



Efficient removal of antibiotic ciprofloxacin by catalytic wet air oxidation using sewage sludge-based catalysts: Degradation mechanism by DFT studies

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ABSTRACT

In this work, the sewage sludge-derived activated carbon (SAC) loaded with iron nanoparticles (FeSAC) showed a highly effective catalytic activity in the degradation of the antibiotic ciprofloxacin by the CWAO reaction. The properties of FeSAC catalyst were studied by using N₂ adsorption-desorption measurements at 77 K, scanning electron microscopy, X-ray fluorescence spectroscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis. The CWAO reaction was evaluated at different temperatures (120–140 °C), total pressure (10–30 bar) and catalyst doses (0.1–0.7 g/L) in a batch reactor. In this regard, temperature and catalyst dosage showed a significant impact on the removal of the tested antibiotic. By using a catalyst dose of 0.7 g/L, ciprofloxacin degradation and CO₂ selectivity were higher than 99 % and 60 %, respectively, and were achieved within two hours at 140 °C and 20 bar. The loss of the active phase (Fe) of the catalyst in the reaction medium was measured, obtaining negligible values (less than 24 ppb). This catalyst showed high stability under the tested reaction conditions. In addition, a potential equation was proposed to correctly describe the evolution of ciprofloxacin degradation. The calculated activation energy of the CWAO process was 53.8 kJ/mol. Additionally, Density Functional Theory (DFT) calculations were performed to illustrate the degradation mechanism of ciprofloxacin, where the electronic energies indicated the compounds that are most difficult to degrade by CWAO. Finally, a proof of concept using an environmentally-relevant matrix was carried out, verifying the technical feasibility of the synthesized catalyst for its application with more complex matrices, consecutive reaction cycles and at a low treatment cost.

1. Introduction

In 2021 alone, a total of 8.7 million tons of dry sewage sludge were generated in Europe [1]. The amount and characteristics of sludge generated in a WWTP is largely depended on the influent and type of used treatment processes. It has been estimated that sewage sludge production will increase rapidly annually in the coming years [2].

The traditional methods for sewage sludge management include landfill, incineration, composting, anaerobic digestion (biogas production) and agricultural applications, among others [3,4]. One alternative method gaining particular attention in recent years is the pyrolysis.

Pyrolysis of sewage sludge can substantially reduce the waste volume, carbonize organic compounds, fix heavy metals, as well as destruct pathogens [4]. The carbon material derived from this process could be sustainably used to produce carbonaceous materials such as adsorbents or catalytic supports for potential environmental applications used in the degradation of many pollutants [5,6].

Emerging pollutants are usually defined as natural and synthetic chemicals that are not commonly monitored in the WWTPs effluents and therefore have the potential to enter the aqueous environment. These pollutants are not new in our environments, but they can stay for a long time in the aqueous medium because of their biotransformation,

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formation of metabolites and by-products. This group of compounds includes pharmaceuticals and personal care products, among many other substances used daily [7,8].

In recent years, the use of pharmaceutical products has grown exponentially. Consequently, there has been an increase of these compounds in groundwater, surface water and wastewater [9–11]. Some of these contaminants belong to the fluoroquinolones group, antibacterial drugs firstly used in the 1970 s [12]. Among them, ciprofloxacin is one of the most widely used. Unfortunately, since these types of antibiotics are characterised by their low biodegradability, the conventional biological wastewater treatment processes are not able to successfully remove these compounds from wastewater [13,14]. Therefore, the development of effective treatment methods is of great importance. In this sense, the advanced oxidation processes (AOPs) constitute a promising group of technologies for the treatment of wastewater containing organic refractory compounds, as an additional stage to the conventional biological treatment [15]. Among AOPs, wet air oxidation (WAO) process has already been successfully applied to treat effluents from printing and dye industry. A wide range of products have been treated efficiently due to the capacity of this process to degrade compounds that show low solubility, such as polymers or fatty acids [16]. The main disadvantages of WAO technique are the high requirements of temperature (200–320 °C) and pressure (20–200 bar), which results in high operation costs. The use of a catalyst strongly improves the degradation of organic pollutants by using milder operating conditions. Soluble transition metal salts (such as iron or copper) have been reported as efficient enhancers of the reaction rate [17]. Therefore, the use of a solid catalyst offers a further advantage compared to the homogeneous catalysts, since the solid can be easily recovered, regenerated and reused, after reaction. Besides, in the catalytic wet air oxidation (CWAO) process, the stability and durability of the catalyst under operating conditions must be strictly tested [18].

To our knowledge, there is only one previous study about the treatment of ciprofloxacin-containing waters by CWAO using ruthenium-based catalysts [12]. Therefore, there is a significant knowledge gap in the application of cheaper iron-based catalysts supported on sewage sludge-derived carbon materials for the removal of emerging pharmaceutical compounds from wastewater effluents by CWAO at moderate pressure and temperatures, which would allow the process to be economically viable. This study aims to step into the gap of existing research.

Ciprofloxacin was considered as model compound because it is hardly biodegradable by the conventional biological processes, but it is widely used to treat serious infections, or infections when other antibiotics have not worked. This pollutant showed the highest concentration among more than 200 pharmaceuticals in surface waters worldwide [19,20]. In addition, it has been included in the European Surface Water Watch List under the EU Water Framework Directive (Decision 2020/1161) [21]. Several studies about the removal of ciprofloxacin by other advanced oxidation processes have been reported in the literature. This information is summarized in Table S1 (Supplementary material).

In the present study, iron catalysts were synthesized from sewage sludge in order to contribute valorization of wastewater treatment plants (WWTPs) wastes and the development of environmentally friendly and low cost catalysts. Reaction tests were carried out in a batch reactor with iron supported on sewage sludge-derived activated carbon (FeSAC). The catalyst efficiency was determined by the ciprofloxacin degradation, mineralization rate, TOC removal and iron leaching. Not only was the effect of operating conditions such as temperature, total pressure and catalyst dosage tested, but a conversion rate equation was proposed for the experimental findings. Furthermore, the degradation intermediates of ciprofloxacin were identified by LC-MS technique. Based on experimental and theoretical results (Density Functional Theory calculations), a reaction pathway was proposed for the ciprofloxacin degradation. Finally, a proof of concept using surface water as an environmentally-relevant water matrix, has been accomplished.

2. Materials and methods

2.1. Materials

Ciprofloxacin (≥ 98 wt. %) was purchased from Sigma-Aldrich and the chemical activating agent ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ≥ 98 wt. %) was provided by Panreac. Hydrochloric acid (HCl, 37 wt. %), acetonitrile (≥ 99.9 wt. %), and acetic acid glacial (≥ 99.7 wt. %), were supplied by Fluka, Fisher Chemical and Fluorochem, respectively. Aqueous solutions were prepared with ultrapure water from PURELAB® Flex Water Purification System (Veolia). A proof of concept was also carried out using a surface water matrix collected in the Manzanares river (Madrid, Spain), whose physico-chemical properties were measured following the Standard Methods [22]. These parameters are summarized in Table 1.

2.2. Synthesis of FeSAC catalyst

The industrial sewage sludge was kindly supplied by a local pharmaceutical company located in Spain. This biomass precursor was firstly characterized in terms of Chemical Oxygen Demand (COD), and total (TS), fixed (FS), and volatile (VS) solids content measured according to the Standard Methods [22]. The solid fraction was also undergone to elemental analysis (EA) and X-ray fluorescence spectroscopy (XRF) by using a LECO CHNS-932 analyzer and a PANalytical Axios spectrometer, respectively.

For the catalyst synthesis, the sewage sludge was dried in an oven for 24 h at 105 °C. After a grinding step, the dried sludge powder was chemically activated by using an incipient wetness impregnation technique with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, in a ratio of 1 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$: 1 mg dried sludge. The activation was performed for 24 h at room temperature, followed by drying for 24 h at 105 °C. Next, the impregnated sludge was pyrolyzed in a vertical quartz reactor for 2 h at 800 °C, maintaining a constant N_2 flow rate of 100 mL/min and a heating rate of 10 °C/min. To remove the iron excess (i.e. iron compounds, in any of their oxidation states, which are weakly bound to the carbonaceous matrix and can be released into the aqueous phase leading to high iron leaching), the catalyst was washed with HCl 1 M solution for 1 h under magnetic stirring, and then filtered and rinsed with ultrapure water until neutral pH was reached. The solid was dried in an oven for 24 h at 105 °C, and finally, was ground and sieved to a particle size under 250 μm range.

