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A comparative study among Catalytic Wet Air Oxidation, Fenton, and Photo-Fenton technologies for the on-site treatment of hospital wastewater

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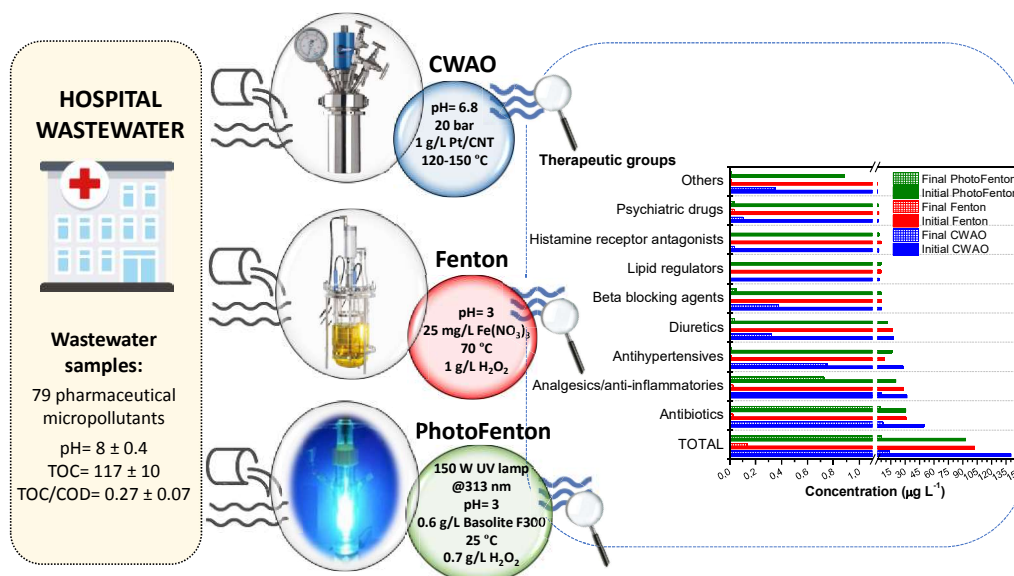
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Graphical Abstract



ABSTRACT

The feasibility of catalytic wet air oxidation, intensified homogeneous Fenton and heterogeneous Photo-Fenton systems for the treatment of real hospital wastewater has been investigated. Wastewater samples were collected from a hospital sewer, during a weekly monitoring program, and fully characterized. Up to seventy-nine pharmaceuticals, including mostly parent compounds and some of their transformation products, were analyzed. Catalytic wet air oxidation allowed the complete removal of several pharmaceutical groups, but it did not allow to eliminate analgesics/anti-inflammatories and antibiotics, whose average removal was around 85%. Intensified Fenton oxidation was the most efficient process for all the drugs removal with an almost complete reduction of the initial pharmaceutical load (99.8%). The heterogeneous Photo-Fenton system reached

a 94.5% reduction of the initial pharmaceutical load. The environmental risk of the treated samples by the hazard quotient (HQ) method was also evaluated. Fenton oxidation was the most effective system with a final \sum HQ of 5.4. Catalytic wet air oxidation and Photo-Fenton systems achieved total \sum HQ values of 895 and 88, respectively. This fact was related to the presence of refractory antibiotics in the treated catalytic wet air oxidation samples. On the opposite, the Photo-Fenton system provided the elimination of most pharmaceutical pollutants that pose a high environmental risk such as antibiotics. Simplified cost estimation was finally performed as a preliminary approach of the economy of the three oxidation processes for the hospital wastewater treatment.

Keywords: Catalytic wet air oxidation; Fenton; Photo-Fenton; Hospital wastewater; Pharmaceutical compounds.

1. Introduction

The research on the characterization, management, risk assessment, and treatment of hospital wastewaters has received increasing attention in the last decade (Verlicchi et al., 2018; Daouk et al., 2016; Ferrando-Climent et al., 2014; Verlicchi et al., 2013 b; Santos et al., 2013; Verlicchi et al., 2012a; Verlicchi et al., 2012b; Pauwels, 2006). These complex aqueous matrices are loaded with large amounts of biological and chemical agents. They contain, among other things, high concentrations of pharmaceutical compounds, up to 10 – 100 times higher than regular urban wastewater (Verlicchi et al., 2016). Nevertheless, due to the lack of regulation that establishes the specific management and treatment of these hazardous effluents, they are commonly discharged into municipal sewer systems (Boillot et al., 2008; Verlicchi et al., 2010). Analyses of the contribution of hospital wastewaters in the influents of wastewater treatment plants (WWTPs) have revealed that hospitals represent one of the primary sources of pharmaceuticals, particularly antibiotics, lipid regulators, and receptor antagonists (Verlicchi et al., 2012b). As these pollutants are relatively resistant to conventional treatments, they commonly appear in WWTP discharges, posing a significant threat to the aquatic environment. On the other hand, hospital wastewaters also represent an important source of pathogenic microorganisms, leading to the dissemination of multiple antibiotic resistance (Majumder et al., 2021; Beattie et al., 2020).

The hazardous nature of hospital wastewater, which is mainly related to its high pharmaceutical load but also the presence of pathogenic microorganisms, would require its specific management and treatment. On-site treatments to reduce the micropollutants load and to warrant the effluent disinfection is usually considered as the most promising approach, overall dealing with large hospitals. Applying a highly active technology at a small scale can be more cost-effective and environmentally friendly than a cheaper technology at a large scale with limited effects on the diluted hospital discharges (Pauwels, 2006). Accordingly, the development of cost-effective processes for hospital wastewater treatment represents an important field of research nowadays.

Advanced oxidation processes (AOPs) are regarded as promising alternatives for hospital wastewater treatment (Kanakaraju et al., 2018; Klavarioti et al., 2009). In particular, intensified Fenton oxidation at temperatures between 50 – 70 °C has proved to be highly effective in terms of mineralization, disinfection, and ecotoxicity abatement (Munoz et al., 2016). On the other hand, the application of UV light in the so-called Photo-Fenton process has allowed operating under milder conditions due to the faster Fe^{3+} reduction provoked by light irradiation (Mirzaei et al., 2017); which at the same time, would ensure the disinfection of the wastewater. The use of solid catalysts in Photo-Fenton processes avoids the continuous loss of catalyst and the generation of iron sludge after the treatment. In recent work, García-Muñoz et al. (2017) demonstrated the high efficiency of the heterogeneous Photo-Fenton process for hospital wastewater treatment using

ilmenite as a catalyst. On the other hand, novel iron-containing materials based on metallic organic frameworks such as Fe-BTC has recently shown a remarkable activity for the oxidation of methylene blue in Fenton systems using circumneutral pH conditions and low oxidant (H_2O_2) dosages (Martínez et al., 2017).

