HCO_3^- production from 17β-estradiol oxidation by photo-Fenton as a strategy to avoid the generation of greenhouse gases

Producción de HCO_3^- derivado de la oxidación de 17β-estradiol por foto-Fenton como una estrategia para evitar la generación de gases de efecto invernadero

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Abstract

17β-estradiol (E2) is a natural estrogen considered the major endocrine disruptor in the environment at ng L^{-1}. Advanced oxidation processes (AOP) such as photo-Fenton, have shown promising results for E2 oxidation. However, in AOP and conventional process, the final destination of E2 is not reported, nor is it mentioned if it has been transformed into simpler species such as CO_2, a greenhouse gas. Therefore, the aim of this work was to evaluate the production of HCO_3^- from the oxidation of 17β-estradiol by a photo-Fenton process as a strategy to avoid the generation of greenhouse gases in water. Batch assays were realized with E2-C concentrations (mg L^{-1}) of 3.5, 4.5, and 7.5 at pH values of 5, 10, and 7.5, using $FeSO_4 \cdot 7H_2O$ (4) and H_2O_2(10), respectively. An E_{E2-C} of 64.99 % was obtained, and the oxidation of E2 followed a first-order reaction model, where coefficients of 84.30×10^{-3} min^{-1}. A predominant production of 3.73 ± 0.21 mg HCO_3^--C L^{-1} was observed, compared to 0.45 ± 0.01 mg CO_2-C L^{-1} (pH 10). The Fenton process predominantly oxidized E2 to HCO_3^-, which it is considered innocuous for the environmental. The process was not inhibited at pH 10.

Keywords: 17β-estradiol, advanced oxidation, photo-Fenton, dioxide carbon, bicarbonate.

Resumen

17β-estradiol (E2) es un estrógeno natural considerado como el mayor disruptor endócrino a concentraciones de ng L^{-1}. Procesos de oxidación avanzada (POA) como el foto-Fenton ha mostrado resultados prometedores para la oxidación de E2. Sin embargo, en procesos convencionales y POA, el destino final de E2 no es reportado o si este fue transformado hasta CO_2, un gas de efecto invernadero. Por ello, el objetivo de este trabajo consistió en evaluar la producción de HCO_3^- proveniente de la oxidación de 17β-estradiol por un proceso de foto-Fenton como una estrategia para evitar la generación de gases de efecto invernadero en agua. Se realizaron ensayos en lote con (mg L^{-1}) E2-C (5, 4.5 y 7) a pH 5, 10 y 7.5 con $FeSO_4 \cdot 7H_2O$ (4) y H_2O_2 (10), respectivamente. Se obtuvieron E_{E2-C} del 64.99 % y la oxidación de E2 se ajustó a un modelo de reacción de primer orden, donde se obtuvieron coeficientes de hasta 84.30×10^{-3} min^{-1}. Se obtuvo una producción mayoritaria de hasta 3.73 ± 0.21 mg HCO_3^--C L^{-1}, comparado con 0.45 ± 0.01 mg CO_2-C L^{-1} (pH 10). El proceso foto-Fenton oxidó E2 hasta HCO_3^- mayoritariamente, el cual es considerado como inocuo para el medio ambiente. El proceso no fue inhibido por el pH 10.

Palabras clave: 17β-estradiol, oxidación avanzada, foto-Fenton, dióxido de carbono, bicarbonato.

1 Introduction

Every day, a considerable quantity of commonly used products is discharged into the environment via wastewater systems. Due to their physical and chemical properties, these substances have significant effects on aquatic biota even at trace concentrations (ng L^{-1} - μg L^{-1}) (Zolkefli *et al*., 2020; Fang *et al*., 2019b). Among these compounds are emerging contaminants (ECs), defined as organic chemical compounds of various nature that are commonly used and continually introduced into water sources (Srikanth *et al*., 2019). These contaminants lack updated toxicological data and are not subject to regulation due to their low concentrations (ng L^{-1}) (Valdez *et al*., 2020). It has been reported that ECs have the potential to generate environmental problems and impact human or animal health due to their physical and chemical properties (Olatunde *et al*., 2020). The contaminants falling into this category include pharmaceutical compounds, cleaning products, personal care products, artificial sweeteners, flame retardants, hydrocarbons, pesticides, dyes, among others (Gonzales *et al*., 2023; Parida *et al*., 2021).