2.3. Catalyst characterization

Elemental analysis and X-ray fluorescence spectroscopy were performed in order to determine the chemical composition of the synthesized catalyst, using the same equipment mentioned for the characterization of the raw industrial sludge. The textural properties of the material were explored by N_2 adsorption-desorption isotherms at 77 K in an ASAP 2020 equipment. Before measurement, the samples were out-gassed for 3 h at 250 °C. The specific surface area of the solids (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) equation and micropore volume (V_{Mic}) was estimated using the Dubinin–Radushkevich equation. The morphology and elemental analysis of the solid was studied by scanning electron microscopy with energy

Table 1
Physico-chemical characterization of the surface water.

Parameters	Value
pH	6.9
Chemical Oxygen Demand (mg/L)	<15
Total Organic Carbon (mg/L)	3.2
Total Carbon (mg/L)	7.4
Total Nitrogen (mg/L)	0.6
Total Dissolved Solids (mg/L)	64
Conductivity at 20 °C (OS/cm)	38.1

dispersion X-ray spectrometry (SEM-EDX) on a JEOL JSM 6335 F microscope. The binding energies of the elements in the catalyst were determined by X-ray photoelectron spectroscopy (XPS) in a SPECS GmbH electron spectroscopy system with a PHOIBOS 150 9MCD energy analyzer, and Mg X-ray source. Thermogravimetric analysis (TGA) was carried out in a Perkin Elmer STAR 6000 analyzer. The measurements were accomplished in a temperature range between 30 and 1000 °C, under nitrogen flow rate of 30 mL/min and a constant heating rate of 10 °C/min.

2.4. Catalytic wet air oxidation tests of ciprofloxacin in aqueous solution

CWAO experiments were performed using ciprofloxacin solutions with an initial concentration of 50 mg/L, in a Hastelloy autoclave reactor equipped with a heating jacket and a mechanically controlled paddle stirrer. This range of concentration has been previously reported in the literature [14,23–28]. The measured pH of ciprofloxacin aqueous solutions in ultrapure water was found around 6.8. In order to ensure no mass transfer limitations in the liquid phase, the stirring speed was set at 700 rpm. The experiments were performed by loading 100 mL of ciprofloxacin solution and the selected catalyst dose into the reactor. The reactor was then purged with nitrogen to remove any traces of air and to prevent the reaction from initiating before the operating conditions were reached. Subsequently, the stirring was started, and the heating jacket was switched on. Once the reaction temperature was reached, the reactor was pressurized with air up to the operating pressure, considering this step as zero reaction time. Liquid samples were collected periodically for 3 h and immediately filtered through 0.45 µm PTFE filters for further analysis. The influence of different reaction conditions, such as catalyst dose (0.1–0.7 g/L), temperature (120–160 °C) and total pressure (10–30 bar) was investigated. In addition, a proof of concept with a surface water matrix, which can be considered a real and environmentally-relevant aqueous matrix, was accomplished. In this latter case, the measured pH of the initial ciprofloxacin aqueous solution was of 7.0.

2.5. Analytical methods

Ciprofloxacin concentration was analyzed using a High Pressure Liquid Chromatograph 1260 Infinity II coupled with a diode array detector (Agilent) using a Poroshell 120 EC-C18 column (4.6 × 150 mm; 4 µm). The mobile phase was a mixture of acetonitrile (17.5 %) and a 75 mM acetic acid solution (82.5 %) at a flow rate of 0.85 mL/min, using an injection volume of 50 µL. The column temperature and the detection wavelength were set at 30 °C and 275 nm, respectively.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to analyze the iron leaching into the reaction medium. The total organic carbon (TOC) content was measured by a Shimadzu TOC-V CPH analyzer. Finally, the reaction intermediates and by-products were identified in a Bruker LC-QTOF-MS Impact II spectrophotometer.

2.6. Computational studies

The molecular structure of the reactants and the observed intermediates were optimized by the Density Functional Theory (DFT)/M06–2X method with a 6–311 + +G(2df,2pd) basis set level, obtaining the corresponding E_{HOMO} values and positive frequencies in all the possible conformations evaluated, corresponding to minima energy. Here we show, of all these conformations, those that have turned out to be more stable under the conditions of the study. The calculations have been carried out using the Gaussian 16 program [29], including Natural Bond Orbitals (NBO) analysis [30,31]. The experimental conditions considered were 20 bar and 140 °C. The SMD model (universal solvation model based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface

tensions) was used to address the solvent effects of water [32]. Gauss-View 6.0 software was used to visualize the computed and optimized structures [33].

3. Results and discussion

3.1. Sewage sludge characterization

Regarding to the main macroscopic properties of the industrial sewage sludge, a TS concentration of 36.6 g/L was found. The high COD (34.8 g/L) and VS (80 % of TS) values indicated the presence of a relevant organic matter content in the sewage sludge. Generally, this aspect is convenient for the synthesis of biomass-derived catalysts as the more organic matter in the precursor, the higher the efficiency in the production of biomass-based catalyst [34].

Chemical characterization of the sewage sludge solid fraction showed a carbon content of 42.4 wt. %, which is within the carbon concentration range reported in the literature for high char yields [35]. Other elements detected in higher proportions were oxygen (14.6 wt. %), calcium (11.6 wt. %), or hydrogen (5.8 wt. %). Furthermore, the raw sludge presented a low iron content (0.7 wt. %).

3.2. Catalyst characterization

Elemental analysis of the synthesized catalyst provided the content of carbon (70.9 wt. %), nitrogen (3.8 wt. %) and hydrogen (1.8 wt. %). From the results of XRF analysis, other main elements, such as oxygen (8.5 wt. %) and iron (5.1 wt. %) were identified. As expected, the pyrolysis step increased the carbon content of the raw sewage sludge to around 67 % from its initial value. During this process, the oxygen and hydrogen content was also considerably reduced compared to the biomass precursor values. The synthesis of the carbonaceous material by chemical activation required the application of an iron-based activating agent. The use of this metal salt allowed a sufficiently high iron content to act as the active phase of the catalyst in the CWAO process. Although the initial calcium content in the biomass precursor was high, the concentration in the resulting material was practically negligible, possibly due to the catalyst rinsing. Finally, it should be noted that the product yield, after the rinsing step, was found about 61 %.

The textural properties of the FeSAC catalyst were determined by the N₂ adsorption-desorption isotherms at 77 K (Fig. 1a). According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the carbonaceous material showed a type IV isotherm, which is representative of mesoporous materials. In addition, the large initial adsorption of nitrogen at low relative pressure values ($P/P^0 < 0.05$) indicates the occurrence of a considerable amount of micropores in the solid structure. At relative pressure values above 0.4, the isotherm also exhibits an H4-type hysteresis loop, indicating capillary condensation in the mesopores [36]. As has been reported in the literature, hysteresis occurs when the pore width exceeds a critical value (which depends on adsorbate, temperature, and pore networks); and it has been determined that nitrogen at 77 K exhibits this phenomenon when the pores are larger than 4 nm [37].

The measured BET surface area of FeSAC catalyst was of 582 m²/g, which is within the range reported in the literature for similar carbonaceous materials synthesized from sewage sludge [38]. Furthermore, a micropore volume value of 0.17 cm³/g was obtained, corresponding to 47.5 % of the total pore volume. As can be seen in the pore size distribution (Fig. 1b), the maximum value was found in the narrow mesopore zone, i.e. around 4 nm. Thus, the mean pore diameter, calculated from the BJH method, was of 7.2 nm.

The thermal stability of the synthesized catalyst was evaluated by TGA, as illustrated in Fig. 2a. The degradation pattern showed three clearly defined zones. The first one was found at 100 °C, where a weight loss of about 7 % was reached due to the evaporation of the adsorbed water in the sample. The second degradation zone could be found in the

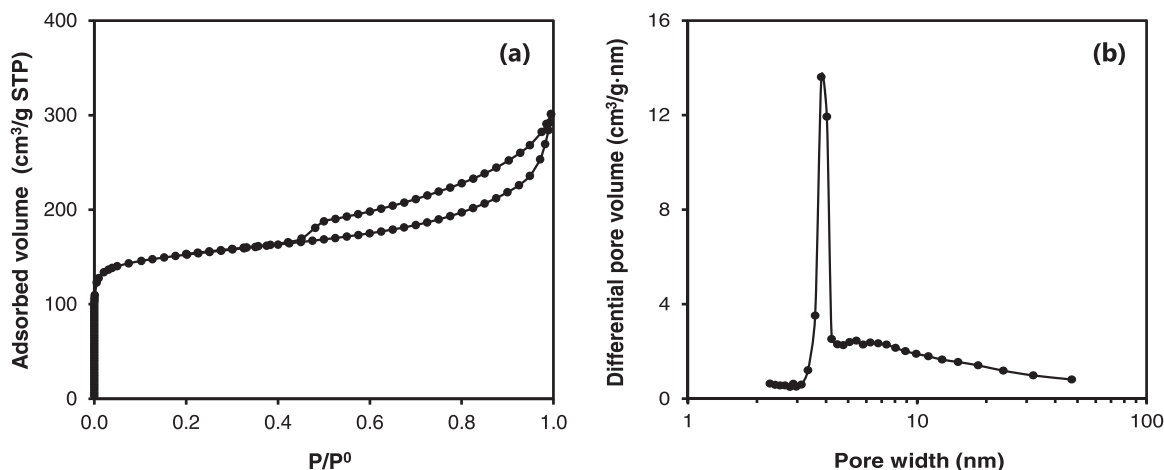


Fig. 1. N_2 adsorption-desorption isotherms at 77 K (a) and pore size distribution (b) of the FeSAC catalyst.