Although so far catalytic wet air oxidation (CWAO) has received comparatively less attention than AOPs for hospital wastewater treatment, its efficiency for the removal of a wide range of pharmaceutical compounds has been demonstrated in several works (Benitez et al., 2011; Zhan et al., 2013; Li et al., 2013; Serra-Pérez et al., 2019). CWAO is highly effective for the degradation of non-biodegradable and/or toxic organic pollutants at moderate temperature ($T = 140\text{-}200\text{ }^\circ\text{C}$) and partial oxygen pressure (1.5-10.5 bar), using air or oxygen as oxidant (Levec et al., 2007; Abid et al., 2016). In the last decades, several heterogeneous catalysts, including noble (Pd, Pt, Ru, Rh) and transition metals (Fe, Co, Ni, Cu) deposited on different supports (carbon materials, Al_2O_3 , ZrO_2 , TiO_2 , and CeO_2) have been successfully applied (Abid et al., 2014; Devard et al., 2019; Bensouilah et al., 2020). However, the catalytic activity of these materials has not been assessed for the treatment of real hospital wastewaters.

Although the most critical challenge in treating hospital wastewaters is the removal of pharmaceuticals, most of the works in the literature have been focused on the evolution of global pollution parameters *viz.* COD and/or TOC (Sun et al., 2011; Gadipelly et al., 2014). Some studies have also considered the ecotoxicity

abatement and/or the microbial load reduction (Munoz et al., 2016; Berto et al., 2009), but there is a lack of knowledge on the actual elimination of the real pharmaceuticals load, which is mainly due to the complex analytical equipment required for such goal. In this sense, most attempts have been focused on treating hospital wastewaters spiked with one or a few pharmaceuticals (Martins et al., 2009; Wilde et al., 2013; García-Muñoz, 2017; Della-Flora, 2020; Ahmadzadeh, 2018; Lima Perini, 2018; Dolatabadi et al., 2019; Sanabria et al., 2021). As it has been explained, catalytic wet air oxidation, intensified homogeneous Fenton and heterogeneous Photo-Fenton systems are promising technologies for the removal of pharmaceutical compounds. All of them can also ensure the disinfection of the wastewater but their ability to eliminate the actual load of pharmaceuticals for these complex matrices has not been previously demonstrated (Munoz et al., 2016; Khan et al., 2019; Sanabria et al., 2021). Thus, a comparative study among these systems would represent an important step forward in this field.

This work aimed to evaluate the feasibility of three types of oxidation water treatment technologies (CWAO, Intensified Fenton, and heterogeneous Photo-Fenton) for the on-site treatment of real hospital wastewater. Although the evolution of global pollution parameters (TOC and COD) was considered, the main attention was focused on the removal of the pharmaceutical compounds present in the real wastewater. Up to 79 pharmaceuticals were analyzed from different therapeutic families. Apart from analyzing the reduction of pharmaceuticals concentration, the environmental impact of the final effluents

via an environmental risk assessment was performed. This evaluation considered both the measured concentration and ecotoxicity of each pharmaceutical to estimate its potential effect on the environment (Carlsson et al., 2006; Lucas et al., 2016). Finally, a preliminary estimation of the main operating costs associated with each water treatment technology was also carried out.

2. Materials and methods

2.1. Hospital Wastewater

2.1.1. Sampling design

The samples were taken from a hospital sewer during a weekly monitoring program using a typical sampling protocol as described elsewhere (Cruz del Álamo et al., 2020). The hospital located in the south of Madrid (Spain) generates three effluents from different activity areas of the hospital which are discharged into the sanitary public network. One of them corresponds to primary care, X-ray and digestive areas. The other two are from laboratories and intensive care (ICU), anatomic, sterilization and pharmacology units. To collect representative samples of the hospital daily discharged, three automatic water sampler systems were used to take 330 mL (110 mL each) of wastewater every 10 min for 24 hours and mixed. All the samples were kept at 4 °C immediately after sampling. The procedure was repeated daily along three different days in April 2015 to obtain enough volume of hospital wastewater for each experimental treatment. The

wastewater collected each day was called HW-1 (20th of April 2015), HW-2 (22nd of April 2015) and HW-3 (21st of April 2015).

2.1.2. Physico-chemical characterization

Table 1 shows the physicochemical characterization of the three water samples collected in this work. Each sample was subjected to a different treatment: HW-1 to catalytic wet air oxidation; HW-2 to intensified homogeneous Fenton oxidation; and HW-3 to heterogeneous Photo-Fenton oxidation. All the samples were kept at 4 °C immediately after sampling. A detailed procedure of the used physicochemical characterization methods has been included in the Supplementary Material.

Table 1. Physico-chemical characterization of the hospital wastewater samples.

Parameter	HW-1	HW-2	HW-3
pH	6.8 ± 0.2	8.6 ± 0.2	8.7 ± 0.04
TOC (mg L ⁻¹)	111 ± 10	110 ± 12	130 ± 8
Total COD (mg L ⁻¹)	332 ± 25	365 ± 25	650 ± 88
TOC/COD Ratio	0.33	0.30	0.20
TSS (mg L ⁻¹)	126 ± 35	138 ± 30	733 ± 138
Conductivity (mS cm ⁻¹)	2.36 ± 0.01	1.18 ± 0.05	1.17 ± 0.01
Aromaticity (A _{UV_254})	0.53 ± 0.1	1.17 ± 0.1	*n.a.
PO ₄ ³⁻ (mg L ⁻¹)	*n.a.	20.6 ± 0.5	5.8 ± 0.3
Total-N (mg L ⁻¹)	90 ± 1	94 ± 5	79 ± 4
Toxicity (TU)	5.6 ± 0.5	4.8 ± 0.5	*n.a.

