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 grandiflorum), canangucha (Maurita Flexuosa), and coffee (Coffea arabica) were explored as enhancers of the solar photo-Fenton process to eliminate acetaminophen, sulfamethoxazole, carbamazepine, and diclofenac in raw municipal wastewater. The process, at pH 6.2 and 5 mg L⁻¹ of iron without the presence of extracts, had a very limited action (~35% of the pollutants degradation at 90 min of treatment) due to the iron precipitation. Interestingly, the extract addition increased the soluble iron forms, but only copoazu extract improved the pollutant degradation (~95% of elimination at 20 min of the process action). The copoazu extract components acted as natural complexing agents, maintaining the soluble iron up to 2 mg L⁻¹ even after 90 min and, consequently, enhancing the pollutant degradation. The effect of copoazu extract dose on the process performance was also assessed, finding that an iron:polyphenols (from the copoazu extract) at a molar ratio equal to 1:0.16 was the most favorable condition. Then, the process improved by copoazu extract was applied to raw municipal wastewater. Remarkably, the process led to ~90% of total pharmaceuticals degradation at 20 min of treatment. This work evidenced the feasibility of amazonian fruit 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 · Raw municipal wastewater treatment · Natural enhancers

Introduction
Untreated municipal wastewater (UMWW) 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 UMWW (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 UMWW 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).

The photo-Fenton process 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). The photo-Fenton process has shown to be very efficient in the degradation of pollutants in wastewater (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 Fe³⁺ 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 Fe³⁺-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 can contribute to the oxidation of organic substances) (Miralles-Cuevas et al. 2014; Clarizia et al. 2017; Villegas-Guzman et al. 2017a).

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{HO}^\cdot + \text{HO}^- \quad (1) \\
\text{Fe}^{3+} + \text{H}_2\text{O} + h\nu_{(UV-vis)} &\rightarrow \text{Fe}^{2+} + \text{HO}^\cdot + \text{H}^+ \quad (2) \\
\text{Fe}^{3+} + \text{HO}^- &\rightarrow \text{Fe(OH)}_3 \text{ (insoluble solids)} \quad (3) \\
[\text{Fe}^{3+}-\text{L}]_{\text{complex}} + h\nu &\rightarrow \text{Fe}^{2+} + \text{L}^\cdot \quad (4) \\
\text{L}^\cdot + \text{O}_2 &\rightarrow \rightarrow \text{O}_2^\cdot \quad (5)
\end{align*}
\]

Several poly-carboxylic acids that act as chelating agents of iron (such as oxalic acid, citric acid, ethylenediamine-N,N-disuccinic acid (EDDS), and ethylene-diamine-tetra-acetic acid (EDTA)) have been successfully utilized to improve the solar photo-Fenton process performance at near-neutral pH (Arzate et al. 2020). Nonetheless, EDTA is non-biodegradable and persistent in the environment (Sillanpää 1997; Papoutsakis et al. 2015). Meanwhile, chelation with citric or oxalic acid requires reduced pH for their best performance (for instance, the optimal behavior for the Fe³⁺-citrate and Fe³⁺-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 this reagent. Thus, to overcome these issues, polyphenol-rich natural substances have been recently evaluated (Ruiz-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 (Klameth et al. 2013). Indeed, juices of orange or lime and coffee extract (organic acids-rich juices) have been evaluated as solar photo-Fenton enhancers with promising results for the elimination of CECs and bacteria (Villegas-Guzman et al. 2017b).

In this context, natural products or agro-industrial wastes 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 their affordability could lead to an environmentally sustainable SPF with the potential to propose a large-scale application in future (Klameth et al. 2013). Some of the abundant native products from Colombian Amazonia contain polyphenols and organic acids (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 grandiflorum), canangucha (Mauritia Flexuosa), and husk coffee (Coffea arabica), were considered.

Copoazu and canangucha are typical fruits of the Amazonian 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 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 addition of extracts of three amazonian fruits to enhance the performance of the SPF process at near-neutral pH to simultaneously degrade four representative pharmaceuticals (acetaminophen, diclofenac, sulfamethoxazole, and carbamazepine) in raw municipal wastewater (RMWW) without any previous treatment. Under the authors’ knowledge, this work is the first study about the use of amazonian fruits for enhancing the degradation of the pharmaceuticals in raw municipal wastewater, which pretends to provide a starting point about the future utilization of amazonian agro-industrial products and wastes as iron complexing agents in the photo-Fenton process. Our work covers 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 iron:extract ratio on the pollutant degradation and iron availability, and (iv) enhancement of the pharmaceutical degradation in RMWW by the best extract.