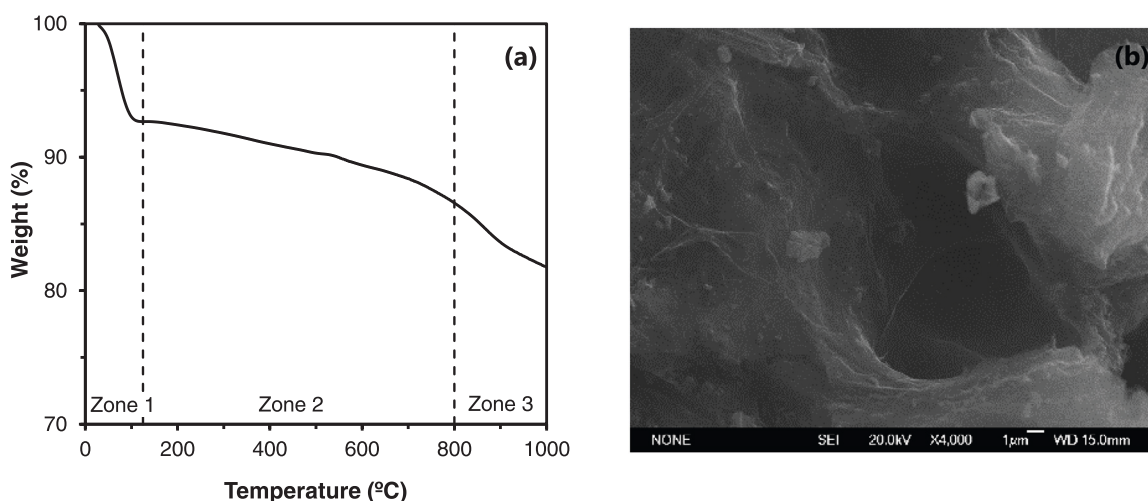


Fig. 2. Thermogravimetric analysis (a) and SEM micrograph (b) of the FeSAC catalyst.

range 150–750 °C, obtaining a weight loss between 7 % and 12 %. The pyrolysis temperature during the catalyst synthesis was of 800 °C, which could explain the narrow weight loss in the previously mentioned temperature range, associated with both volatile and high molecular weight compounds that were not completely eliminated during pyrolysis process. Finally, at temperatures above 800 °C, the thermal degradation of the catalyst increased substantially, reaching a weight loss of around 18 % at 1000 °C. This increase in the thermal degradation compared to the second zone might be related to the removal of high molecular weight compounds that had no time to be degraded during the catalyst synthesis and those that required a higher temperature to do so. The thermal study demonstrated that the synthesized iron-based catalyst could be heated up to 750 °C without significant decomposition.

The morphological properties of the FeSAC catalyst were determined by scanning electron microscopy. Thus, a SEM micrograph of the sample is shown in Fig. 2b, and further information with different magnifications has been included in Fig. S1 (Supplementary material). As can be observed, the carbonaceous material presents a rough and porous surface, with a heterogeneous structure consisting of small iron particles of different size and shape adhered to the carbon matrix. Furthermore, the activating agent, $FeCl_3 \cdot 6H_2O$, appears to have formed a complex network of pores in the catalyst, presenting cavities and crevices on its surface. Fig. S2 (Supplementary material) shows the EDX spectrum of the catalyst. The presence of iron, silicon, oxygen, and carbon elements clearly confirmed the synthesis of the carbon-based catalyst.

The oxidation state of surface iron was determined by X-ray photoelectron spectroscopy (XPS) analysis by deconvolution of the Fe2p spectra of fresh and spent catalyst. Fig. S3 (Supplementary material) represents the deconvoluted Fe2p spectra of the fresh and after used catalyst in the oxidation experiment. A main band is observed centered at approximately 712 eV accompanied by a secondary band at higher binding energy (725 eV). These bands correspond to the characteristic values of Fe^{3+} , in addition to two satellite peaks located around 717 and 728 eV confirming the presence of Fe^{3+} species on the catalyst surface [39]. XPS analysis also detected C and O as major surface components.

3.3. Catalytic performance

3.3.1. Preliminary tests

Initially, preliminary tests were conducted to determine the adsorption contribution of ciprofloxacin onto the synthesized catalyst. Three catalyst doses, between 0.10 and 0.70 g/L, were tested under an inert nitrogen atmosphere to avoid the compound oxidation. Fig. 3 illustrates the adsorption blanks of ciprofloxacin at 140 °C and 20 bar. As can be seen, during conditioning time until the operating temperature is reached, the equilibrium concentration is already attained. Therefore, the concentration of ciprofloxacin remains constant from zero time onwards.

On the other hand, the effectiveness of the synthesized catalyst requires not only to assess the adsorption contribution in the process, but

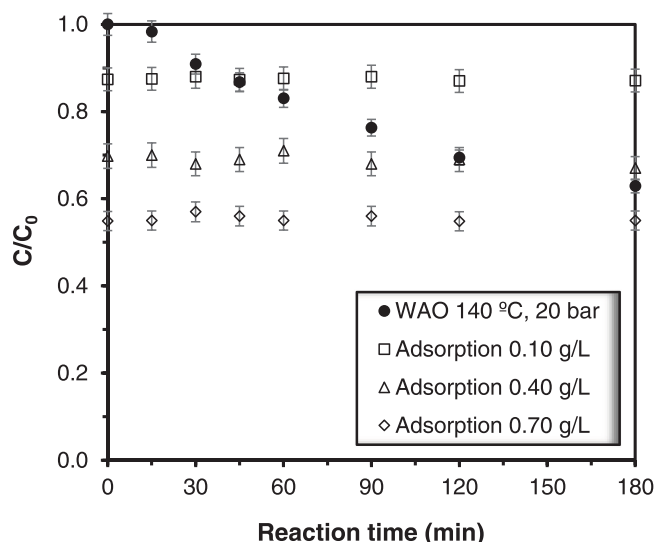


Fig. 3. WAO process and adsorption blanks for different FeSAC catalyst doses at 140 °C and 20 bar (under inert atmosphere).

also to evaluate the degradation reaction without the use of the catalyst and using air as the oxidizing atmosphere. For this purpose, a non-catalytic WAO test was carried out at 140 °C and 20 bar, as shown in Fig. 3. The results revealed considerably slow reaction kinetics, requiring a reaction time of around 1 h to remove less than 17 % of the initial concentration of ciprofloxacin.

During the first 15 min, an initial induction period in which hardly any contaminant degradation occurs can be observed. This pattern has been previously reported in the literature for non-catalytic wet air oxidation reactions, where the generation of a minimum concentration of hydroxyl radicals is necessary for the reaction to occur [40–43]. In addition, as will be mentioned hereafter, the use of catalyst in the reaction eliminates this induction period.

3.3.2. Influence of temperature on the catalytic activity

Temperature is one of the operating variables with the most significant effect on the CWAO processes [44]. The analysis of this parameter was carried out by varying the temperature from 120 to 180 °C, and maintaining the rest of the operating conditions constant, i.e. total pressure (20 bar) and catalyst dose (0.7 g/L). In addition, the TOC degradation efficiency was analyzed to evaluate the mineralization of ciprofloxacin. The TOC degradation efficiency was slower than that of

ciprofloxacin, suggesting a prolonged time to achieve a complete mineralization [45]. Selectivity towards non-organic compounds was also evaluated, being defined as $(X_{\text{TOC}}/X_{\text{Ciprofloxacin}})$. The evolution of the normalized ciprofloxacin concentration, as well as the TOC removal and selectivity to CO_2 at 180 min can be seen in Fig. 4b.