The adverse effects associated with the presence of ECs in water are primarily related to endocrine disruption. This consists of the alteration of hormonal, metabolic, and reproductive functions in living organisms, precipitating a systematic imbalance, which could generate issues such as cancer, metabolic syndrome, among other effects on aquatic fauna (Khan *et al*., 2020; Vilela *et al*., 2018).

Among the ECs with significant disruptive potential, natural estrogens such as estrone (E1), 17β-estradiol (E2), estriol (E3), alongside synthetics like 17α-ethinylestradiol (EE2) (Castellanos *et al*., 2021). These compounds enter natural water continously through various routes, including wastewater from the pharmaceutical industry, domestic use, or naturally occurring secretions from the adrenal glands and ovaries of females (Fang *et al*., 2019a). Numerous studies have highlighted the adverse environmental impacts of estradiol in water, leading to global environmental issues such as the feminization of animal species, neuriligical harm, and immune systems disruption (Ren *et al*., 2022). For instance, zebrafish and medaka fish in river waters of Israel have been exposed to concentrations from 48 to 313 ng L^{-1}, resulting in morphological alterations in the testicles and a tendency to feminize males (Sun *et al*., 2019). Furthermore, the presence of E2 in the environment has compromised water quality for human consumption and the infiltration of the pollutant through cultivated soils (Ren *et al*., 2022). The physicochemical properties of 17β-estradiol (E2)

facilitate its adsorption in sediments, contributing to its high persistence (Brion *et al*., 2004). Consequently, conventional wastewater treatment plants (WTPs) often fail completely eliminate this compound, with quantified concentrations reaching up to 630 ng L^{-1} in WTP effluents in Asia, 3000 ng L^{-1} in Europe, 2300 ng L^{-1} in Latin America, and up to 9000 ng L^{-1} in Africa. Additionally, conventional WTPs serve as sources greenhouse gas emotions, continuously generating COX, NOX, and SOX (Medrano *et al*., 2022; Du *et al*., 2020).

Diverse physical, chemical, and biological processes are currently under investigation as alternatives for the removal of E2 and other pharmaceuticals from contaminated water. Technologies for removal, including reverse osmosis, nanofiltration, membrane filtration, electrochemical process, and various adsorption techniques, have demonstrated significant efficacy in E2 removal from water samples. For instance, the application of granular sludge under anaerobic conditions, as studied by Zhao *et al*. (2020), achieved degradation percentages of up to 42.2% of E2. Similary, Aziz and Ojumu (2020) reported removal percentages of up to 95% of E2 through the utilization of technologies such as membrane nanofiltration. Despite the promising results observed with these technologies, it is essential to consider some notable drawbacks, including high energy requirements, the potential formation of unwanted by-products must be considered, such as their high energy requirement, formation of unwanted products, and the unreported final disposition of the removed pollutant (Lyubimenko *et al*., 2022).

Advanced oxidation processes (AOP) have been considered as a promising solution for eliminating E2 from water, transforming this toxic compound into simpler substances. Some of the most studied AOPs include photocatalysis, Fenton oxidation and photo-Fenton, all of which involve the generation of hydroxyl radicals (·OH) (Gonzalez *et al*., 2023; Mansouri *et al*., 2021). These radicals play a crucial role in oxidizing organic compounds, including ECs, into less complex molecules (Medrano *et al*., 2022; Gowtham *et al*., 2021; Laverde-Cerda *et al*., 2020). Among the various photo-Fenton systems, UV-Vis/H$_2$O$_2$/Fe(II) stands out for its advantages, such as low operating costs and easy implementation on an industrial scale (Brienza *et al*., 2014). Some studies on E2 removal through AOPs include the work of Bennet *et al*. (2018), where the oxidation of 10 μg L^{-1} of 17β-Estradiol using UV and UV/H$_2$O$_2$ with a Mercury lamp (1 kW) was investigated. A removal efficiency of up to 90% was reported, although the oxidation products remained unidentified. Orozco *et al*. (2019) achieved an 85 % removal efficiency of 1 μg E2 L^{-1} in 60 minutes using UV 400 W (254 nm) with 100 mg L^{-1} of TiO$_2$, although the final oxidation product was