**Materials and methods**

**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®. Citric acid and ascorbic acid were provided by Sigma-Aldrich. All solutions were prepared using deionized water (RMWW) without any previous treatment. Under the authors' knowledge, this work is the first study about the use of amazonian fruits for enhancing the degradation of the pharmaceuticals in raw municipal wastewater, which pretends to provide a starting point about the future utilization of amazonian agro-industrial products and wastes as iron complexing agents in the photo-Fenton process. Our work covers 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 iron:extract ratio on the pollutant degradation and iron availability, and (iv) enhancement of the pharmaceutical degradation in RMWW by the best extract.
water or raw municipal wastewater without any previous treatment from Florencia-Colombia (RMWW, which main characteristics are provided in Table 1).

**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 determined, and the pondered removal percentage for the simultaneous degradation of the target pollutants was calculated as described by Serna-Galvis et al. (2019).

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 H₂O₂ 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). The raw municipal wastewater (RMWW) from Florencia-Caquetá Colombia was characterized using analytical standard methods (APHA et al. 2012), as summarized in Table S1.

**SPF 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 raw municipal wastewater (RMWW) in a beaker. Fe (III) at 5 mg L⁻¹ and H₂O₂ from 68 to 120 mg L⁻¹ were added to the reactor. Degradation experiments were done using a Suntest CPS+ (Atlas) containing an air-cooled xenon lamp equipped with proper filters to cut off the wavelengths below 300 nm, to simulate the sunlight. The illumination surface was 560 cm² and the light intensity (global irradiance) was 250 W m⁻².

**Extract characterization**

Three amazonian fruits (canangucha “Mauritia flexuosa,” coffee “Coffea arábica,” and copoazu “Theobroma grandiflorum”) 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, and 30 g of the pulp fruit was 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.

To characterize the extracts, the content of total polyphenols, citric acid, and ascorbic acid was established. Total phenols were measured by the Folin-Ciocaltel method. Citric acid and ascorbic acid were measured using a UHPLC.

**Table 1 Physicochemical characteristics of the RMWW from Florencia-Caquetá Colombia**

| Parameter                      | Minimum value | Maximum value |
|--------------------------------|---------------|---------------|
| Nitrates (NO₃⁻) (mg L⁻¹)       | 4.62          | 14.38         |
| Ammonia nitrogen (NH₄⁺), (mg L⁻¹) | 17.73         | 43.34         |
| Total nitrogen (TN), (mg L⁻¹)  | 124           | 210.3         |
| Orto-phosphates (PO₄³⁻), (mg L⁻¹) | 1.46          | 3.21          |
| Sulfates (SO₄²⁻), (mg L⁻¹)     | 45.60         | 188.3         |
| Chlorides (Cl⁻), (mg L⁻¹)      | 62.05         | 103.34        |
| Alkalinity (mg L⁻¹)             | 53.49         | 146.76        |
| Hardness (mg L⁻¹)               | 57.1          | 119           |
| pH                             | 6.45          | 6.75          |
| Total organic carbon (TOC, mg C L⁻¹) | 28            | 89.32         |
| Chemical oxygen demand (COD, mg O₂ L⁻¹) | 256           | 580           |
| Biochemical oxygen demand (BOD₅, mg O₂ L⁻¹) | 126           | 302           |
| Total suspended solids (TSS, mg L⁻¹) | 54.12         | 147.67        |
| Total solids (TS, mg L⁻¹)       | 128.56        | 258.78        |
(Thermo Scientific Ultimate 3000) equipped with an Agilent Hi-Plex H column, and sulfuric acid (0.01 M) at 0.6 mL min$^{-1}$ as mobile phase, and its DAD was operated at 210 nm. Extracts of the amazonian fruit were added to the aqueous samples to be treated by the SPF systems considering the same molar ratio between the iron and total polyphenols (i.e., Fe:polyphenols ratio).

**Results and discussion**

**Performance of SPF in absence and presence of COFE, CANE, and COPE**

The capability of the SPF process to degrade a mix of the four representative pharmaceuticals in deionized water (at pH 6.2) was tested initially, and the results are presented in Fig. 1. 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 elimination of pollutants, the evolution of iron and the consumption of hydrogen peroxide were also followed during the SPF process (Fig. 1). The analysis of dissolved iron in the SPF system indicated that iron was not available in the solution (Fig. 1) was limited due to the non-availability of dissolved iron (Pignatello et al. 2006; Serna-Galvis et al. 2020). Consequently, the elimination percentage of pollutants was low, and so, as a strategy to improve the performance of the SPF process, extracts of amazonian fruits were added to the reaction system.