The CWAO reactions exhibited some removal of ciprofloxacin at zero time reaction, which might be due to the contribution between thermal degradation and adsorption effects of the pharmaceutical during the time the reactor reached the operating temperature. According to the blank tests conducted at 140 °C and 20 bar (Fig. 3), the WAO reaction showed a ciprofloxacin removal below 1 % at zero time reaction, thus non-catalytic thermal degradation appears to be negligible. The liquid sample at zero time from CWAO reaction was also analysed by LC-MS to identify thermal degradation compounds in the catalytic process (Fig. S4). In this regard, no other compounds were detected that were not already in the 50 mg/L initial ciprofloxacin solution (Fig. S5), so the removal at this time in the catalytic process can only be attributed to the adsorption contribution. In addition, it should be noted that the use of the catalyst eliminates the induction period observed in the WAO tests, minimizing the time required to start degrading the pollutant.

The experimental results revealed that the degradation of ciprofloxacin is notably temperature-dependent. This is consistent with the results found in the literature, since the production of free radicals, which initiate the oxidation reaction, is enhanced as the temperature increases [44]. In this regard, the antibiotic concentration reached values around 20 % of its initial value at 15, 30 and 60 min, for temperatures of 160, 140 and 120 °C, respectively. This difference was particularly pronounced at high ciprofloxacin conversions when operating at 120 °C, reaching a removal around 95 % at 3 h, while the other temperatures (140 °C and 160 °C) reached yields above 99 % between 1 and 2 h earlier.

However, although an increase in temperature favors ciprofloxacin degradation, this trend seems to be the opposite for TOC removal. Consequently, since the concentration of ciprofloxacin at 180 min is very similar at the three temperatures, an increase in the final TOC concentration would lead to a lower selectivity to CO_2 , i.e. a lower drug mineralization. This might be due to a modification of the reaction pathway or to an enhancement of the production rate of some intermediate which is highly recalcitrant to oxidation [45].

The variation in the removal rate of ciprofloxacin as the operating temperature changes could be due to the contribution of two factors, the influence on the kinetic constant and the solubility of oxygen in the aqueous medium, i.e. the concentration of one of the reagents. According to the literature, the solubility of oxygen in water above 100 °C and at high pressure exhibits an increasing trend when the temperature

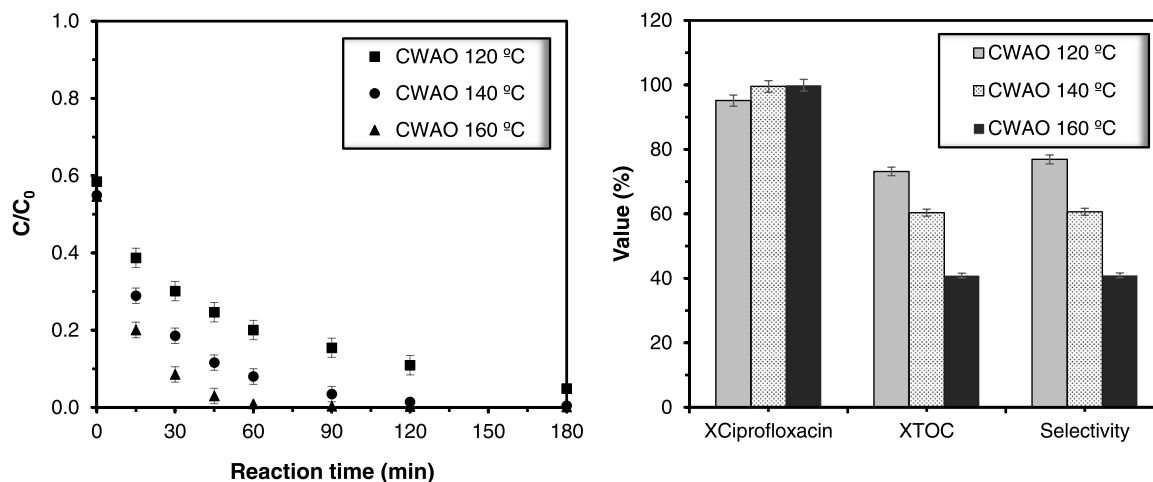


Fig. 4. Temperature effect on ciprofloxacin removal versus time (a); and ciprofloxacin conversion, TOC conversion and selectivity to CO_2 at 180 min (b). Experiments performed at $P = 20$ bar, $C_{\text{Ciprofloxacin},0} = 50$ mg/L and $C_{\text{Catalyst}} = 0.7$ g/L.

rises. This behavior is increasingly noticeable at higher pressures. However, oxygen solubility at a total air pressure around 20 bar shows a slight increase between 120 °C (54.7 mg O₂/L) and 160 °C (67.4 mg O₂/L) [46]. Therefore, it seems that the effect of temperature has a greater contribution on the kinetic constant than on the concentration of the oxidizing agent.

The initial reaction rate was determined by numerical derivation from the concentration profile of ciprofloxacin versus reaction time. As shown in Table 2, the initial reaction rate rises as the temperature increases, keeping constant all the other variables. As previously mentioned, this fact could be due to the temperature effect on the kinetic constant. In addition, after 180 min the catalyst showed negligible iron leaching, less than 24 ppb in all reactions, and the final pH remained constant in the range 3.9–4.2. Considering the aspects mentioned above, a temperature of 140 °C has been established as the optimum for this study.

3.3.3. Influence of total pressure on the catalytic activity

The hydroxyl radicals generation in CWAO processes depends on the amount of dissolved oxygen, i.e., on the concentration of the oxidizing agent in the reaction medium [44,47]. As previously mentioned, the gas-liquid equilibrium depends, besides the temperature, on the pressure value. Therefore, the ciprofloxacin removal could be affected by this variable. In this study, the total pressure has been evaluated from 10 to 30 bar.

As shown in Fig. 5a, ciprofloxacin degradation appears to be slightly improved with increasing the total pressure, but this variation might be considered negligible for the pressure range evaluated. According to the literature, the oxygen solubility in water ranges from 29.8 to 89.4 mg O₂/L for a total pressure of 10 and 30 bar at 140 °C, respectively [46]. Therefore, the ciprofloxacin conversion did not seem to depend on the dissolved oxygen concentration (Fig. 5b). Furthermore, these results are consistent with what was mentioned in the analysis of the temperature influence. In this regard, the variation of oxygen solubility between 120 and 160 °C at 20 bar is within the values obtained between 10 and 30 bar at 140 °C, confirming the previously discussed idea that the increase in the ciprofloxacin removal rate with rising temperature is mainly due to the kinetic constant, and not to the concentration of the dissolved oxidizing agent. As observed with ciprofloxacin conversion values, the pressure seems to have a negligible effect on TOC conversion and selectivity.

As has been reported in Table 3, the initial reaction rate of ciprofloxacin, calculated by numerical differentiation, could be considered constant for the pressure range analyzed. This is consistent with the overlap of the concentration profiles versus time shown in Fig. 5a. In addition, the catalyst showed a very low concentration of leached active phase and a roughly constant pH at 180 min. For the results mentioned above, the optimum pressure was set at 20 bar, since an increase of this parameter did not substantially improve the ciprofloxacin degradation.

3.3.4. Influence of catalyst dose on the catalytic activity

The catalyst dose was studied in the range of 0.1–0.7 g/L, and all other parameters, i.e., temperature and total pressure, being maintained constant. As illustrated in Fig. 6a, the catalyst dose has a significant impact on the removal of ciprofloxacin, even at relatively low values. In this regard, a higher catalyst dosage in the reaction medium resulted in a

Table 2

Temperature influence on initial reaction rate, iron leached and pH of the reaction medium after 180 min. Experiments performed at P = 20 bar, C_{Ciprofloxacin,0} = 50 mg/L and C_{Catalyst} = 0.7 g/L.

	CWAO 120 °C	CWAO 140 °C	CWAO 160 °C
r _{Ciprofloxacin,0} (mg/g _{Catalyst} ·min)	951	1259	1590
Fe _{Leached} (mg/L)	< 0.024	< 0.024	< 0.024
pH	3.9	4.1	4.2

greater degradation of the antibiotic. Moreover, this variation seems to be more noticeable for a catalyst dose under 0.40 g/L. After 1 h of reaction, normalized concentrations around 65 %, 27 % and 8 % were reached using catalyst doses of 0.1, 0.3 and 0.7 g/L, respectively. According to this trend, increasing the dose above 0.7 g/L may not compensate for the slight enhancement in the ciprofloxacin removal.

As expected, increasing the catalyst dose not only reduces the final concentration of ciprofloxacin in the reaction medium, but also results in a lower TOC content. This fact indicates a higher antibiotic mineralization when operating at a catalyst concentration of 0.7 g/L.

Regarding the initial reaction rates, given in Table 4, a drop in these values was observed with increasing catalyst loading. This behavior could be explained due to the decrease of ciprofloxacin concentration in the bulk fluid at zero reaction time as a result of the higher adsorption contribution. That is, a concentration drop of the reagent would lead to a decline in the initial reaction rate. In the literature, it has been reported that the oxidation processes occur by a radical pathway, generating hydroxyl radicals on the catalyst surface. However, if the reaction occurred only on the catalyst surface, the reaction rate per unit mass of catalyst would be independent of the dosage. As will be determined in Section 3.3.5, the reaction rate depends on the catalyst concentration according to an order smaller than unity. Thus, this behavior would imply that a combination of homogeneous and heterogeneous free radical mechanism is involved in the reaction [48–51].