* n.a.= non-available

2.1.3. Pharmaceuticals Analysis

Seventy-nine pharmaceuticals, including mostly parent compounds and some of their known transformation products and human metabolites (see Table S1), were analyzed in the wastewater samples by triplicate. Hospital wastewater samples were kept at -20°C until analysis, which was performed within 1-2 weeks. On the day of analysis, they were defrosted at ambient temperature and then filtered using PVDF filters (0.45 µm, Millex-GV, Millipore). The analysis of pharmaceuticals was carried out using a method based on solid-phase extraction (SPE) followed by ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-ESI-MS/MS) (Gros et al. 2012). Details on the sample pre-treatment (SPE), chromatographic separation, and MS/MS detection, as well as the validation parameters, are given in the abovementioned article. Quantification was performed based on the standard internal approach by adding the corresponding deuterated compounds (the ones indicated in Table S1) to all the samples and aqueous standards for the calibration curve at a concentration of 0.01 ng L⁻¹ before analysis. For quality assurance, three replicates per sample were analyzed to determine the analytical variability, and both MeOH and chromatographic blanks were used. Despite limits of detection (LODs) and limits of quantification (LOQs) are detailed elsewhere (Gros et al. 2012), new values were estimated for the water samples analyzed in this study, as the minimum detectable amount of analyte with signal-to-noise ratios of 3 and 10, respectively. LODs ranged from 0.02 to 50 ng L⁻¹ (further details in Table S2). Likewise, the

accuracy of the method was also evaluated for this study and given as the recovery values (R%) obtained after spiking the different surface waters (n = 3) with a standard mixture at 50 ng L⁻¹. Recovery values ranged between 35 and 153%.

2.1.4. Environmental risk assessment

The environmental risk of the pharmaceutical compounds present in the raw and treated hospital wastewaters was studied using the hazard quotient (HQ) method. The HQs were calculated for each target compound according to European guidelines (Commission, 2003) as shown in equation 1 (Lucas et al., 2016):

$$HQ = \frac{MEC}{PNEC} \quad [1]$$

Where MEC is the measured environmental concentration, in this case, the measured pharmaceutical concentration of the hospital wastewater or treated wastewater (Table S3). It must be stressed that the individual concentration of some pharmaceutical compounds exceeded the maximum measured concentration of our analytical technique. In those cases, the maximum detected concentration was taken as MEC (Santos et al., 2013). On the other hand, if the quantified concentration was below the limit of detection (LOD) or the limit of quantification (LOQ) (Table S2), half of the LOQ was considered as the potential harmful concentration (Mendoza et al., 2015). PNEC is the predicted no-effect concentration. PNEC values derived from available aquatic toxicity data

(EC₅₀/LC₅₀) of three different species from distinct trophic levels (algae, crustaceans and fish), applying the pertinent Assessment Factors (AFs) according to European Commission Guidelines (Commission, 2003). In this work, PNEC values were taken from a previous study (Lucas et al., 2016). This study considers an AF of > 990 times lower than the toxicity concentration values found for the most sensitive microorganisms (*Fish, Daphnia, and Algae*) (Mendoza et al., 2015). At least one high toxicity datum is available for the three trophic levels. When data were not available, they were calculated using U.S. EPA Ecological Structure-Activity Relationships (ECOSAR) software (Sanderson et al., 2003). Values of PNEC for each pharmaceutical compound are shown in Table S4. The total HQs have been calculated taking into account the contribution of each pharmaceutical compound present in the initial hospital wastewater and the final effluents after each treatment, considering the sum of the initial and final values of the different studied therapeutic groups following the procedure used in the literature (Lucas et al., 2016).

2.2. Catalytic wet air oxidation and advanced oxidation Fenton-like treatments

Catalytic wet air oxidation (CWAO) experiments were carried out in a Hastelloy high-pressure micro-reactor (i.d. 50 mm, the volume of 100 mL). The reactor was equipped with an electrically heated jacket, a turbine agitator, and a variable speed magnetic drive. The temperature and the stirring speed were controlled by using a PID controller. The reactor was first loaded with 100 mL of wastewater,

and initially pressurized with nitrogen to ensure an inert atmosphere inside the reactor. Afterwards, the system was heated to the desired temperature. This was considered zero time for the reaction, and TOC conversion during this time can be neglected. Air from the cylinder was then sparged into the liquid phase, and samples were withdrawn periodically after enough flushing of the sample line. Pressure drop was monitored, and additional air was charged to maintain constant total pressure during 120 minutes of the catalytic run. All the catalytic oxidation experiments were developed at 20 bar of pressure using 1.0 g L^{-1} of platinum. Multi-walled carbon nanotubes (Pt/CNT, 3% wt.) were used as catalyst according to the previous results obtained in the literature (Ovejero et al., 2007; Ovejero et al., 2010). The pH of the hospital wastewater (6.8) was not modified and the temperature was studied from 120 to 150 °C.

The homogeneous Fenton experiments were carried out batch-wise in stoppered glass flask reactors (75 mL reaction volume) shaken at 200 rpm in a constant-temperature bath. Dissolved $\text{Fe}(\text{NO}_3)_3$ (98% assay, Panreac) was used as the catalyst. The operating conditions of the experiments in terms of temperature, catalyst and H_2O_2 concentrations were established according to the results obtained in previous work (Munoz et al., 2016). In this sense, the temperature was fixed at 70 °C, the Fe^{3+} concentration was established at 25 mg L^{-1} , and the dose of H_2O_2 was 1.25 times the stoichiometric amount relative to the COD of the hospital wastewater ($2.125 \text{ g H}_2\text{O}_2 \text{ g}^{-1} \text{ COD}$). The initial pH of the reaction medium was adjusted with nitric acid to the optimum value ($\text{pH} = 3$) for the

homogeneous Fenton process (Pignatello et al., 2006). Samples were taken throughout the reaction time for 240 min.

The heterogeneous Photo-Fenton experiments were performed in a cylindrical glass reactor filled with 0.5 L of the hospital wastewater and using a 150 W medium pressure mercury lamp (Heraeus TQ-150). The lamp was surrounded by a quartz jacket in which a copper sulfate aqueous solution circulates to block radiation at wavelength values shorter than 313 nm. The temperature was controlled at room temperature during the process. The process used a Basolite F300-like semi-amorphous Fe-BTC material as a heterogeneous catalyst, which is a metal-organic framework (MOF) described elsewhere (M. Sanchez-Sanchez et al., 2015). The catalyst was then suspended into the aqueous solution (0.6 g L^{-1}) and the pH was initially adjusted to ca. 3. The initial hydrogen peroxide dosage was 0.7 times the stoichiometric amount ($1.125 \text{ g H}_2\text{O}_2 \text{ g}^{-1} \text{ COD}$). Samples were taken throughout the reaction time for 120 min.

