palma:*** Conceptualization, Writing-review & editing, Resources, Funding acquisition.

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Figures

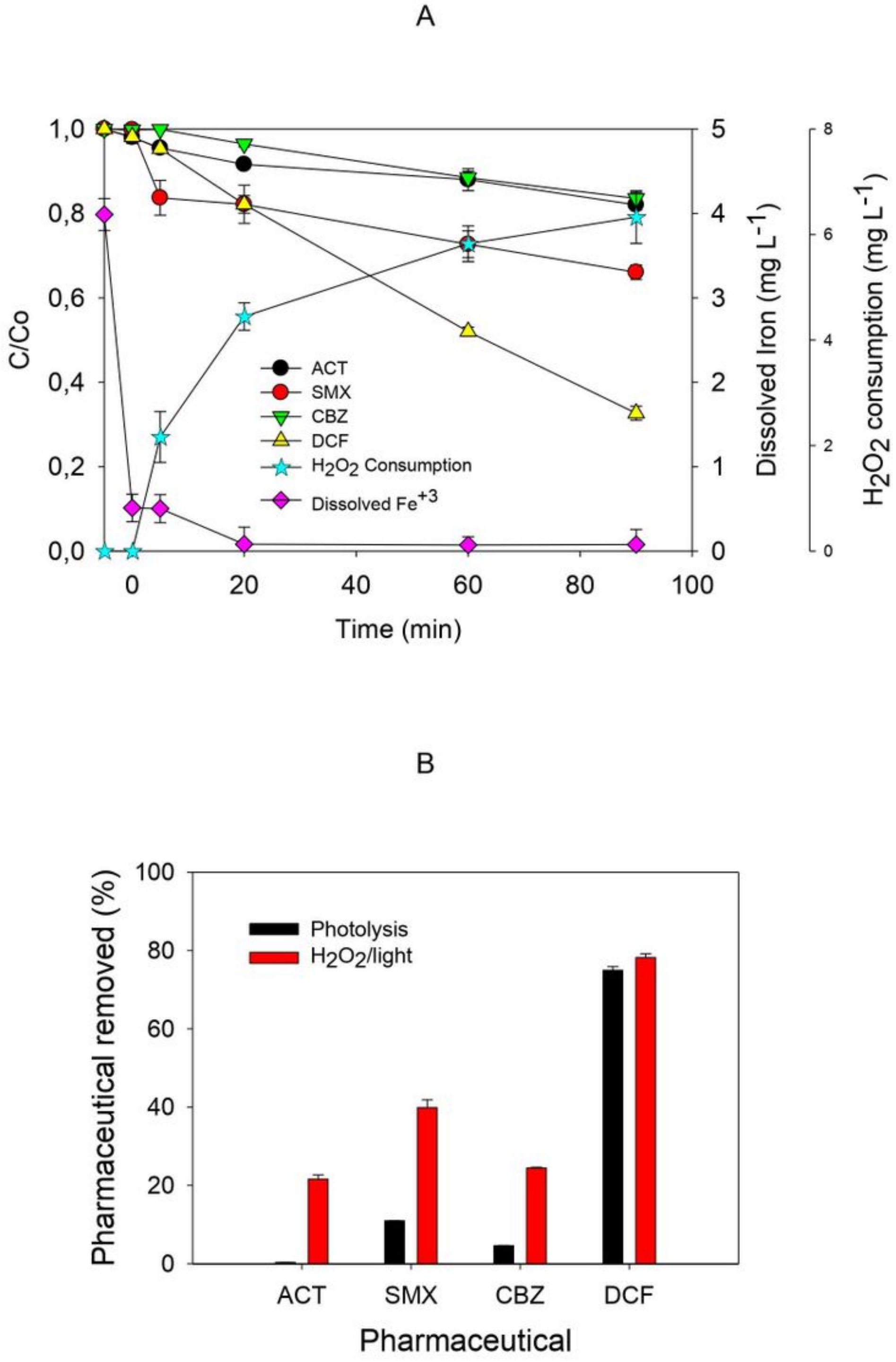

Figure 1

Treatment of pharmaceuticals mixture in deionized water by SPF at near-neutral pH. B. removal of pharmaceuticals by control systems. Experimental conditions [Fe3+]o = 5 mg L-1 (90 µmol L-1). [Pharm]o = 0.0066 mM. [H2O2]o = 120 mg L-1, and pHinitial = 6.2.