not disclosed. Similary, Butt *et al.* (2021) evaluated the oxidation of the methyl orange dye through a photo-Fenton process, achieving removal percentages of up to 37% in 60 minutes of reaction. Singa *et al.* (2021) highlighted the efficacy of this process for eliminating polycyclic aromatic hydrocarbons in landfills, with oxidation efficiencies ranging from 84.43 to 92.54%. However, a common limitation in these studies is the lack of information regarding the AOP products and the whether the organic compounds are transformed into simple species like CO_2. This information is important for assessing the completeness of the process and the potential toxicity of the formed metabolites. Environmental conditions, including light radiation, H_2O_2 concentration, and pH are main factors in controlling the oxidation process and the formation of compounds like HCO_3^- and CO_2 (Pinoargote *et al.*, 2022). HCO_3^- is considered environmentally innocuous and is not a greenhouse gas, in contrast to CO_2. Therefore, the objective of this study was to evaluate the production of HCO_3^- from the oxidation of 17β-estradiol through a photo-Fenton process as a strategy to avoid generating greenhouse gases in water.

2 Material and methods

2.1 Batch assays

Assays were performed in 60 mL serological bottles, with a working volume of 36 mL and the remaining volume as headspace (Figure 1). The oxidation of E2 was evaluated at concentrations of 3.5 (I), 4.5 (II) and 7.5 (III) mg L^{-1} of E2-C at pH 5, 10, and 7.5, respectively, adding to each one 4 mg L^{-1} of $FeSO_4 \cdot 7H_2O$ as catalyst and 10 mg L^{-1} of H_2O_2, according to what was reported by Pinoargote *et al.* (2022). The concentrations of catalyst and hydrogen peroxide used were selected according to the lowest concentrations evaluated in the literature to optimize the process (Gowtham and Pauline, 2021). Assays were exposed to direct natural sunlight for 1 hour and liquid and gas samples were taken every 5, and 10 minutes for subsequent analysis. It is worth mentioning that the bottles were exposed to natural sunlight from 12:30 pm to 1:30 pm, during the months of February and March 2023 in the city of Mineral de la Reforma, Hidalgo, Mexico. Additionally, an assay was carried out to evaluate the stability of E2 when exposed to sunlight, consisting of maintaining a concentration of 15 mg E2-C L^{-1} for 3 h.
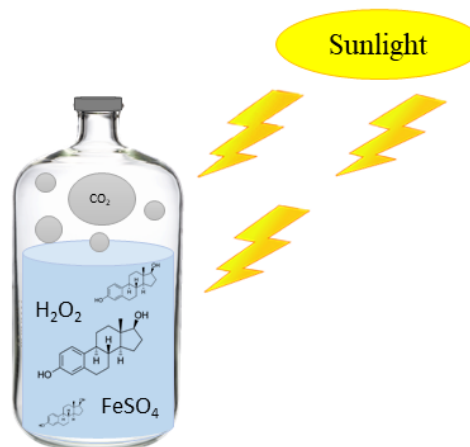

Figure 1. The reaction system for batch assays.

2.2 Kinetic evaluation of the photo-Fenton process

To evaluate the oxidation of E2 in the process, response variables was performed, such as efficiency of estradiol consumption (E_{E2-C}), using equation 1.

$$E_{E2-C} = \frac{mg_{C-E2} \; consumed}{mg_{C-E2} \; initial} \times 100 \qquad (1)$$

The reaction of the assays carried out was evaluated by a linear regression analysis with a first order reaction equation, as shown in equations 2.

$$\ln C_{E2} = -kt + \ln C_{E2_0} \qquad (2)$$

Where C_{E2} corresponds to the concentration of E2 at each unit of time, C_{E20} was the initial concentration of E2, k was the kinetic constant in min^{-1}, and t was the time in minutes, respectively. For each regression, the determination coefficient ($R^2 > 0.9$) was calculated, to demonstrate the fitting of the model with the experimental data. Finally, a mass balance was performed in all assays to assess the final fate of E2, including the formation of products formatted.