2.3. Preparation and characterization of the heterogeneous catalysts

The Pt supported on multi-walled carbon nanotubes (Pt/CNT) used in the catalytic wet air oxidation experiments was synthesized from oxidized carbon nanotubes (CNTs) and a further impregnation of the active phase (Pt) by incipient wetness impregnation method. The solid presented a Pt content of 1% wt. and a BET surface area value of $198 \text{ m}^2\text{g}^{-1}$ (Ovejero et al., 2007; Ovejero et al., 2010). The Fe-BTC material used in the Photo-Fenton experiments is an inorganic-

organic hybrid material based on iron-containing nodes connected by trimesic acid molecules to form a stable metallic organic framework (MOF), as described elsewhere (Martínez et al., 2018). It shows a semi-amorphous structure previously reported in the literature (Sanchez-Sanchez et al., 2015), with ca. 1002 m² g⁻¹ of BET surface area. The iron content of as-made Fe-BTC material was ca. 12 %wt.

3. Results and Discussion

3.1. Main features of the hospital wastewaters

As it can be seen in Table 1, the hospital wastewater samples showed the typical characterization data of this kind of effluents, such as a slightly alkaline pH (between 7-9), moderate organic load (soluble COD and TOC between 332-650 mg L⁻¹ and 110-130 mg L⁻¹, respectively), and low ecotoxicity (~5 TU). Likewise, the aromaticity was low indicating a relatively low proportion of aromatic compounds in the pool of molecules that comprise COD with values between 0.5-1.2. Regarding the fluctuation of the characterization data of the three different hospital wastewater samples, the organic load and the TSS varied significantly whereas the total nitrogen and phosphate loads displayed a less important difference. Up to seventy-nine pharmaceutical compounds were identified in the samples from their analysis by UHPLC-ESI-MS/MS. Among them, widely prescribed drug families such as lipid regulators and cholesterol-lowering statin drugs, histamine H1 and H2 receptor antagonists, diuretics, beta-

blocking agents, anti-hypertensives, antibiotics and analgesics, and anti-inflammatory compounds, were detected. Fig. 1 depicts the average contribution in the three hospital wastewater samples (HW-1, HW-2, and HW-3) for the different therapeutic families. Concentrations of detected pharmaceutical compounds can be found in Table S3 of the Supplementary Material. The antibiotics and analgesics and anti-inflammatories were the most abundant compounds with percentages ranging from 22 to 35%, corresponding to concentrations between 20 - 50 $\mu\text{g L}^{-1}$. Anti-hypertensive drugs and diuretics also represent significant proportions between 8 and 20% (concentrations ranging from 8 to 28 $\mu\text{g L}^{-1}$). The rest of the therapeutic families showed percentages below 5% and concentrations between 5 and 1.5 $\mu\text{g L}^{-1}$.

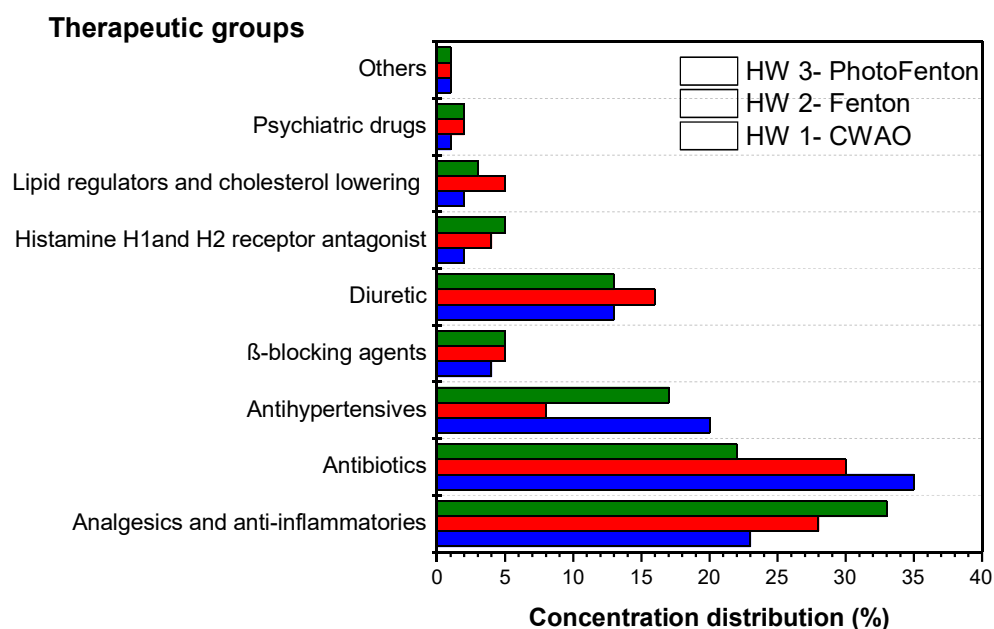


Fig. 1. Distribution of pharmaceutical compounds by therapeutic families for the three hospital wastewater samples.

3.2. Removal of organic matter

Fig. 2 depicts the performance of CWAO, intensified homogeneous Fenton and heterogeneous photo-Fenton systems in terms of the removal of the organic loads of the hospital wastewater. Fig. 2.a shows the performance of the CWAO experiments for the COD removal under the studied operational conditions. As can be seen, an increase of the reaction temperature from 120 to 150 °C led to a significant increase in the COD removal, achieving a 98% elimination at the highest temperature. Regarding the final TOC conversion after 2 hours of reaction, the increase of temperature from 120 to 140 °C promoted the enhancement from 55 to 75%. The increase of temperature at 150°C hardly improved the TOC conversion. It is well known that the treatment of organic compounds by CWAO is based on radical chain reactions (Serra-Pérez et al., 2020). In this process, as has been reported, oxygen could be adsorbed and dissociated on the basal planes of the graphite sheets to form the dissociated oxygen atoms (Rivas et al., 1998) and react with the surface carboxylic groups of the CNTs to produce hydroperoxide radicals (HO_2^\bullet). These radicals can promote the oxidation and breakdown of the soluble organic pollutants, reducing the organic matter to CO_2 , H_2O and low molecular weight organic compounds (Abid et al., 2016). The first-order apparent rate constants (k) for the COD removal were $2.08 \cdot 10^{-2}$, $2.57 \cdot 10^{-2}$, $2.68 \cdot 10^{-2}$, $2.72 \cdot 10^{-2} \text{ min}^{-1}$ at 120, 130, 140 and

150 °C, respectively. As can be observed, an increase in the reaction temperature led to an augmentation in the initial reaction rate due to the production of free radicals within the oxidative process (Ovejero et al., 2013). Likewise, the increase of temperature conditioned the type of intermediate by-products, mainly the short-chain organic acid fraction (Martín-Hernández et al., 2012).