Finally, as previously observed for temperature and pressure, the leached iron concentration, and the pH of the reaction medium at 180 min remained practically constant for the catalyst dosage range evaluated.

3.3.5. Kinetic modelling for ciprofloxacin degradation

The reaction rate for heterogeneous catalytic systems, such as the CWAO process in this study, is usually expressed in terms of the amount of catalyst, and therefore the material balance in the batch reactor would be as follows:

$$(-r_{\text{Ciprofloxacin}}) = \frac{1}{W_{\text{Catalyst}}} \left(-\frac{dn_{\text{Ciprofloxacin}}}{dt} \right) = \frac{1}{C_{\text{Catalyst}}} \left(-\frac{dC_{\text{Ciprofloxacin}}}{dt} \right) \quad (1)$$

where $r_{\text{Ciprofloxacin}}$ is the removal rate of ciprofloxacin (mg_{Ciprofloxacin}/g_{Catalyst}·min), W_{Catalyst} is the mass of catalyst (g_{Catalyst}), C_{Catalyst} is the concentration of catalyst in the reaction medium (g_{Catalyst}/L), $n_{\text{Ciprofloxacin}}$ is the mass of ciprofloxacin (mg_{Ciprofloxacin}), $C_{\text{Ciprofloxacin}}$ is the concentration of ciprofloxacin (mg_{Ciprofloxacin}/L), and t is the reaction time (min).

On the other hand, potential kinetic models have been widely proposed in the literature for CWAO processes. Considering the influence of variables such as temperature, pressure and catalyst dosage, the following conversion rate equation has been proposed:

$$(-r_{\text{Ciprofloxacin}}) = k \cdot C_{\text{Ciprofloxacin}}^n \cdot P_{\text{Total}}^m \cdot C_{\text{Catalyst}}^z \quad (2)$$

where, k is the kinetic constant (mg_{Ciprofloxacin}⁽¹⁻ⁿ⁾·L^(n+z)·bar^(-m)·g_{Catalyst}^(-z-1)·min⁽⁻¹⁾), P_{Total} is the total pressure (bar), and the parameters n , m and z represent the reaction orders.

Combining Eqs. (1) and (2), and replacing the kinetic constant as a function of temperature according to the Arrhenius equation results in the following expression:

$$\left(-\frac{dC_{\text{Ciprofloxacin}}}{dt} \right) = k_0 \cdot e^{\left(-\frac{E_a}{RT} \right)} \cdot C_{\text{Ciprofloxacin}}^n \cdot P_{\text{Total}}^m \cdot C_{\text{Catalyst}}^{z+1} \quad (3)$$

where, k_0 is the pre-exponential factor (mg_{Ciprofloxacin}⁽¹⁻ⁿ⁾·L^(n+z)·bar^(-m)·g_{Catalyst}^(-z-1)·min⁽⁻¹⁾), E_a is the activation energy (kJ/mol), R is the gas constant (8.314·10⁻³ kJ/mol·K), and T is the reaction temperature (K).

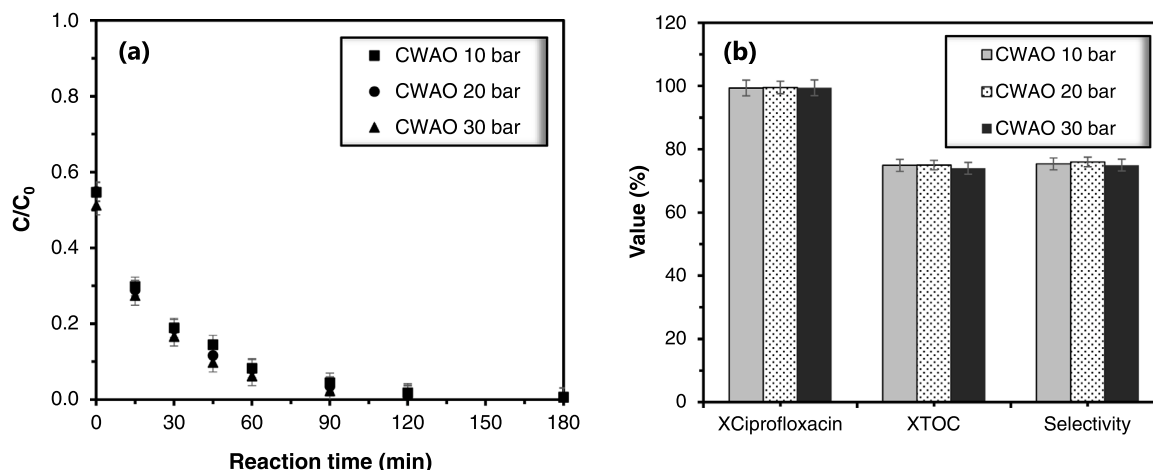


Fig. 5. Pressure effect on ciprofloxacin removal versus time (a); and ciprofloxacin conversion, TOC conversion and selectivity to CO_2 at 180 min (b). Experiments performed at $T = 140\text{ }^\circ\text{C}$, $C_{\text{Ciprofloxacin},0} = 50\text{ mg/L}$ and $C_{\text{Catalyst}} = 0.7\text{ g/L}$.

Table 3

Pressure influence on initial reaction rate, iron leached and pH of the reaction medium after 180 min. Experiments performed at $T = 140\text{ }^\circ\text{C}$, $C_{\text{Ciprofloxacin},0} = 50\text{ mg/L}$ and $C_{\text{Catalyst}} = 0.7\text{ g/L}$.

	CWAO 10 bar	CWAO 20 bar	CWAO 30 bar
$r_{\text{Ciprofloxacin},0}$ (mg/g _{catalyst} ·min)	1193	1259	1146
$\text{Fe}_{\text{Leached}}$ (mg/L)	< 0.024	< 0.024	< 0.024
pH	3.9	4.1	3.9

Furthermore, a parameter named as *effective initial concentration* ($C_{0,\text{eff}}$) has been defined to consider the decrease of ciprofloxacin concentration at zero reaction time due to the pollutant adsorption until the operating conditions are reached. Thus, ($C_{0,\text{eff}}$) is the concentration of ciprofloxacin in the bulk fluid at zero reaction time. As observed in Figs. 4–6, the pharmaceutical concentration at zero reaction time seems to depend predominantly on the catalyst dosage, with negligible influence of temperature and total pressure. Therefore, the initial condition for Eq. (3) could be expressed as indicated in Eq. (4):

$$C_{0,\text{eff}} = C_{\text{Ciprofloxacin}}|_{t=0} = C_{0,\text{real}} - a \cdot C_{\text{catalyst}} \quad (4)$$

where, a is a model parameter (mg_{Ciprofloxacin}/g_{catalyst}), $C_{0,\text{eff}}$ is the effective initial concentration (mg_{Ciprofloxacin}/L), and $C_{0,\text{real}}$ is the initial ciprofloxacin concentration (mg_{Ciprofloxacin}/L), i.e. 50 mg/L.

The parameters of the mathematical model consisting of Eqs. (3) and (4) were determined using a mathematical subroutine with Matlab for the nonlinear multiparameter estimation and the integration of the differential equations. To minimize the error between the experimental data ($C_{\text{Ciprofloxacin},\text{exp}}$) and the model outputs ($C_{\text{Ciprofloxacin},\text{model}}$), the residual sum of squares indicated in Eq. (5) was applied. This objective function is a statistical technique in regression analysis that allows to determine the function that best fits a set of experimental data. In this regard, the function indicates the level of variance in the residuals of a regression model, so the lower the value, the better the model will fit the experimental data. The above mentioned justifies the selection of the residual sum of squares as the optimality criterion.

Table 4

Catalyst dose influence on initial reaction rate, iron leached and pH of the reaction medium after 180 min. Experiments performed at $T = 140\text{ }^\circ\text{C}$, $P = 20\text{ bar}$ and $C_{\text{Ciprofloxacin},0} = 50\text{ mg/L}$.