2.3 Analytical methods

17β-estradiol concentrations were determined in a Perkin Elmer series 200 (USA) high performance liquid chromatograph (HPLC) equipped with a UV-visible detector at a wavelength (λ) of 230 nm, using a C18 column. A methanol-water mixture (70:30 v/v) was used as the mobile phase with a flow rate of 1 mL min^{-1}. For the analysis of total organic carbon (Total Carbon (TC), Total Organic Carbon (TOC), and HCO_3^-) in all the assays, a Shimadzu TOC-Analyzer was used. Where the total carbon was oxidized in a reactor at a temperature of 720 ºC and for the analysis

of inorganic carbon two solutions were used: one of HCl (1N) and H_2PO_4 (25%) with a flow of extra-dry air at 150 mL min^{-1} and a pressure of 200 kPa. CO_2 concentrations were analyzed in a Perkin Elmer gas chromatograph (GC), model Autosystem XL (USA), equipped with a thermal conductivity detector (TCD), as well as an HP-PLOT/Q capillary column, Agilent Technologies (USA), 30 m long, 0.530 mm internal diameter and 40 μm particle size. The temperatures of the oven, injector and detector were set at 60°C, 100°C, and 200°C, respectively. Ultra-high purity helium was used as the mobile phase at a flow rate of 10 mL min^{-1}. The injection volume was 50 μL, and data acquisition was performed using TC Nav software version 6.3.1.

2.4 Statistical analysis of the data

The batch assays, as well as each of the calibration curves, were conducted in duplicate and, the data represented represent average of the experimental group. For each linear regression performed, the determination coefficient (R^2) was calculated, and in all cases, it was higher than 0.99. In addition, the standard deviations and the coefficient of variation (CV) were estimated for each set of data, with the CV was less than 10% in all cases.

3   Results and discussion

3.1 E2 stability evaluation under natural sunlight

The results of the stability evaluation of 17β-estradiol are shown in Figure 2, where 15 mg E2-C L^{-1} in water were exposed to natural sunlight for 3 h. This was done to rule out photolysis of E2 under natural sunlight before conducting assays with FeSO$_4 \cdot$7H$_2$O and H$_2$O$_2$. During the 3-hour assay, it was observed that the concentration of E2 remained constant with a mean of 15.40 ± 0.65 mg E2-C L^{-1} (CV of 4.24%). It is worth mentioning that, in the analytical techniques employed, the production of E2 metabolites was not observed. This indicates that the formation of metabolites and new products during the photo-Fenton process will be directly related with the oxidation of E2 through the addition of FeSO$_4 \cdot$7H$_2$O, and H$_2$O$_2$ (Fernandez *et al.*, 2017).

On the other hand, the assay carried out with 2 mg E2-C L^{-1}, adjusted to a pH of 10, showed simultaneous production of inorganic carbon and a decrease in the concentration of E2. The results of these assays are shown in Figure 3. The alkaline pH led to a decrease in the concentration of E2, with up to 490 μg L^{-1} of inorganic carbon produced, originating from the decrease in estradiol concentration. An

increase in pH greater than10 has been considered a factor that does not promote Fenton-type reactions, as high efficiencies have been reported at pH values lower than 3 (Qian *et al.*, 2020). However, the assay samples containing 2 mg E2-C L^{-1} were analyzed by HPLC, revealing the accumulation of carbonated metabolites throughout the process, although specific metabolites were not identified. This indicates that the pH adjustment of 10 has a direct effect on the E2 bonds, leading to the formation of HCO$_3^-$. Furthermore, it is important to mention that the pKa of E2 has been reported in the range of 10.23 - 10.4 (Yang *et al.*, 2023; Shareef *et al.*, 2006). When estradiol is in a medium where pH $\geq$ pKa, it tends to undergo a strong effect of electron loss and dissociation, due to the weak bonds in the polar functional groups of its structure, as indicated by Gong *et al.* (2022). This loss of electrons is so intense that the lost functional groups combine with inorganic compounds such as HCO$_3^-$ or other organic compounds, resulting from the partial oxidation of E2, according to the results found in the present work. Likewise, it has been reported that compounds such as the bicarbonate ion tend to generate radicals scavengers that promote the oxidation of E2 (Kim *et al.*, 2015; Frontistis *et al.*, 2011). It is worth mentioning that the pH in the assays increased over time from 10 to 10.93, which can be attributed and is verified by the formation of inorganic carbon compounds such as HCO$_3^-$.
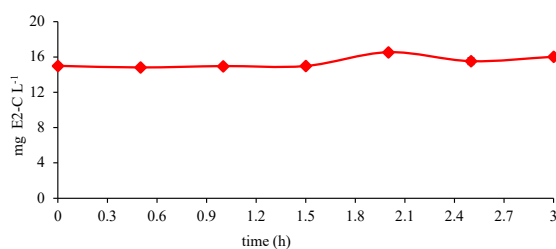