Intensified Fenton oxidation at 70°C using $\text{Fe}(\text{NO}_3)_3$ as Fe^{3+} source was effective for treating the hospital wastewater in terms of physicochemical parameters removal. The evolution of COD and TOC conversions as well as the H_2O_2 decomposition along the experiment ($[\text{Fe}^{3+}] = 25 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 1000 \text{ mg L}^{-1}$; $\text{pH}_0 = 3$) can be seen in Fig. 2.b. Fairly high COD reduction (70%) and significant TOC mineralization (50%) were achieved at the end of the reaction. Almost complete consumption of H_2O_2 was also reached. Nevertheless, it should be mentioned that the efficiency on the consumption of H_2O_2 (defined as TOC mass removal per unit mass of H_2O_2 decomposed) was slightly low ($60 \text{ mg TOC g}^{-1} \text{ H}_2\text{O}_2$) compared to those previously obtained with sawmill and pesticides wastewaters (83 and $88 \text{ mg TOC g}^{-1} \text{ H}_2\text{O}_2$, respectively; Munoz et al., 2014; Pliego et al., 2012). This could be related to the high content of urea in the hospital wastewater as this compound is quite refractory to hydroxyl radicals attack (Munoz et al., 2016). In terms of kinetics, the first-order apparent rate constant for COD removal was calculated, obtaining a value of $1.15 \cdot 10^{-2} \text{ min}^{-1}$.

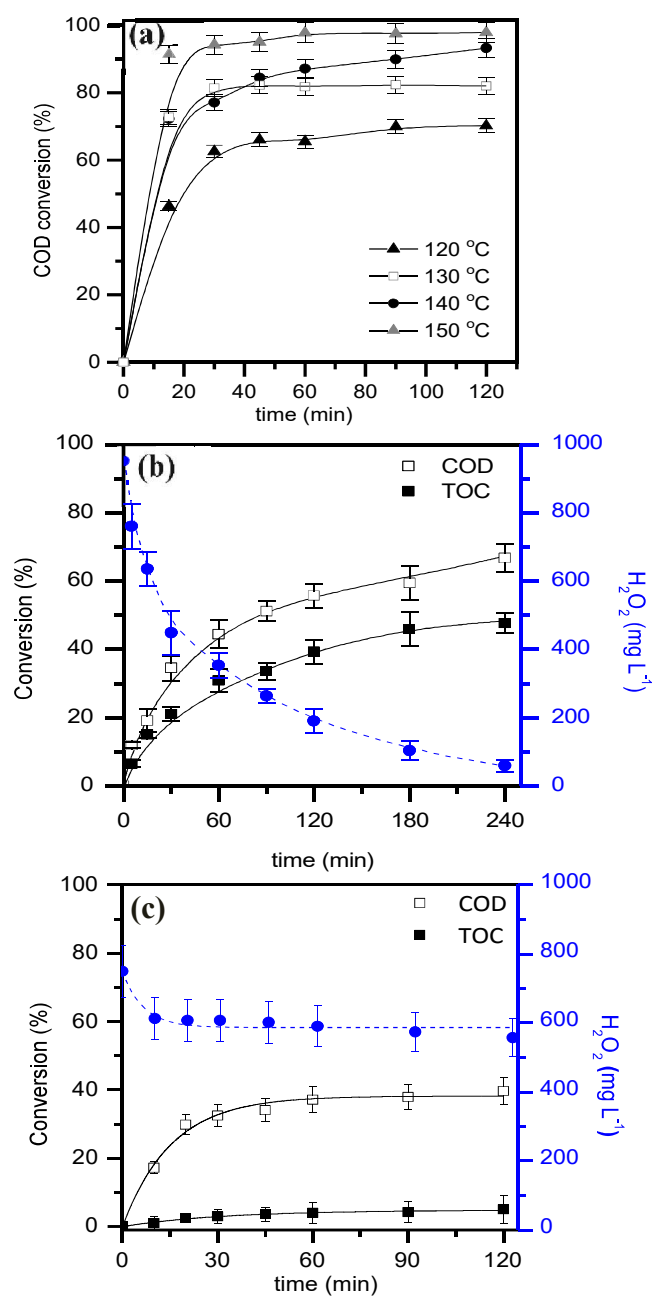


Fig. 2. Evolution of % conversion in (a) catalytic wet air oxidation (CWAO) in terms of COD (20 bar, [catalyst] = 1.0 g L⁻¹ T = 120-150 °C), (b) Fenton oxidation in terms of COD and TOC conversion and H₂O₂ concentration at 70 °C ([Fe³⁺] = 25 mg L⁻¹; [H₂O₂]₀ = 1000 mg L⁻¹; pH₀ = 3), and (c) Photo-Fenton oxidation at 25 °C ([Fe-BTC] = 0.6 g L⁻¹; [H₂O₂]₀ = 750 mg L⁻¹; pH₀ = 3) of the hospital wastewater.

Fig. 2.c shows the performance of the Photo-Fenton process for TOC and COD removals, as long as the hydrogen peroxide decomposition during the time of reaction, under the operational conditions studied herein ($[\text{Fe-BTC catalyst}] = 0.6 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 750 \text{ mg L}^{-1}$; $\text{pH}_0 = 3$ and $T = 25^\circ\text{C}$). Although the Fe-BTC catalyst evidenced a successful performance for the elimination of methylene blue under Fenton conditions (Martínez et al., 2018), when it has been used for the treatment of real hospital wastewater assisted by UV irradiation, the catalytic activity decreased significantly. The catalyst reached a COD removal of 30% and a hardly 5% of TOC reduction after 120 min. The refractory TOC character was previously reported by Munoz et al. 2016, associating this behaviour to the presence of relevant amounts of urea in the hospital wastewater. But the most relevant aspect was the sudden slowdown of the COD removal after hardly 10-20 min of reaction, which is under the decrease of the oxidant consumption. The turbidity of HW-3 due to the relatively high content of TSS ($733 \pm 138 \text{ mg/L}$), the highest of the three hospital wastewater samples as compared to the other two (126 ± 35 and $138 \pm 30 \text{ mg/L}$), is undoubtedly a limiting factor for the performance of the photocatalytic system. This fact affects the transparency of the water, reducing the effectivity of UV radiation. Moreover, the drastic reduction of oxidant consumption and COD removal after 20 minutes of reaction revealed a clear deactivation of the Fe-BTC catalyst probably due to the complex composition of the hospital wastewater. On the other hand, the COD removal obtained for the first 20 minutes of reaction is related to the heterogeneous photo-