The extracts of three amazonian fruits, CANE (canangucha extract), COFE (coffee extract), and COPE (copoazu extract), were tested. To compare the performance of the extracts, their addition was defined by maintaining the same concentration of total polyphenols. Therefore, it was added 2.45 mg GAE L$^{-1}$ of polyphenols (which are 14.4 μmol GAE L$^{-1}$) coming from each extract (Table 2), and 5 mg L$^{-1}$ of Fe$^{3+}$ (i.e., 90 μmol L$^{-1}$) to obtain a Fe:polyphenols molar ratio of 1:0.16.

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 significantly enhanced the degradation of the four pharmaceuticals (Fig. 2D). From Fig. 2D, it can be also noted that despite COFE and CANE kept iron in soluble forms, these two extracts had a detrimental effect on the process performance for the elimination of pollutants (with an exception for ACT in CANE presence).

Table 2 contains the amounts of relevant components added to the reaction system through the extracts. It must be mentioned that COFE addition induced more intense color to the water than the other extracts (Fig. S2). This is probably due to the content of tannins and chlorogenic acid in COFE (Genaro-Mattos et al. 2015). Thus, the stronger coloration could provoke a decrease in the light penetration, with the consequent limitation of the catalytic cycle of iron (Eq. 4) and the degradation of pharmaceuticals.

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 ones 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. 6), which favors redox reactions for hydroquinone-type or analogous structures as presented by hydroquinone-type products

$$
{\text{CANE}} - \text{Fe}^{3+}\text{complex} + \text{ACT} \rightarrow \text{Fe}^{2+} + \text{quinone-type products}
$$

On the other hand, when COPE was added, an acceleration of the degradation of pharmaceuticals and a significant increase in the H$_2$O$_2$ consumption were observed (Fig. 2C,D). To investigate the possible action of COPE as a photosensitizer, the treatment of the pharmaceuticals in the 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 pharmaceutical degradation (Porras et al. 2016).

COPE contained polyphenols and citric acid but no ascorbic acid (Table 2). The significant presence of polyphenols and citric acid was consistent with what is reported in the literature about COPE characterizations (Hernández Londoño 2010; Contreras-Calderón et al. 2011; Pérez-Mora et al. 2017; Carmona-Hernandez et al. 2018; Pereira et al. 2018). Citric acid acts as a complexing agent of ferric ions (Eq. 4), keeping the iron in soluble forms (Fazary et al. 2009; Papoutsakis et al. 2016). Such complexes are photo-active and promote the catalytic cycle of iron at near-neutral pH (Eqs. 1, 4–5). Also, polyphenols can 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 H2O2 consumption (Fig. 2C), which confirms the interactions indicated by Eqs. 1 and 8. Hence, the role of COPE as a source of complexing agent of iron and regenerator of ferrous ions favored the production of radicals in the system; then, an enhancement of the

| Extract                  | Total phenols (mg GAE L⁻¹) | Citric acid (mg L⁻¹) | Ascorbic acid (mg L⁻¹) |
|--------------------------|----------------------------|---------------------|------------------------|
| Canangucha extract (CANE)| 2.45 ± 0.08                | < 0.05              | < 0.05                 |
| Coffee extract (COFE)    | 2.45 ± 0.17                | < 0.05              | < 0.05                 |
| Copoazu extract (COPE)   | 2.45 ± 0.11                | 357.22 ± 8.60       | < 0.05                 |

Fig. 2 Treatment of the pharmaceuticals mix in deionized water by SPF at natural pH in the presence of extracts. A. COFE. B. CANE. C. COPE. D. Enhancing effect of three extracts. Experimental conditions: Molar ratio Fe:polyphenols = 1:0.16. [Fe³⁺]₀ = 5 mg L⁻¹. [Pharmaceuticals]₀ = 0.0066 mM. [H₂O₂]₀ = 120 mg L⁻¹, and pH_initial = 6.2
degradation of target pollutants was observed (more details about the role of polyphenols and citric acid are discussed in the next section).

\[
\begin{align*}
\text{Fe}^{3+} + \text{Polyphenols} & \rightarrow (\text{Fe}^{3+}-\text{Polyphenols})_{\text{complex}} \\
(\text{Fe}^{3+}-\text{Polyphenols})_{\text{complex}} + \text{H}_2\text{O}_2 & \rightarrow (\text{Fe}^{2+}-\text{Polyphenols})_{\text{complex}} + \text{HOO}^* \\
+ \text{H}^+ & 
\end{align*}
\] (7) (8)

It can be mentioned that the dissolved iron in the presence of COPE remained lower than in the cases of CANE and COFE (see Fig. 2A–C), suggesting that CANE and COFE exerted an iron complexation stronger than COPE. However, our results suggest that the complexes with CANE and COFE are less photocative than the formed with COPE. Consequently, in the case of COPE, this makes the iron more available to interact with the hydrogen peroxide (Eqs. 1 and 8). Additionally, as HO* is non-selective, it 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, variations of the Fe:polyphenols ratio in COPE were performed, and their outcomes are presented and discussed in the next subsection.