	CWAO 0.1 g/L	CWAO 0.4 g/L	CWAO 0.7 g/L
$r_{\text{Ciprofloxacin},0}$ (mg/g _{catalyst} ·min)	3578	1806	1259
$\text{Fe}_{\text{Leached}}$ (mg/L)	< 0.024	< 0.024	< 0.024
pH	5.3	5.3	4.1

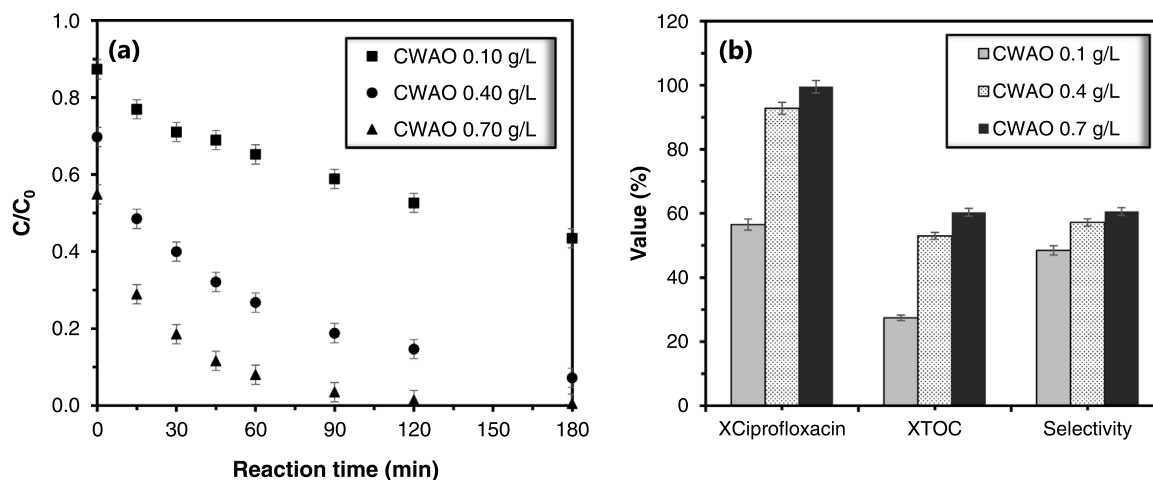


Fig. 6. Catalyst dose effect on ciprofloxacin removal versus time (a); and ciprofloxacin conversion, TOC conversion and selectivity to CO_2 at 180 min (b). Experiments performed at $T = 140\text{ }^\circ\text{C}$, $P = 20\text{ bar}$ and $C_{\text{Ciprofloxacin},0} = 50\text{ mg/L}$.

$$f_{obj} = \sum (C_{Ciprofloxacin, exp} - C_{Ciprofloxacin, model})^2 \quad (5)$$

The calculated parameters of the proposed conversion rate equation are summarized in Table 5. The small influence of the total pressure on the kinetics of the ciprofloxacin degradation process, as shown in Fig. 5, results in an order with respect to pressure close to zero ($m = 0.13$). The order of catalyst dose obtained ($z = 0.2$) was less than unity, being within the values found in the literature for similar CWAO processes and taking into account both heterogeneous and homogeneous contributions to the pollutant removal rate [12,49–51].

On the other hand, the activation energy of the catalytic process considered in this study (53.8 kJ/mol) is relatively close to that found by other authors using catalysts with more expensive metals as active phase. Specifically, Serra-Perez et al. (2020) studied the degradation of ciprofloxacin using ruthenium and platinum catalysts supported on carbon nanospheres, whose activation energy was around 40 kJ/mol [12]. Besides requiring more costly and toxic metals than the one proposed in this study, i.e. iron, the ruthenium catalysts exhibited a higher metal leaching in the reaction medium. Therefore, the approach suggested in this study not only allows the valorization of a biomass waste such as sewage sludge, but also seems to present a catalytic activity and a loss of the active phase that is comparable to that obtained for catalysts based on more expensive and toxic metals than iron. Finally, it is worth to highlight that the use of the iron sludge-based catalyst employed in this study allowed to decrease the activation energy of the ciprofloxacin degradation process compared to the non-catalytic WAO process of this pollutant, whose value reported in the literature was around of 70 kJ/mol [12].

The parity plot of the experimental ciprofloxacin concentration values versus those obtained with the conversion rate equation (Table 5) is shown in Fig. 7. As can be seen, the experimental data exhibited small, random and non-systematic deviations from the model prediction. Moreover, the high R^2 value obtained indicated a good fit of the experimental data. In general, it could be concluded that the proposed conversion rate equation described the entire measured data set under the tested operating conditions.

3.3.6. Possible degradation pathway of ciprofloxacin removal by CWAO

The identification of reaction intermediates and by-products was accomplished after a reaction time of 180 min by LC-MS analysis. The molecular ion peak of ciprofloxacin ($m/z = 332$) showed a retention time of 9.4 min. In addition, two reaction intermediates, intermediate 1 and intermediate 2, with m/z values of 319 and 263, respectively, were detected. The degradation compounds identified in the analyzed sample are summarized in Table 6. LC-MS chromatogram and mass spectra of ciprofloxacin solution after 180 min of reaction time and at t_R 9.4, 0.9 and 10.5 min are shown in Figs. S6, S7, S8 and S9 (Supplementary Material).

In the first degradation pathway proposed, m/z 319 can be formed by

Table 5

Conversion rate equation and calculated parameters for ciprofloxacin removal by CWAO using the iron sludge-based catalyst.

Conversion rate equation	
$\left(-\frac{dC_{Ciprofloxacin}}{dt}\right) = k_0 \cdot e^{\left(-\frac{E_a}{R \cdot T}\right)} \cdot C_{Ciprofloxacin}^n \cdot P_{Total}^m \cdot C_{Catalyst}^{z+1}$	
$C_{0, eff} = C_{Ciprofloxacin} _{t=0} = C_{0, real} - \alpha \cdot C_{Catalyst}$	
$k_0 \left(\frac{L^{n+z}}{mg_{Ciprofloxacin}^n \cdot bar^m \cdot g_{Catalyst}^{z+1} \cdot min}\right)$	$7.8 \cdot 10^4$
E_a (kJ/mol)	53.8
n	1.40
m	0.13
z	0.20
α ($mg_{Ciprofloxacin}/g_{catalyst}$)	33.2
R^2	0.990

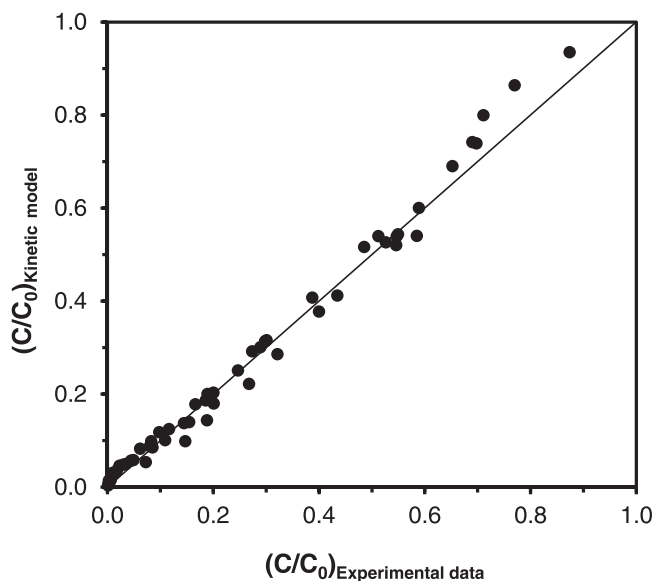


Fig. 7. Parity plot for the tests using the proposed conversion rate equation.

the decarboxylation and hydroxylation of the ciprofloxacin molecule in other pathway. The oxidation process can lead to nitrates, and then continue until mineralization into CO_2 and H_2O [52]. Similar results have been reported by Serra-Perez et al. for the catalytic degradation of ciprofloxacin [12]. On the other hand, the cleavage of the piperazine ring caused by the attack of $\bullet OH$ groups on the carbons between the 1' and 4' position producing stepwise oxidative degradation. This is consistent with the order of oxidability of the functional groups (piperazine ring > benzo ring > pyridine ring). After this, the compound with m/z 263, could be formed after the loss of both formaldehydes and loss of the secondary nitrogen, as well as the subsequent oxidation and loss of formaldehyde from amine side chain from ciprofloxacin [12,53]. A defluorination process could be produced in m/z 263, and further oxidation would lead to low molecular weight carboxylic acids (LMWC), i.e., oxalic, formic and acetic acid. Fig. 8 illustrates, for the first time, the proposed reaction pathway of ciprofloxacin degradation by CWAO process using the synthesized sewage sludge-based catalyst.

It should be noted that, from the molecular point of view, several studies based on Density Functional Theory (DFT) have been carried out with various functional groups. In the case of experimental studies, DFT investigations accurately predicted chemical bonding, band structures, surface character, and the effect of doping, among others.

The calculations showed, both in the reactants and the intermediates, a planar structure from which the substituents at positions 1 and 7 protrude. This plane generates a symmetry that gives rise to some conformations with equivalent energy minima. The different conformations optimized for these substituents have very similar energies, with differences of the order about 0.2 kcal/mol, practically negligible (Fig. 9a).