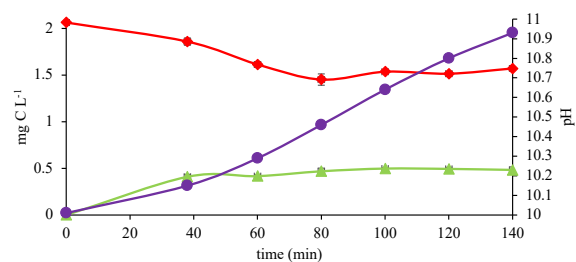Figure 2. Stability evaluation of 15 mg E2-C L^{-1} under natural sunlight. (♦) E2-C

Figure 3. Stability evaluation of 2 mg E2-C L^{-1} at pH 10, in the absence of FeSO$_4$ and H$_2$O$_2$. Primary axis: (♦) E2-C, (▲) HCO$_3^-$-C, Secondary axis: (●) pH.
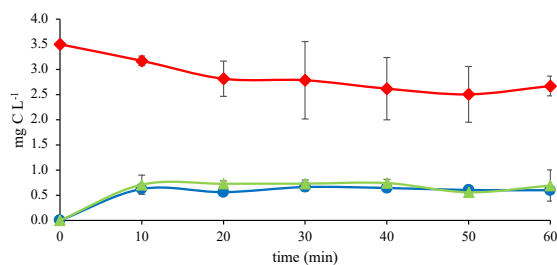
Figure 4. Kinetic profile of oxidation test with 3.5 mg E2-C L^{-1} with 4 mg L^{-1} of $FeSO_4 \cdot 7H_2O$ as catalyst and 10 mg L^{-1} of H_2O_2, at pH 5. (♦) E2-C, (●) CO_2-C, (▲) HCO_3^--C.

Figure 6. Kinetic profile of oxidation test with 7.5 mg E2-C L^{-1} with 4 mg L^{-1} of $FeSO_4 \cdot 7H_2O$ as catalyst and 10 mg L^{-1} of H_2O_2, at pH 7.5. (♦) E2-C, (●) CO_2-C, (▲) HCO_3^--C.

Figure 5. Kinetic profile of oxidation test with 4.5 mg E2-C L^{-1} with 4 mg L^{-1} of $FeSO_4 \cdot 7H_2O$ as catalyst and 10 mg L^{-1} of H_2O_2, at pH 10. (♦) E2-C, (▲) HCO_3^--C, (●) CO_2-C.

3.2 Oxidation of 17β-estradiol in batch assays

Figure 4 shows the results obtained from the kinetic profile of the oxidation assay with 3.5 mg E2-C L^{-1} at pH 5, where the oxidation of 960 μg E2-C L^{-1} is observed in the first 10 min of the assay and remains constant for the rest of the hour. Along with consumption, 690 μg HCO_3^--C L^{-1} and 610 μg CO_2-C L^{-1} were produced in the first 10 min of reaction, and these concentrations remained constant until the end of the assay. This study represents one of the first attempts to evaluate the production of inorganic carbon in advanced oxidation processes with Fe^{2+}/H_2O_2, aming to assess whether E2 is completely or partially oxidized.