Fenton oxidation and UV photo-degradation. Previous studies reported that 15-20 % of the COD reduction in a photo-treatment process of pharmaceutical effluents was due to direct photolysis (Bansal et al. 2018), which involves the interaction of the light with the organic substrate molecules to trigger their photo-dissociation (Mandavagane et al. 2020). In terms of kinetics, using only the first data, the first-order apparent rate constant for COD removal was $0.77 \cdot 10^{-2} \text{ min}^{-1}$. To get better insights about the organic load oxidation degree achieved in each of the technologies investigated, the evolution of TOC vs. COD was also assessed (Fig. 3). A diagonal line in this relationship corresponds to ideal complete oxidation *i.e.*, COD decreases linearly with TOC; while a horizontal line corresponds to partial oxidation, *i.e.*, COD decreases along the reaction and TOC remains unchanged (Mantzavinos et al., 1997; Fotiadis et al., 2007; Pliego et al., 2012). The diagonal trend observed in CWAO and Fenton experiments indicate that the oxidation reactions mainly occurred through total rather than partial oxidation. Nevertheless, all experimental data points were below the ideal diagonal line. This behaviour could be related to the transformation of the original carbon content to refractory compounds, e.g., short-chain organic acidic compounds, which are highly resistant to oxidation (Ma et al., 2017; Bilinska et al., 2020). The presence of high contents of urea in the hospital wastewater can also explain these results as this compound is quite refractory to hydroxyl radicals attack (Munoz et al., 2016). In any case, the presence of such species in the final effluent would not represent a limitation as they are expected to be further

degraded at WWTP facilities, given their high biodegradability. In contrast to CWAO and intensified homogeneous Fenton oxidation, partial oxidation governed the treatment in the Photo-Fenton process (Fig. 3). In this case, COD conversion was not accompanied by relevant mineralization of the organic matter, which can be explained by the limiting penetrability of UV irradiation and catalyst deactivation for the treatment of the real hospital wastewater.

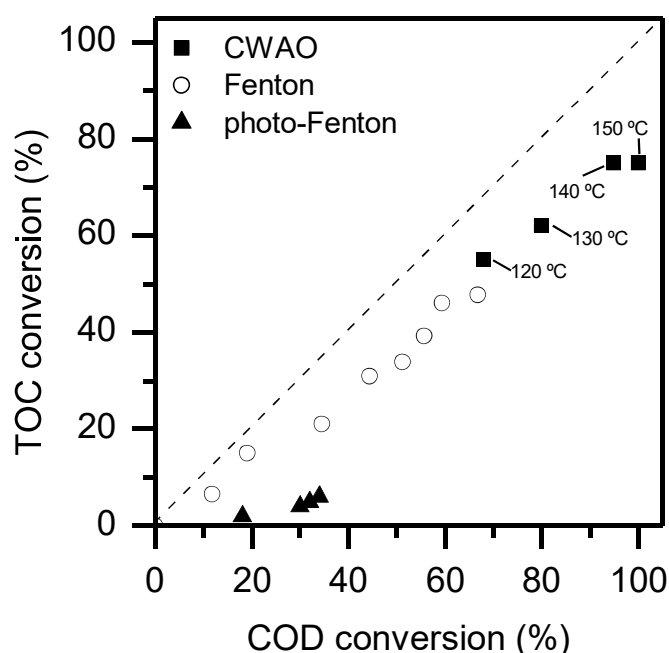


Fig. 3. Evolution of TOC vs. COD upon CWAO (at different temperatures), Fenton oxidation, and Photo-Fenton oxidation of hospital wastewater.

3.3. Removal of pharmaceutical compounds of emerging concern

Fig. 4 summarizes the results obtained in the removal of all the pharmaceutical micropollutants analyzed in this work classified by therapeutic groups. The

average concentration of pharmaceutical compounds in the hospital wastewater samples after treatment can be found in Table S3. Among the investigated advanced processes, intensified Fenton oxidation was the most efficient for drug removal with an almost complete reduction of the total initial concentration (99.8%). Except for citalopram, trazodone, and losartan, all the pharmaceuticals were eliminated in this treatment. It should also be noted that those refractory compounds appeared in the final Fenton effluents at negligible concentrations (4.0, 7.5, and 8.5 ng L⁻¹, respectively; see Table S3). The high efficiency of this process for the removal of pharmaceuticals can be attributed to the action of the *in-situ* generated hydroxyl radicals in the liquid phase, which are quite reactive towards those pollutants (Kanakaraju et al., 2018). Accordingly, although total oxidation of the TOC present in the wastewater was not achieved due to the occurrence of refractory substances like urea or short-chain organic acids (Fig. 2), pharmaceuticals were eliminated to a high extent.

Catalytic wet air oxidation allowed the complete removal of several pharmaceuticals groups such as histamine H1 and H2 receptor antagonist compounds and lipid regulators at 130°C. In contrast, analgesics/anti-inflammatories and antibiotics, which represented the most abundant groups of pharmaceuticals, were not completely eliminated. In this case, removals of those therapeutic pharmaceutical families were 84.6 and 85.9%, respectively (Fig. 4), concerning the total removal of 90% for the initial concentration of pharmaceutical compounds. In any case, it must be noted that acetaminophen,

ciprofloxacin, and ofloxacin were detected in the effluent at relevant concentrations (see Table S3).

The Photo-Fenton process, despite the moderate catalytic performance previously discussed in terms of the COD removal, showed an efficient removal of the pharmaceutical compounds, reaching a 94.5% reduction of the total initial concentration (from 92.9 to 5.2 $\mu\text{g/L}$). All the studied therapeutic groups achieved a removal above 98%, except for analgesic and anti-inflammatories (86.8%), β -blockers (94.9%), and antibiotics (96.4%). Among those groups, acetaminophen, atenolol, hydrochlorothiazide, azithromycin and ciprofloxacin are the most recalcitrant compounds to this process. It should also be mentioned that only acetaminophen was detected at a relevant concentration in the effluent. Unlike catalytic wet air oxidation, the photo-Fenton process allowed reducing almost completely the presence of some antibiotics such as ciprofloxacin, ofloxacin, metronidazole, or sulfamethoxazole. These results evidenced that pharmaceutical compounds are oxidized or partially decomposed by the heterogeneous photocatalytic system. Thus, the elimination of pharmaceuticals could be happened by the oxidizing hydroxyl radicals generated in the photo-Fenton process during the initial active period of the heterogeneous catalyst. But additionally, photodecomposition processes promoted by UV-light irradiation can also have an important role as reported elsewhere (Mandavagane, 2020). So, for example, ciprofloxacin reached 92 % of removal in the heterogeneous photo-Fenton treatment of this study, which is quite similar to the values obtained in

other works. The half-life of ciprofloxacin by direct photolysis was found to be 13 ± 2 minutes (Lam et al. 2013), indicating an important by photodegradation. The fast removal of ciprofloxacin through a photo-Fenton treatment was also reported by De Lima Perini et al. (2013) that obtained removal rates higher than 90 % in 10 minutes.