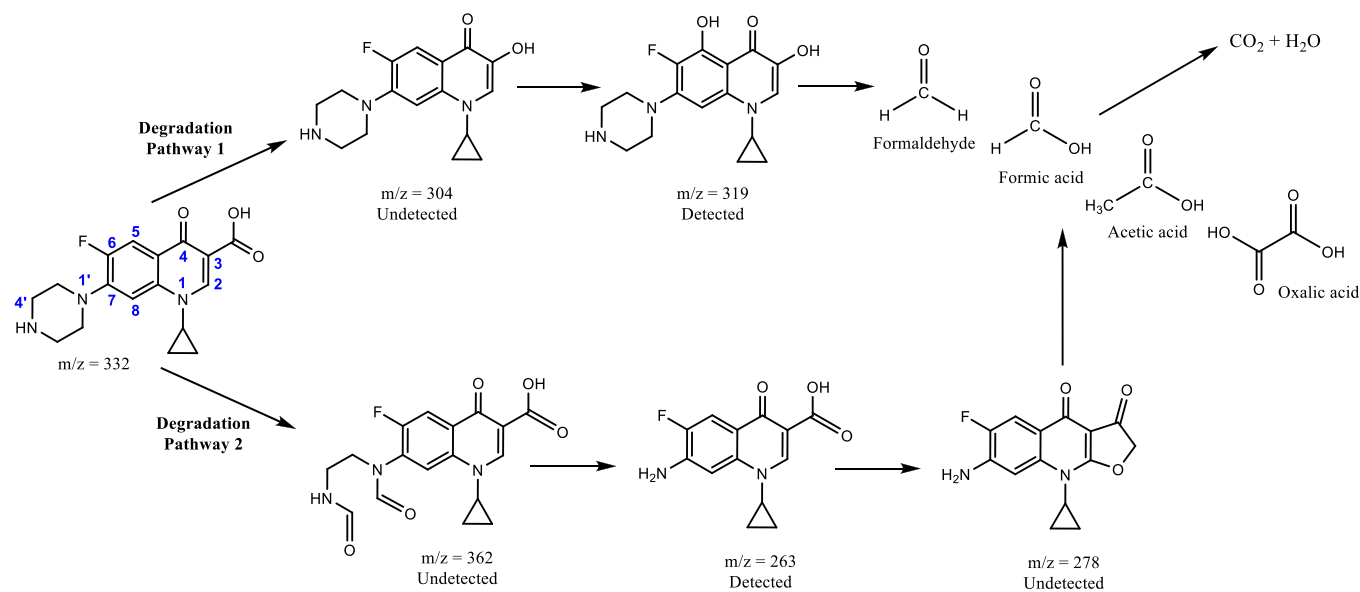
Considering the carboxylic group, calculations have shown that the most favorable conformations are those in which the OH group is directed towards the oxygen at C4 to interact through hydrogen bridging, being favored by about 8–9 kcal/mol over those that do not contemplate that possibility. This fact is supported by NBO (Natural Bond Orbitals) analysis, which shows stabilizing interactions between the orbitals of the oxygen lone pairs and the anti-bonding orbital of the O-H bond. In addition, electrostatic repulsions between oxygen atoms are reduced in this way. The most representative optimized structures can be seen in Fig. 9b, and their coordinates are collected in Tables S2, S3 and S4 (Supplementary material).

The E_{HOMO} values of the electronic energies corresponding to ciprofloxacin and the reaction intermediates, as well as the HOMO orbital

Table 6

Properties of some identified intermediate compounds during the ciprofloxacin degradation by LC-MS.

Compound	t_R (min)	$[M+H]^+$ (m/z)	Molecular Formula	Name	Structure
1	9.4	332	$C_{17}H_{18}FN_3O_3$	Ciprofloxacin	
Intermediate 1	0.9	319	$C_{16}H_{18}FN_3O_3$	1-cyclopropyl-6-fluoro-3,5-dihydroxy-7-(piperazin-1-yl)quinolin-4(1H)-one	
Intermediate 2	10.5	263	$C_{13}H_{11}FN_2O_3$	7-amino-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylic acid	

**Fig. 8.** Proposed reaction pathway of ciprofloxacin degradation by CWAQ process.

energies (Table 7) and the optimized geometrical configuration of the organic intermediates calculated using the DFT method are shown in Fig. S8. For comparison purposes, caffeine was used, since it is a typical emerging organic contaminant that has been studied by many researchers in catalytic oxidation [54,55]. Therefore, caffeine was also evaluated using the DFT method for comparison with ciprofloxacin intermediates. Further details are collected in Table S5 (Supplementary material).

From the diagram of E_{HOMO} values, the acidic compounds, i.e., formaldehyde, formic, acetic, and oxalic acids have the lowest E_{HOMO} values among all the organic compounds, with values as low as -10.0 eV. This fact demonstrates the difficulty of oxidizing this type of low molecular weight compounds (that are refractory to oxidation), due to their characteristics, rather than to the oxidation conditions [56]. The organic intermediate 2 showed a lower E_{HOMO} value (-7.56 eV) than intermediate 1 (-6.88 eV). This suggests that intermediate 1 would be easier to degrade, which would be consistent with the mass spectrum data where, being intermediate 1 the major compound after 0.9 min (Fig. S9), it has completely disappeared at 10.5 min, remaining intermediate 2 (Fig. S10). Assuming a faster disappearance of intermediate 1,

the fact that at 0.9 min it is the major compound suggests that the reaction would proceed mainly (although not exclusively) by pathway 1.

3.3.7. Proof of concept and catalyst stability

In the literature, CWAQ processes of aqueous solutions prepared in ultrapure water have been widely reported. Effectively, this should be the initial study to evaluate the kinetics of the process. However, it is essential to assess the effect that an environmentally-relevant matrix may have on the oxidation reaction [12,57], verifying the feasibility of this technology with the synthesized iron sludge-based catalyst. In this regard, a real surface water matrix fortified with ciprofloxacin ($C_0 = 50$ mg/L) has been tested. Thus, the evolution of ciprofloxacin concentration for ultrapure water and surface water at 20 bar, 140 °C and a catalyst dosage of 0.70 g/L can be seen in Fig. 10a.

The surface water matrix does not seem to have a significant influence on the degradation of ciprofloxacin. As expected, the conversion of the antibiotic is slightly lower with the surface water matrix compared to ultrapure water, possibly due to the presence of other organic contaminants that compete with ciprofloxacin during the CWAQ process. That is, the hydroxyl radicals generated are involved in the oxidation of