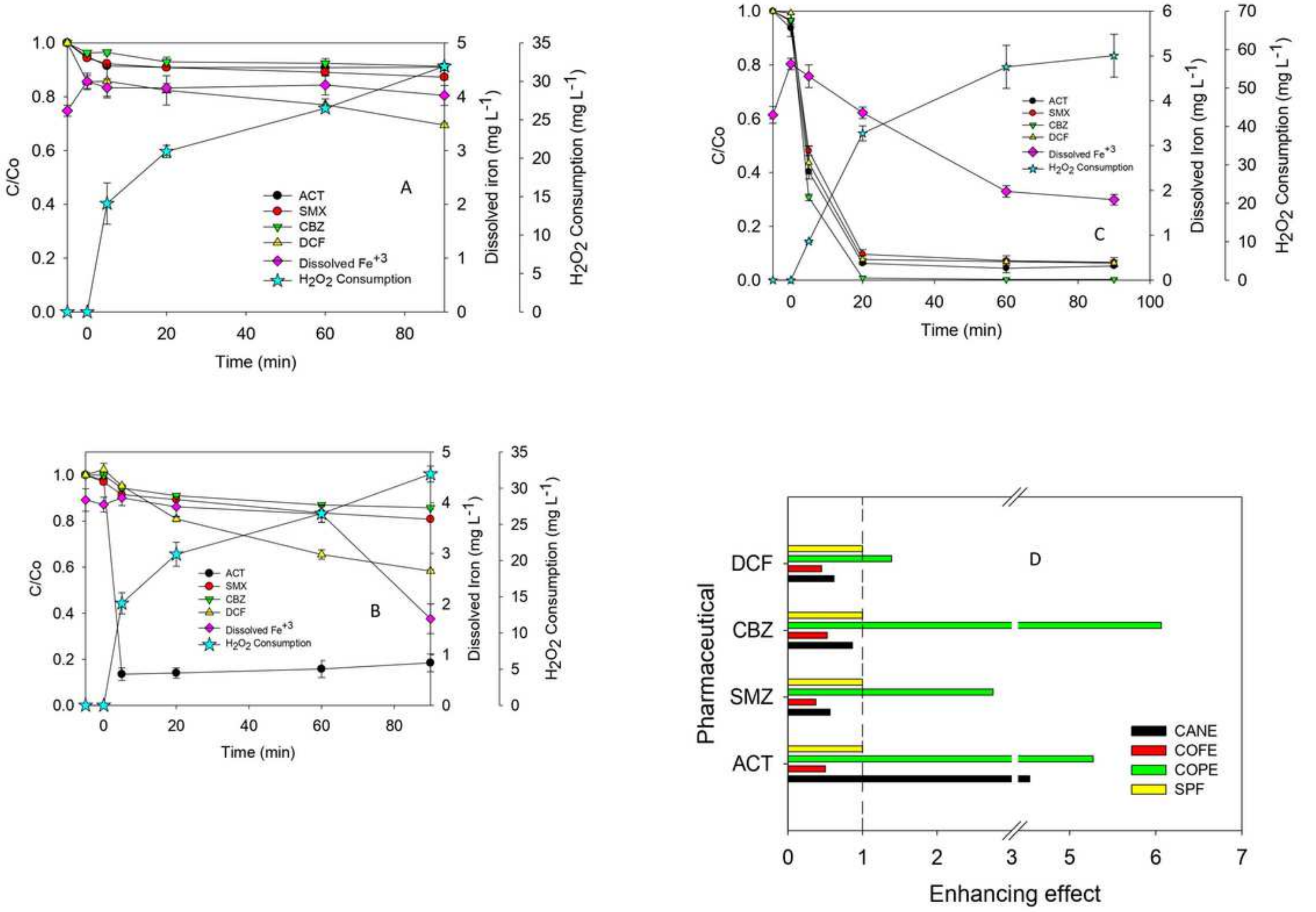

Figure 2

Treatment of the pharmaceuticals mix in deionized water by SPF at natural pH in presence of extracts. A. COFE. B. CANE. C. COPE. D. Enhancing effect of three extracts. Molar ratio Fe:extract = 1:0.16. [Fe3+]o = 5 mg L-1. [Pharm]o = 0.0066 mM. [H2O2]o = 120 mg L-1, and pHinitial = 6.2.