Figure 5 shows the results obtained from the kinetic profile of the oxidation assay with 4.5 mg E2-C L^{-1} at pH 10, where the maximum oxidation of up to 4.04 mg E2-C L^{-1} was observed during the first 10 min of the assay. Along with consumption, up to 3.90 mg HCO_3^--C L^{-1} and 0.45 mg CO_2-C L^{-1} were generated during the reaction, and these concentrations remained constant until the end of the assay. Compared with the previous assays at pH 5, a higher production of inorganic carbon was observed, suggesting that Fenton reactions with Fe^{2+}/H_2O_2 lead to oxidation up to HCO_3^- at alkaline pH. The Fenton process was not inhibited in a pH 10 medium.
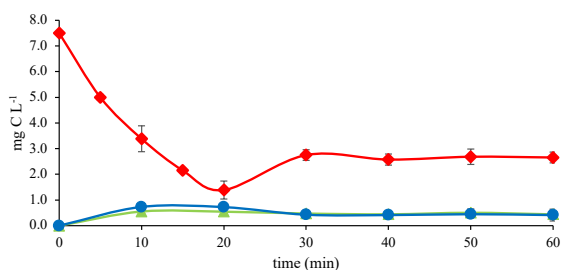
Assays with 7.5 mg E2-C L^{-1} were evaluated under a neutral pH (7.5) to understand the influence on the oxidation of E2 and the formation of inorganic carbon compounds. The results obtained from the kinetic profile of this assay are presented in Figure 6, where the maximum oxidation of up to 3.75 mg E2-C L^{-1} was observed in the first 10 min. The result was similar to that obtained in the assays with 4.5 mg E2-C L^{-1} at pH 10. Simultaneously, up to 0.55 mg HCO_3^--C L^{-1} and 0.73 mg CO_2-C L^{-1} were generated, starting from the first 10 minutes of the reaction. In these assays, the decrease in the concentration of E2 is directly attributed to a precipitation effect, as the production of inorganic carbon was lower than the concentration of the organic carbon consumed, as reported Camacho *et al.* (2022).

It should be noted that this study stands as one of the initial works demonstrating the complete E2 oxidation by photo-Fenton to carbon compounds such as HCO_3^- and CO_2. It is not just a proposal for the E2 oxidation pathway. Additionally, it was observed that the concentrations of E2 in the first 20 and 30 minutes of the reaction followed a first-order reaction behavior. However, when the reaction reaches equilibrium, the oxidation changes from first order to zero order. A mass balance (Table 1) was conducted in all assays, revealing that E2 was primarily converted into HCO_3^-. The production of inorganic carbon was pH-dependent. In the assay with 3.5 mg E2-C L^{-1} at pH of 5, the maximum production of HCO_3^--C was 690 μg L^{-1}. However, when the pH was increased to 10 in the assays with 4.5 mg E2-C L^{-1}, the maximum production of HCO_3^--C was to 3.90 mg L^{-1} (Table 1). This represented 4.6 times increase and is correlated with the zone curves of predominance of carbonaceous species, where, at pH values above 8, the production of species such as HCO_3^- increases. For this reason, environmental conditions promote the formation of HCO_3^- from the oxidation of E2 at pH 10. The photo-Fenton process was not inhibited (Yang *et al.*, 2023; Camacho *et al.*, 2022). Moreover, under alkaline conditions, Fe^{2+}, SO_4^{2-}, UV from sunlight, and the formation of HCO_3^- were the primary active oxidation species generating $\cdot OH$ from H_2O_2 and OH-

Table 1. Results of the mass balance in the batch assays with 3.5, 4.5, and 7.5 mg E2-C L^{-1}.

Conditions		Initial concentration (mg L^{-1})	Final concentration (mg L^{-1})		
E2-C (mg L^{-1})	pH	E2-C	E2-C	CO_2-C	HCO_3^--C
3.5	5	3.50 ± 0.01	2.46 ± 0.16	0.61 ± 0.03	0.69 ± 0.06
4.5	10	4.50 ± 0.01	1.69 ± 0.12	0.45 ± 0.008	3.90 ± 0.34
7.5	7.5	7.50 ± 0.01	2.66 ± 0.07	0.42 ± 0.01	0.06 ± 0.04

species (Zhu *et al.*, 2021). Although, HCO_3^- is consider as a suppressor of ·OH generation, this study found that the presence of Fe^{2+}, SO_4^{2-}, UV from sunlight and H_2O_2 promoted ·OH production (Liu *et al.*, 2023; Zhu *et al.*, 2021). Furthermore, under alkaline conditions, the formation of Fe(III)-hydroxyl complexes was promoted for ·OH production, given than $Fe(OH)^{2+}$ is the most potent photoactive species (Feng *et al.*, 2005). In all assays, the final concentration of CO_2 remained around 0.5 ± 0.1 mg L^{-1}, regardless of changes in the pH values. The results indicate that the photo-Fenton with Fe^{2+}/H_2O_2 and sunlight did not produce greenhouse gases such as CO_2 at pH > 7, and it was not inhibited due to the predominant generation of HCO_3^-. According to these results, the use of photo-Fenton process in real systems could be an alternative to mitigate greenhouse gases generation in wastewater treatment plants and eliminate contaminants from wastewater.