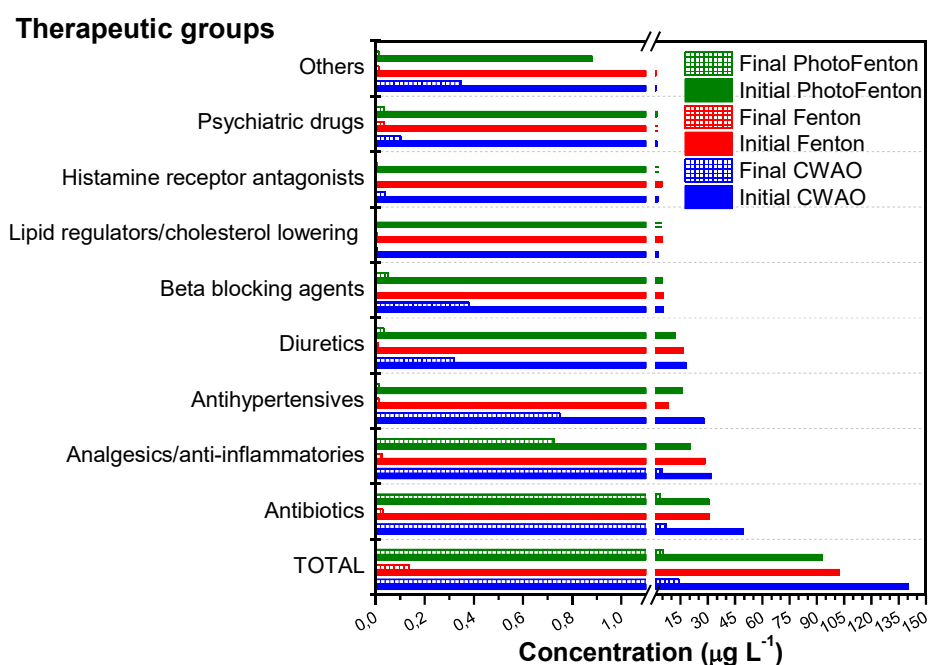


Fig. 4. Concentration of therapeutic pharmaceutical groups for hospital wastewater before and after catalytic wet air oxidation, intensified homogeneous Fenton, and heterogeneous photo-Fenton processes.

3.4. Environmental risk assessment of treated hospital wastewaters

Total hazardous quotients (ΣHQ) before and after each treatment are shown in Fig. 5. Individual HQs of each pharmaceutical are summarized in Table S5 of the

Supplementary Material. A higher Σ HQ value was obtained for the initial hospital wastewater HW-1 sample used for the CWAQ process (Σ HQ= 2986), as compared to HW-2 (Σ HQ = 1897) and HW-3 (Σ HQ = 1886) used for intensified homogeneous Fenton and heterogeneous photo-Fenton systems, respectively. The HQs' difference among the hospital wastewater samples was due to the concentration of some antibiotics such as azithromycin and trimethoprim present in the HW-1 sample. These are compounds of high environmental risk due to their extremely low PNEC values (0.019 and $0.0058 \mu\text{g L}^{-1}$, respectively).

Fenton oxidation achieved the lowest environmental risk after treatment with Σ HQ of 5.4. The reduction of the Σ HQ was 99.7%. On the other hand, although both CWAQ and heterogeneous photo-Fenton processes achieved a similar reduction of the initial load of pharmaceutical concentrations (90 and 94.5%, respectively), the Σ HQ differs significantly after treatment with values of 895 and 88, respectively. The CWAQ process only accomplished a reduction of 70% of the total initial Σ HQ value, while heterogeneous Photo-Fenton treatment reduced the Σ HQ by 95%. These results are due to the presence of refractory and hazardous antibiotic compounds with low PNEC values in the HW-1 employed for the CWAQ experiments. Especially ciprofloxacin, which only achieved a 7% removal, contributed 80% to the total HQ value of the CWAQ treatment effluent. However, the heterogeneous photo-Fenton attained the reduction of most pharmaceutical compounds with high environmental risk such as antibiotics

(azithromycin, ciprofloxacin, ofloxacin, sulfamethoxazole, and trimethoprim). Therefore, this process seems to be more efficient for eliminating hazardous drugs (reduction of final HQ values) despite the moderate COD conversion accomplished after the treatment.

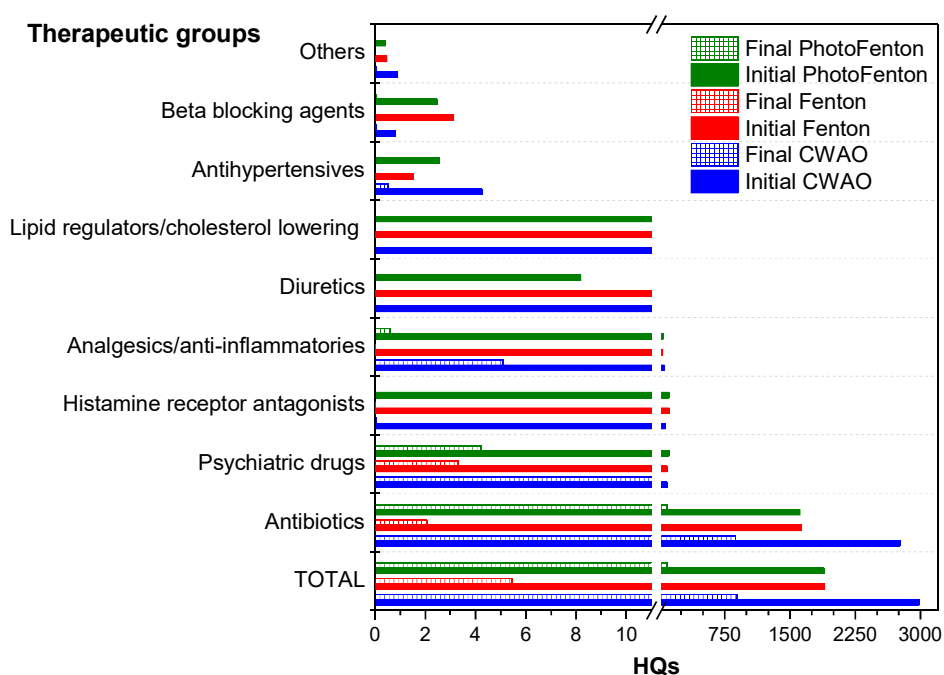


Fig. 5. Hazardous quotients (HQ) of therapeutic pharmaceutical groups for hospital wastewater before and after catalytic wet air oxidation, intensified homogeneous Fenton, and heterogeneous photo-Fenton processes.