**Unraveling the COPE effect and the influence of Fe:COPE ratio on the degradation of pollutants**

To better understand the enhancing role of the copoazu extract, experiments in distilled water, adding the two most relevant components of COPE at the SPF system, were performed. The degradation of ACT (which is the most common pharmaceutical in Colombian wastewater (Botero-Coy et al. 2018)), with the individual presence of gallic acid (a well-known model of polyphenols and organic matter (Lucas et al. 2008)) and citric acid at the same concentrations added to the reaction system in copoazu extract, was carried out.

Fig. 3A compares the elimination of ACT, after 5 min of treatment, in the absence and presence of COPE, gallic acid, and citric acid. It can be noted that in the presence of COPE and its relevant components, the elimination of ACT was strongly improved (achieving removals >95% in 5 min of treatment). Also, it must be highlighted that in the presence of COPE, citric acid, and gallic acid, the soluble iron and consumption of hydrogen peroxide were higher than in the absence of these substances (Fig. 3B,C). These results indicate that the enhancing role provided by the addition of COPE can be associated with the action of citric acid and polyphenols (such as gallic acid) contained in the extract added to the reaction system. Indeed, the citric acid had an effect higher than gallic acid, keeping the soluble iron (Fig. 3B).
be explained considering that ferric complexes with citric acid have a high capability of absorbing UVA and visible light and undergoing photolytic processes, which easily reduce Fe$^{3+}$ toward Fe$^{2+}$ (Clarizia et al. 2017).

As mentioned above, both relevant components of COPE are able to complex ferric ions, avoiding the iron precipitation and favoring the catalytic cycle of iron in the SPF process (as evidenced in Figs. 2C and 3B (Fazary et al. 2009; Oakes 2013; Papoutsakis et al. 2016)). Consequently, these COPE components act as complexing agents and promoters of the regeneration of ferrous ions (Eqs. 4, 7, and 8), leading to a higher production of radicals in comparison with the system without COPE. Thereby, the elimination of target pharmaceuticals in the COPE presence (Fig. 2C) is better than in its absence (Fig. 1).

On the other hand, considering the best performance of COPE observed in Fig. 2, the pharmaceutical mix in deionized water was treated by SPF at pH 6.2, using different amounts of the extract (Fig. 4A). It can be noted that the efficiency of SPF for the degradation of the pharmaceuticals significantly increased as the Fe:polyphenols (from 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$_2$O$_2$ consumption were measured during the SPF process at the different Fe:polyphenols from COPE ratios (Fig. 4B). These measurements showed that both the iron in solution and hydrogen peroxide consumption were higher as the COPE amount increased. In fact, in the presence of the highest COPE extract, 80% of the initial iron remained in the solution during the whole experiment (on the contrary, in the absence of COPE, more than 95% of iron was quickly precipitated).

As the COPE amount was higher, more quantity of complexing agents (especially citric acid) were available to keep the iron as soluble forms that can react with H$_2$O$_2$, thus favoring the generation of radicals (Eqs. 1–5), and consequently, the elimination of the pharmaceuticals was enhanced. At the Fe:polyphenols ratio of 1:0.25, despite the iron remained in solution by interaction with the COPE (Fig. 3), there was only a little improvement in the removal of pollutants concerning 1:0.16. The highest addition of the amazonian fruit extract may represent an increase in the organic matter load, which would compete for 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 did not occur. Indeed, it would be expected that a Fe:polyphenols ratio higher than 1:0.25 will induce a detrimental effect on the removal of pharmaceuticals by the SPF process. Therefore, the above results indicated that 1:0.16 is the suitable ratio for the subsequent experiments.