The results of oxidation efficiencies of E2 of each assay are shown in Table 2. The E2 removal efficiencies in assays with initial concentrations of 3.5, 4.5 and 7.5 mg L^{-1} of E2-C were 25.75 ± 2.43, 59.34 ± 7.32, and 64.44 ± 0.97 %, respectively. The removal efficiency exhibited an increase with higher initial concentrations, and the oxidation process was not inhibited across varying pH conditions. Notably, the results obtained in this study are better than reported in certain studies, such as the one conducted by Kovacic *et al.* (2018), which reported oxidation efficiencies of 30% for $5\mu M$ E2 over 95 minutes using advanced oxidation processes with a 450 W Xenon lamp. These results were lower than it was obtained in the present study, but also their study not disclose the final fate of E2. Similarly, Bennett *et al.* (2018) reported efficiencies of 64 % in the removal of 10 μg L^{-1} of E2 through oxidation with UV light and H_2O_2. However, their study also did not provide information on the final fate of the contaminant, and the concentration evaluated was 450 times lower than the concentration of E2 used in our study. Feng *et al.*, (2005) reported an oxidation efficiency of 61.7 % from an initial concentration of 36.7 μmol E2 L^{-1} after 160 min of UV-vis irradiation with a 250 W metal halide lamp ($\lambda \geq 313$ nm) at pH 3. While the efficiencies reported by Feng *et al.*, (2005) are similar with the results of our study, the oxidation was 1.6 times higher than that achieved in this work using Fe^{2+}/H_2O_2 and sunlight at pH 10.
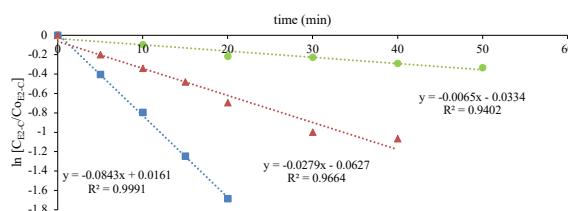

Figure 7. Linear regression of a first-order reaction of trials with 3.5 (●), 4.5 (▲) and 7.5 (■) mg E2-C L^{-1}.

3.3 Oxidation kinetics of 17β-estradiol

The results of the kinetic evaluation of the concentrations of E2 were analyzed using linear regression to assess the fit of a first-order reaction model. It is important to remember that the concentrations of E2 in the first 30 minutes of the reaction followed a first-order reaction behavior and when the reaction reaches equilibrium, the oxidation changes from first order to zero order. The findings, represented in Figure 7 and Table 2, reveal that the kinetic constants were greater than 10^{-2} min^{-1} at pH values of 7.5, and 10. The highest constant was obtained in the assay with 7.5 mg E2-C L^{-1} at a pH of 7.5, followed by the assay with 4.5 mg E2-C L^{-1} at a pH of 10, while the lowest constant was obtained in the assay with 3.5 mg E2-C L^{-1} at pH 4.5. In comparison, Zhu *et al.*, (2021) reported kinetic constants (min^{-1}) of 0.0464 and 0.0308 during the oxidation of 0.1 mmol of E2 at pH values of 9, and 10, respectively, using UV light from a mercury lamp (254 nm) in both freshwater and seawater. The constants reported by Zhu *et al* (2021) are 0.81, and 1.73 times lower than the kinetic constants obtained in our work at pH values of 10 and 7, respectively. Kovacic *et al.*, (2018) reported a k value of 15.39×10^{-3} min^1 with 5 μM E2, TiO_2-FeZ and a 50 μM H_2O_2 concentration in assays conducted under sunlight exposure.