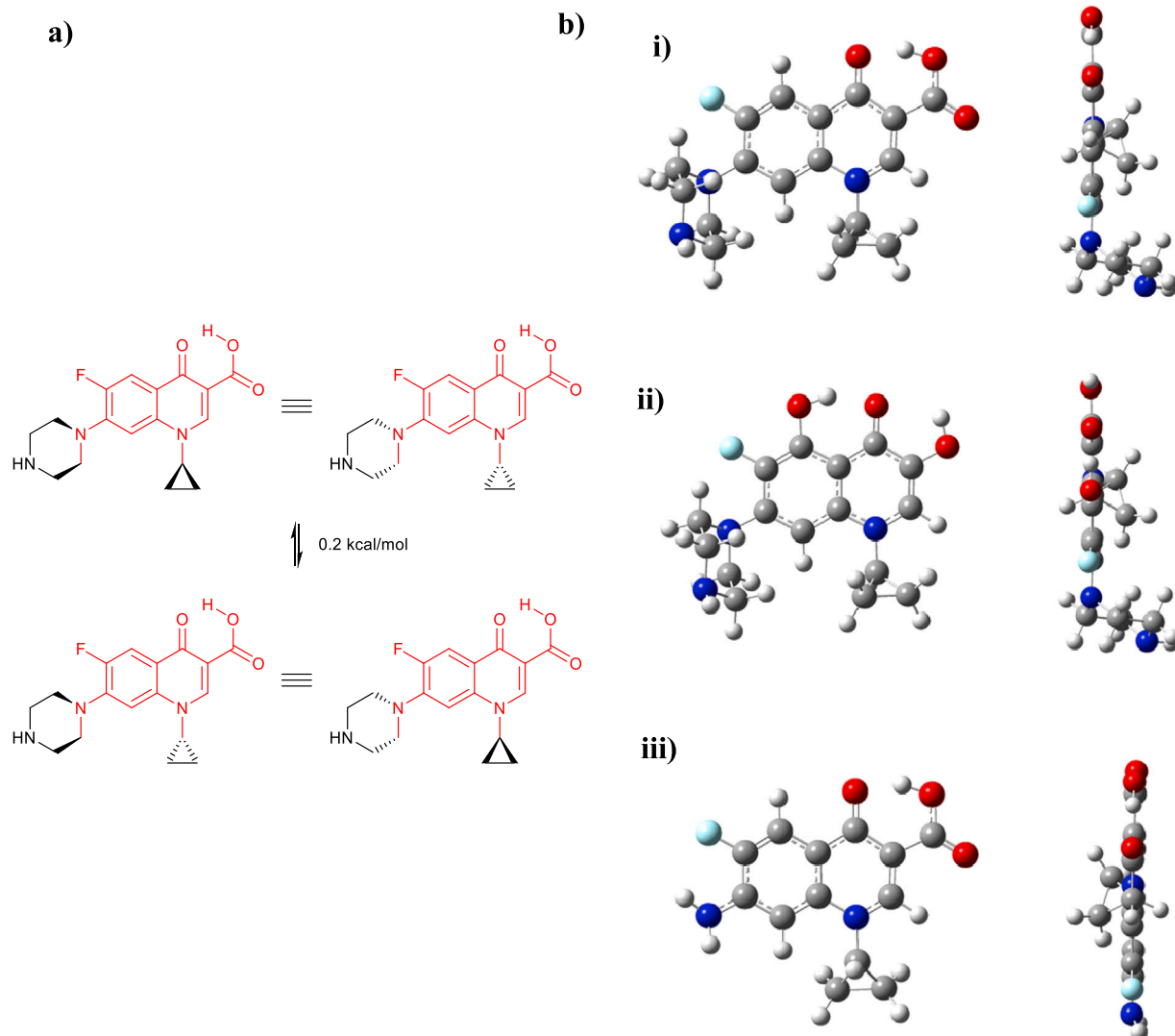


Fig. 9. Most stable conformations of ciprofloxacin (a) and most stable conformations of ciprofloxacin (i); intermediate 1 (ii); and intermediate 2 (iii) (b).

Table 7
Electronic energies and E_{HOMO} values of ciprofloxacin and intermediates.

Compound	Electronic energies (kcal/mol)	E_{HOMO} (eV)
Ciprofloxacin	-720626.16	-7.22
Intermediate 1	-696697.04	-6.88
Intermediate 2	-587998.39	-7.56

other compounds existing in the surface water matrix. It should also be highlighted that the matrix has a small influence on pollutant adsorption, showing a small increase of ciprofloxacin concentration in the bulk fluid at zero reaction time.

On the other hand, the leaching of the active phase in the reaction medium was the same regardless of the matrix, i.e., leached iron concentrations lower than 0.024 mg/L were measured. This iron concentration is significantly lower than the limit value set by the European Directive 2020/2184 for water intended for human consumption, which is 0.2 mg/L [58]. Supported iron catalysts generally exhibit a high metal leaching, so there is a large background in the literature related to the use of noble metal-based catalysts, which are more costly and toxic but present lower losses of active phase [59–63]. Therefore, it seems that the synthesis procedure of the catalyst proposed in this study enables the correct attachment of the active phase to the carbonaceous matrix,

ensuring a concentration of leached iron in the aqueous phase that does not pose an environmental risk.

Catalyst deactivation is considered one of the most critical issues in heterogeneous catalytic processes, determining in most cases the technical and economical feasibility. In this research, the stability of the catalyst was assessed by three consecutive reuse cycles for the removal of ciprofloxacin in surface water matrices, as shown in Fig. 10b. As can be seen, the synthesized catalyst exhibited high stability, appreciating a slight decrease in ciprofloxacin conversion over the three cycles. During the first reuse, a removal value close to 94 % was achieved, i.e. 2 % less than the one obtained with the fresh catalyst. Then, for the second and third reuse cycles, the conversions obtained after a reaction time of 120 min were 90 % and 87 %, respectively.

All the aforementioned evidences the potential of the catalyst proposed in this study to be applied in CWAO processes for the removal of several emerging contaminants, such as ciprofloxacin, from aqueous medium.

4. Conclusions

The research described in this work proposes a feasible technique for the valorization of a solid waste, i.e., sewage sludge, contributing to the circular economy in wastewater treatment plants and to the removal of emerging pollutants, such as ciprofloxacin. In this regard, the catalyst

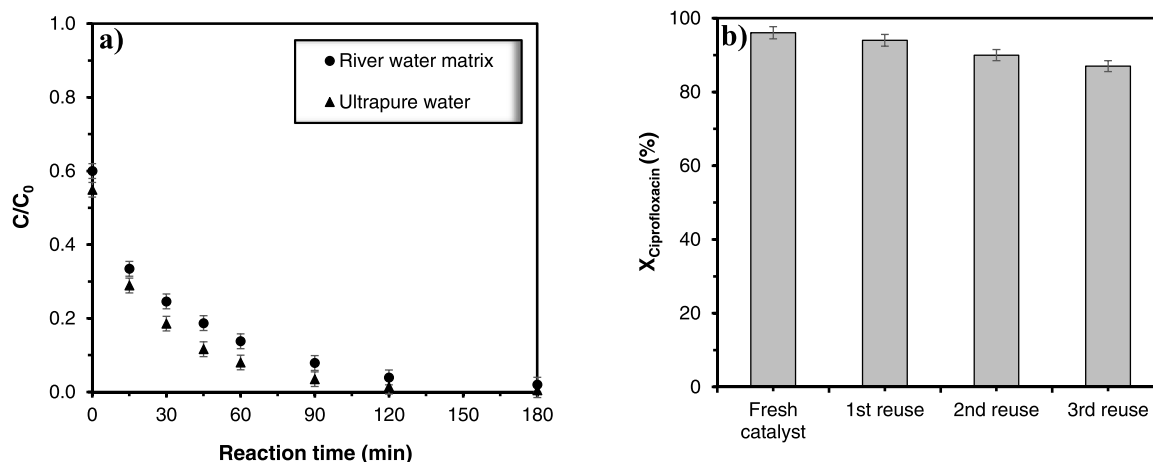


Fig. 10. Matrix effect on ciprofloxacin removal by CWAO experiments at $T = 140\text{ }^{\circ}\text{C}$, $P = 20\text{ bar}$ and $C_{\text{Ciprofloxacin},0} = 50\text{ mg/L}$ (a) and Influence of catalyst reuse on ciprofloxacin conversion for CWAO experiments at $T = 140\text{ }^{\circ}\text{C}$, $P = 20\text{ bar}$, $C_{\text{Ciprofloxacin},0} = 50\text{ mg/L}$, reaction times of 120 min, and using a surface water as aqueous matrix (b).

synthesized from sewage sludge exhibited an iron content and textural and morphological properties suitable for its application in CWAO processes. The iron-based catalyst showed high catalytic activity, oxidizing the emerging pollutant almost completely within 2 h at the following operating conditions: $140\text{ }^{\circ}\text{C}$, 20 bar and $0.7\text{ g}_{\text{Catalyst}}/\text{L}$. The reaction temperature and catalyst dose showed a significant influence on the ciprofloxacin removal from aqueous solution, while total pressure did not play such an important role. In addition, the TOC degradation did not always show the same trend as the ciprofloxacin removal, which may be due to a modification of the reaction pathway. The measurement of leached iron in the reaction medium revealed a low loss of the active phase which does not pose an environmental risk, reaching values of less than 0.024 mg/L . In this way, a longer catalyst lifetime is ensured by increasing the deactivation time. The oxidation state of surface iron on the catalyst, determined by XPS analysis confirmed the presence of Fe^{3+} species on the surface of the fresh and reused catalyst. Regarding the conversion rate equation, a potential model was used to describe the experimental results accurately, with a coefficient of determination (R^2) of 0.990. A Density Functional Theory (DFT) method-based study has been accomplished in order to estimate the stability of the originated intermediates and to elucidate the degree of oxidation by the CWAO process. Furthermore, the synthesized FeSAC catalyst presented a catalytic activity comparable to that reported in the literature for noble metal-based catalysts. Finally, the technical feasibility of the process in environmentally-relevant matrices, such as surface water, was verified, obtaining an almost negligible decreasing in the catalytic activity after three consecutive reaction cycles.

CRediT authorship contribution statement

Pablo Gutiérrez-Sánchez: Conceptualization, Investigation, Formal Analysis, Software, Methodology, Writing - original draft, Writing - review & editing. **Silvia Álvarez-Torrellas:** Writing - review & editing. **Marcos Larriba:** Writing - review & editing. **M. Victoria Gil:** Software, Writing - review & editing. **Juan M. Garrido-Zoido:** Software, Writing - review & editing. **Juan Garcia:** Conceptualization, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2023.109344](https://doi.org/10.1016/j.jece.2023.109344).

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