Then, it can be concluded that the environmental risk of the treatment effluent does not only depend on the total reduction of the pharmaceutical load but also the specific removal of pharmaceutical compounds of particularly high risk for the environment. All in all, it must be noted that the HQ removal efficiency of the three oxidation technologies (99.7%, 95% and 70% for Fenton, Photo-Fenton

and CWAQ, respectively) can be favourably compared with other treatments previously reported in the literature (Lucas et al., 2016). For instance, Lucas et al. (2016) reported HQ reduction values for urban wastewater of 90% and 53% for fungal (*Trametes versicolor*) and conventional activated sludge treatments, respectively. In this study, two different wastewaters, hospital and veterinary hospital effluents, were also treated with the fungal treatment with HQ reductions of 82-93 and 85-98 %, respectively.

3.5. Cost estimation

To provide a preliminary approach to the economy of CWAQ, Fenton and Photo-Fenton processes for the hospital wastewater treatment, an estimation of the operating costs has been performed considering the operating conditions tested in this work (Table 2).

To calculate the heat expenses in those processes operated at temperatures well above the ambient, *i.e.*, CWAQ and Fenton, the use of a heat exchanger has been considered. Accordingly, a ΔT of 10 °C was taken to estimate the heating requirements as a plausible temperature difference, considering that the inlet stream will be pre-heated by the exit one, and also that the process is operated in continuous flow. Besides, in the CWAQ process, the cost of the catalyst used (Pt/CNT) has been estimated considering a catalyst bulk density value (ρ_{cat}) of 210 kg m⁻³ (Lehman et al., 2011), a catalyst lifetime of 1 year, and a correction factor of taken from www.epa.gov/tri. In this way, the estimated cost of the

catalyst was 4.93 € m^{-3} , significantly lower than other reported values for similar precious-metal based-catalysts (Corti et al., 2005). Moreover, the costs associated with the pumping of the wastewater to the required operation pressure (20 bar) have been considered (Mohammed et al., 2017). All the total operating costs for the CWAO process resulted in 6.67 € m^{-3} .

In the case of the Fenton process, the energy requirements represented the main operating cost. This contrasts with previous works (Pliego et al., 2012; Munoz et al., 2014), where H_2O_2 has been commonly identified as the main operating cost. This can be explained by the low organic carbon concentration of the hospital wastewater, which required relatively low H_2O_2 doses for its oxidation (1000 mg L^{-1}). On the other hand, the management of the iron sludge generated along Fenton oxidation was of minor importance given the low iron concentration employed in the treatment (25 mg L^{-1}).

Regarding the Photo-Fenton process, the price of the catalyst used has been estimated considering the commercial price of Basolite F300 (7.24 €/g) from Sigma-Aldrich. The estimated cost of the employed heterogeneous catalyst was 0.25 € m^{-3} , taken a catalyst lifetime of 180 days for 24 hours per day of operation. As previously mentioned, due to the low organic carbon concentration of the hospital wastewater, a relatively low H_2O_2 dose for its oxidation was needed in this treatment (750 mg L^{-1}). Then, the energy requirements of the UV light represented the main operating cost and were calculated considering the electrical

energy price (0.1325 € kW h⁻¹). Therefore, in short, it resulted in total operating costs of 10.36 € m⁻³, being the most expensive technology.

Table 2. Estimated operating costs for the application of CWAO, Fenton and Photo-Fenton technologies for the treatment of hospital wastewater.

Treatment		Price	Treatment cost (€ m ⁻³)	Total main operating cost (€ m ⁻³)
<i>CWAO</i>	Energy requirements (heat) ^a	0.04282 € kW _t h ⁻¹	0.50	6.67
	Energy requirements (pump) ^b	0.1325 € kW h ⁻¹	1.24	
	Catalyst <i>CWAO</i> ^c	21.6 € g ⁻¹	4.93	
<i>Fenton</i>	Fe(NO ₃) ₃ ·9H ₂ O	0.63 € kg ⁻¹	0.12	0.85
	H ₂ O ₂ ^d	0.23 € kg ⁻¹	0.23	
	Energy requirements (heat) ^a	0.04282 € kW _t h ⁻¹	0.50	
	Sludge management	90 € ton ⁻¹	0.002	
<i>Photo-Fenton</i>	H ₂ O ₂	0.23 € kg ⁻¹	0.17	10.36
	Catalyst <i>Photo-Fenton</i>	7.24 € g ⁻¹	0.25	
	Energy requirements (UV light)	0.1325 € kW h ⁻¹	9.94	

^a Europe's Energy Portal; kW_t (t: thermal)

^b Mohammed et al., 2017

^c Mohammed et al., 2016

^d Cañizares et al., 2009

Conclusions

The intensified homogeneous Fenton oxidation process was the most efficient treatment for the removal of pharmaceutical compounds of hospital wastewaters.

All the pharmaceuticals were eliminated, except for citalopram, trazodone, and losartan, which appeared in the final effluent at negligible concentrations (4.0,

7.5, and 8.5 ng L⁻¹, respectively). In contrast, the efficiency of CWAO and heterogeneous photo-Fenton processes slightly decreased. CWAO achieved the removal of 90% of the initial pharmaceuticals load, but acetaminophen, ciprofloxacin, and ofloxacin remained after the treatment at relevant concentrations. But, it must be noted that the antibiotics load of the hospital wastewater sample used for the CWAO experiment was significantly higher than those quantified for the other two advanced oxidation processes. The heterogeneous photo-Fenton process reached a 94.5% reduction with only acetaminophen detected at a relevant concentration, despite the moderate COD removal of this photocatalytic system. The heterogeneous photo-Fenton oxidation, before catalyst deactivation, and the UV-light decomposition seem to promote an effective elimination of the pharmaceuticals load. The environmental risk assessment of the treated effluents showed a low ΣHQ for the intensified homogeneous Fenton process (5.4) and increased values for CWAO and heterogeneous photo-Fenton systems (895 and 88, respectively). The higher value of CWAO was due to remaining antibiotics after treatment, such as ciprofloxacin which contributed to 80% to the total ΣHQ. Preliminary assessment of the operating costs of the three studied technologies showed the intensified homogeneous Fenton process as the most economical alternative followed by CWAO and heterogeneous Photo-Fenton systems.

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Supplementary data

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