**Pharmaceutical degradation in raw municipal wastewater by SPF in COPE presence**

The performance of the SPF process in the presence of the copoazu extract (COPE) was also evaluated for the treatment of raw municipal wastewater (RMWW, i.e., municipal wastewater without any previous treatment) spiked with the target pharmaceuticals (Fig. 5A). The presence of the COPE led to a high degradation of pollutants (~75% in 20 min of the pharmaceutical treatment in RMWW). Again, the COPE maintained iron in solution in the RMWW matrix and increased the production of the radicals (evidenced indirectly by higher H$_2$O$_2$ consumption, Fig. 5B), which favored pharmaceuticals removal.
To clarify the role of COPE in RMWW, the treatment of spiked ACT by SPF with the presence of gallic acid and citric acid was also carried out (Fig. S5). The results showed that the removal of ACT in RMWW was strongly improved by the presence of gallic acid and citric acid (the relevant components of COPE). This indicates that in the considered RMWW, the improvement of the SPF process for the elimination of the pharmaceuticals can also be associated with the action of these COPE components as complexing agents, which favored the catalytic cycle of iron in the reaction system.

To clarify the role of COPE in RMWW, the treatment of spiked ACT by SPF with the presence of gallic acid and citric acid was also carried out (Fig. S5). The results showed that the removal of ACT in RMWW was strongly improved by the presence of gallic acid and citric acid (the relevant components of COPE). This indicates that in the considered RMWW, the improvement of the SPF process for the elimination of the pharmaceuticals can also be associated with the action of these COPE components as complexing agents, which favored the catalytic cycle of iron in the reaction system.

On the other hand, it is important to mention that the intrinsic presence of organic and inorganic components in RMWW competed for the radicals, slightly decreasing pharmaceuticals elimination percentages compared to their degradation in deionized water (Fig. S6). Organic matter from RMWW (e.g., humic substances) can behave as radical scavengers or can induce a radiation attenuation, affecting the removal efficiencies (Mirzaei et al. 2017). Thus, an interesting alternative, to consider in the future, may be the application of biological treatments to RMWW before the SPF process, to decrease the organic matter content, limiting the competence for the radical species and increasing the removal of the target pollutants by action of the AOP.

Also, at the experimental pH (6.2), the HCO$_3^-$ ion is the main inorganic carbon species in the RMWW (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• ($8.5 \times 10^6$ 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 RMWW, 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 less powerful and less reactive toward the pollutants. Besides, the presence of phosphate limits the pharmaceuticals degradation (see SPF without COPE in Fig. 5A) and decreases the soluble iron (see SPF without COPE in Fig. 5B) by precipitation as iron phosphate (Eq. 9) (Mirzaei et al. 2017).

$$\text{Fe}^{3+} + \text{PO}_4^{3-} \rightarrow \text{FePO}_4(s)$$ (9)

In addition, to evaluate the effect of COPE addition for treating RMWW at different initial iron (III) concentrations, it was also varied from 5 to 8 mg L$^{-1}$ (consequently, the amount of added COPE was increased to keep the Fe:polyphenols ratio in the 1:0.16 proportion). Total removal of pharmaceuticals and consumption of hydrogen peroxide plus iron evolution were also followed (Fig. 5). As the initial concentration of iron increased, the pondered removal percentage of pharmaceuticals and the peroxide consumption augmented. Remarkably, high pondered removal of pollutants (~85%) was achieved during 20 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$_2$O$_2$ consumption at 8 mg L$^{-1}$ of iron. Additionally, the presence of COPE favored the catalytic cycle of iron and its maintenance in the solution (Fig. 5B). However, the SPF system using 8 mg L$^{-1}$ of iron in higher amount of COPE extract generated a higher amount of non-selective HO•, which could 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. 5B).

Finally, it should be mentioned that the high removal of the pollutants in the tested RMWW by SPF in the presence of amazonian fruit extracts evidenced the great feasibility of this

![Fig. 5](image)
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 such 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 organic pollutants in wastewater must be developed, in future works, to obtain a deeper comprehension of the intensification of the SPF system by COPE.

**Conclusions**

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

- The addition of COFE, CANE, and COPE increased the dissolved iron but only COPE significantly improved 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 pollutant 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 RMWW 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 molar ratio of Fe: polyphenols from COPE at 1:0.16) augmented the elimination of pharmaceuticals until 90% at only 20 min of treatment.
- This work showed the high feasibility of using amazonian fruit extracts as enhancers of the photo-Fenton process at near-neutral pH and low iron concentrations to remove pharmaceuticals in aqueous media. Our research also suggested that this process is promising for being applied in developing countries, valorizing agro-industrial materials (considered mainly as raw matters or just as wastes) for wastewater treatment.

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

**Author contribution** L.M.L.: investigation, methodology; formal analysis, writing—original draft, resources, funding acquisition. H.L.S.C.: investigation, methodology; writing-original draft. E.A.S.G.: conceptualization, formal analysis, writing—review & editing. R.A.T.P.: conceptualization, writing—review & editing, resources, funding acquisition.

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**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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