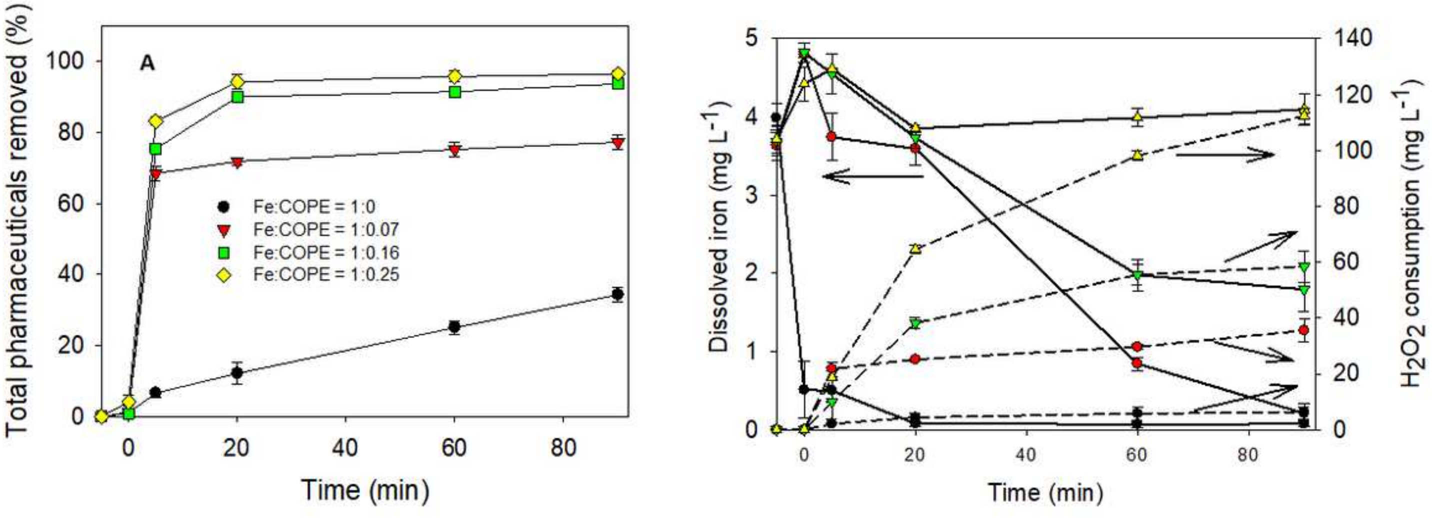

Figure 3

A. SPF at near-neutral pH applied to the elimination of pharmaceuticals in deionized water. [Fe3+]o = 5 mg L-1. [Pharm]o = 0.0066 mM. [H2O2]o = 120 mg L-1, and pHinitial = 6.2. B. Behavior of dissolved iron and H2O2 consumption during SPF at near-neutral pH (6.2) with COPE in different molar relations Fe: COPE. ( ): Dissolved iron and (—): H2O2 consumption.

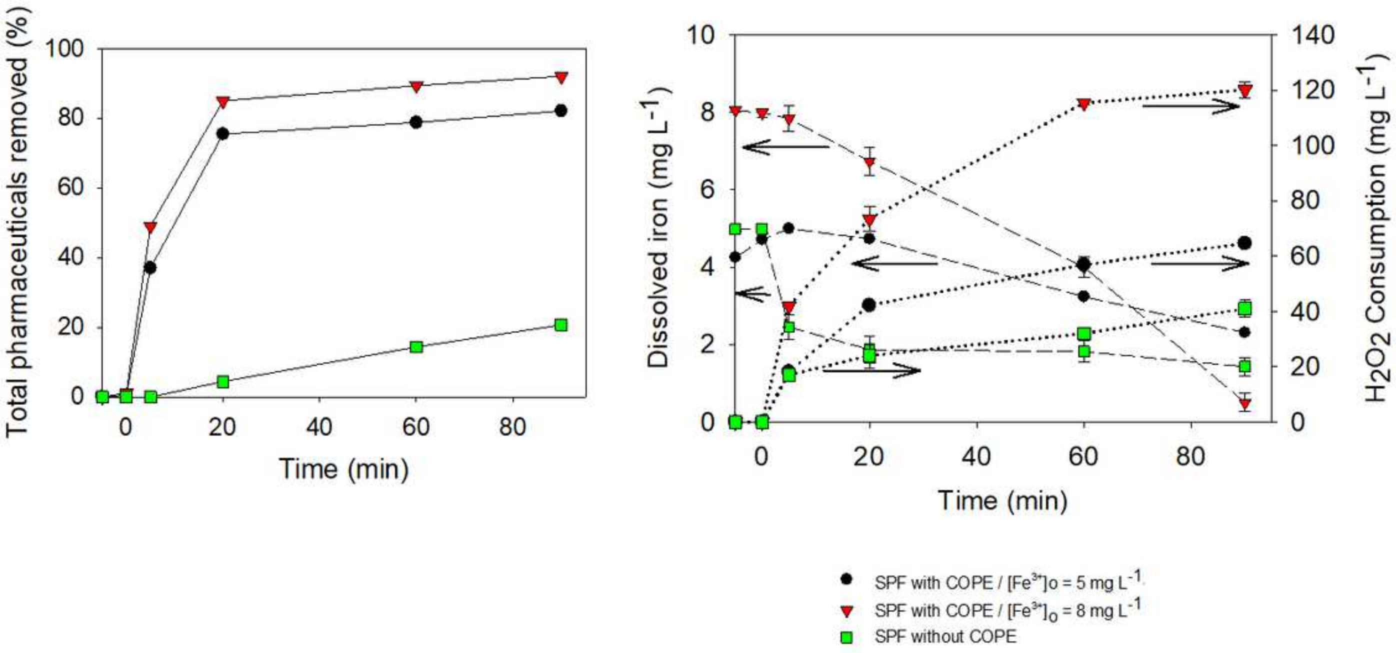

Figure 4

Degradation of the four pharmaceuticals in MWW by SPF at near-neutral pH (6.2) without COPE and with COPE. ( ) Total pharmaceuticals removal; (—) Dissolved iron, and (….) H2O2 consumption. [Pharm]o = 0.0066 mM. Fe:COPE = 1:0.16 and [H2O2]o = 120 mg L-1, for the experiments of SPF without COPE the concentration of Fe3+ was 5 mg L-1.

Supplementary Files

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