The kinetic constant (k) reported by Kovacic *et al.* (2018) is 4.4 times lower than that it found in our work, particularly when compared with the assay involving 7.5 mg E2-C L^{-1}. In a study by Yang *et al.*, (2023), a kinetic constant of 8.79×10^{-7} min^{-1} was reported during the oxidation of 100 μg L^{-1} E2 with humic acids, which is up to 949 times lower compared to the findings in our work. On the other hand, Gong *et al.*, (2022) conducted a study with activated carbon and reported an adsorption rate of 7.5 mg E2 mg Fe/Ni carbonized.

Table 2. Comparison of first-order reaction kinetics constants of batch assays with E2-C at different pH values and oxidation efficiencies obtained.

Assay (mg E2-C L^{-1})	pH	Oxidation efficences E2 (%)	k (k$\times 10^{-3}$ min^{-1})
3.5	5	25.75 ± 2.43	6.5 ± 1.2
4.5	10	59.34 ± 7.72	27.9 ± 4.3
7.5	7.5	64.44 ± 0.97	84.3 ± 2.2
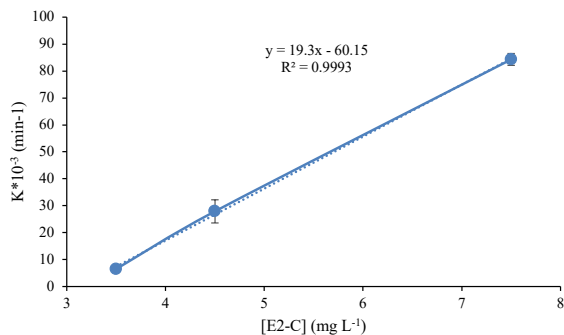
Figure 8. Linear regression of the kinetic constant obtained in the tests with 3.5, 4.5 and 7.5 mg E2-C L^{-1} at pH 5, 10 and 7.5, respectively.

While the adsorption speed reported by Gong *et al.*, (2022) is higher than the results obtained in our work, it is essential to note that E2 was not transformed, instead, it was transferred from one environmental compartment to another, remaining in the environment. Furthermore, the results obtained in this work show that the use of Fe^{2+}/H$_2$O$_2$ with sunlight is superior to the use of TiO$_2$ and UV light. This is an advantage due to the lower cost and simpler infrastructure, making it a more practical approach for application in real systems.

The behavior of the obtained kinetic constants exhibited linearity with a determination coefficient (R^2) of 0.993, as shown in Figure 8. It was observed that as the initial concentration of E2 increased, the kinetic constant (k) also increased according to Equation 3. The linearity of the data suggests that the oxidation of E2 is not dependent on the pH values assessed, aligning findings reported by Kim *et al.*, (2015). According to their observations, as the initial concentration of E2 increases, the kinetic constant shows a linear increase, indicating that pH values do not significantly influence the oxidation of E2 in the system.

$$k = 19.4[E2 - C] - 60.15 \qquad (3)$$

Conclusions

The pH 10 promoted the formation of HCO$_3^-$ during the oxidation of 17β-estradiol. The E2 oxidation efficiencies in assays with initial concentrations of 3.5, 4.5 and 7.5 mg L^{-1} of E2-C at pH values of 5, 10, and 7.5 were 25.75 $\pm$ 2.43, 59.34 $\pm$ 7.32, and 64.44 $\pm$ 0.97 %, respectively. The reaction kinetics was fitted to a first-order reaction model with linear coefficients of determination greater than 0.9. The E2 oxidation constants were found to be independent of the pH in the media but exhibited dependence on the initial concentration of 17β-estradiol with a linear behavior. The maximum oxidation constant found was 84.3$\times 10^{-3}$ min^{-1} in assays with 7.5 mg E2-C L^{-1}. The production of HCO$_3^-$ was found to be pH-dependent. This due to that at pH 5, the maximum HCO$_3^-$-C production was 0.69 $\pm$ 0.06 mg L^{-1}, and at pH 10, it increased to 3.73 $\pm$ 0.21 HCO$_3^-$-C mg L^{-1}. The oxidation of 17β-estradiol by the photo-Fenton process with Fe^{2+}/H$_2$O$_2$ was not inhibited for the pH 10, with the majority of the production being HCO$_3^-$. Therefore, the use of photo-Fenton process in real systems emerges as a viable alternative to mitigate the generation of greenhouse gases in wastewater treatment plants.

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