FENTON-LIKE CATALYST BASED ON A RETICULATED POROUS PEROVSKITE MATERIAL: ACTIVITY AND STABILITY FOR THE ON-SITE REMOVAL OF PHARMACEUTICAL MICROPOLLUTANS IN A HOSPITAL WASTEWATER

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ABSTRACT

Powder $LaCu_{0.5}Mn_{0.5}O_3$ perovskite was successfully conformed in a reticulated macroporous structure to be tested in an up-flow catalytic packed bed reactor as on-site pre-treatment of a hospital wastewater for the removal of emerging pharmaceutical micropollutants. This work has assessed the activity and stability of the powder and reticulated porous perovskite (RPP) material as Fenton-like catalyst. The effect of the initial pH, the temperature and the hydrogen peroxide were studied using the hospital wastewater fortified with carbamazepine (CZP, 15 mg/L) in order to make easier the evaluation of the catalytic activity in terms of the CZP removal. The acidification of pH at 3 enhanced the catalytic performance but also increased the leaching of the constituents of the perovskite material. In contrast, the increase of temperature (from 50 to 90 ^{o}C) and hydrogen peroxide dosage (from 350 to 700 mg/L) also improved the performance of the catalyst, but the stability of the reticulated porous perovskite material hardly was affected. The catalyst evidenced a remarkable activity (ca. 100 % CZP removal) and stability (low leaching of the metal species from the $LaCu_{0.5}Mn_{0.5}O_3$ perovskite) for 70 hours on continuous operation in a catalytic packed bed reactor operated at 70 ^{o}C, initial pH of ca. 5.5 and moderate dosage of hydrogen peroxide (700 mg/L). Finally, the perovskite catalyst showed a notable performance for the removal of the pharmaceutical micropollutants detected in the hospital wastewater in the real range of μg/L (antineoplastic drugs, antibiotics, X-ray contrast agent, psiquiatric drugs or analgesics & anti-inflammatories). Most of them were eliminated with removal degrees above 90-95 %. Metropolol and carbamazepine were the two pharmaceutical compounds removed in less extension, but in any case, the concentration of both after treatment was below to the predicted non-effect concentration (PNEC) for aquatic organisms. Thus, the reticulated porous perovskite material based on $LaCu_{0.5}Mn_{0.5}O_3$ perovskite is considered a promising Fenton-like catalyst for its implementation in fixed bed reactors for on-site pre-treatment of hospital wastewater effluents.

Keywords: Perovskite, reticulated porous ceramic material, heterogeneous Fenton-like catalyst, carbamazepine model pollutant, on-site hospital wastewater treatment.

1. INTRODUCTION

Nowadays hospital wastewater (HWWs) represent one of the main sources of emerging pharmaceutical (EP) micropollutants into the environment [1]. HWWs are between 4 and 150 times more concentrated of these EP micropollutants than urban wastewaters (UWWs) [2–4]. However, as the nature of HWWs are similar in nature than UWWs, they are discharged into the municipal sewer system without any specific pre-treatment [5], and consequently they arrive to the conventional wastewater treatment plants (WWTPs). Unfortunately, conventional WWTPs are not able to remove completely the EP micropollutants in most of the cases, and their effluents become an important source of them in the aquatic ecosystems.

Several works have proposed end-of pipe dedicated wastewater treatments for HWWs as a potential alternative to decrease the load of pharmaceuticals [4]. This has been tested in different studies over Europe, in which different on-site treatments have been developed for specific treatment of HWWs, instead of the direct discharge into the municipal sewer system [5]. In this way, biological treatments based on membrane bioreactors (MBRs) have shown promising results for the treatment of HWWs with removals of EP micropollutants ranging from 19 to 94 %. These biological processes have been effective for some compounds like clarithromycin, but others, such as carbamazepine or diclofenac, were hardly removed [6].

Alternatively, advanced oxidation processes (AOPs) have been tested as pre-treatment for the removal of EP micropollutants present in HWWs. Among AOPs, Fenton oxidation has emerged as a feasible technology for the removal EP micropollutants such as amoxicillin, paracetamol, ofloxacin, diclofenac, etc. in different waster matrixes [7,8]. Fenton oxidation has been also proposed for HWWs, but mainly focused on the reduction of the soluble organic matter or the increase of its biodegradability instead of an efficient removal for EP micropollutants [9,10]. The main drawbacks of Fenton oxidation are the narrow range of operating pH (2.5-3.5) that is required for the efficiency of typical soluble catalytic iron species. The use of heterogeneous Fenton-like catalysts can overcome this limitation as well as the amounts of metallic iron sludge generated after neutralization and precipitation of the dissolved metallic salts [7,11,12].

In this sense, most of heterogeneous Fenton catalysts are based on iron-containing materials based on the immobilization of iron species in different supports such as zeolites [13], pillared clays [14], alumina [15], amorphous mesoporous silica [16,17] and activated carbons [18]. But the use of other low-valency transition-metal ions such as Cu, Mn, Ru, V and Ti may be also extend the scope of the Fenton reaction [19]. In the last decades, perovskites type oxides have been extensively investigated as catalysts for several applications [20], including heterogeneous

Fenton-like catalyst [21–23]. Perovskite materials are characterized by a crystal structure as $CaTiO_3$ and their chemical formula is represented as ABO_3, where A-site is a lanthanide metal (La, Ba, Ca, and Sr) with a 12-coordinated cation and B-site is a transition metal (Ni, Ti, Co, Fe, Mn or Cu) with a 6-coordinated cation as active site [24]. Their catalytic properties are closely related to the nature of the A and /or B cations and can be modified by the partial substitution of A and B, leading to the formation of a variety of mixed oxides. This fact could affect to the chemical state of the cations, the generation of oxygen vacancies, the mobility of oxygen lattice and the formation of structural defects [25]. These features make perovskites promising heterogeneous Fenton-like catalysts.

A preliminary work of $LaCu_{0.5}Mn_{0.5}O_3$ has been reported as an active and stable heterogeneous Fenton-like catalyst for the removal of paracetamol as model pollutant in ultrapure water [26]. However, the feasibility for real and complex wastewater matrixes, like HWWs, has not been studied. Moreover, a critical point for the full-scale implementation of powdered heterogeneous Fenton-type catalysts in fixed-bed reactors and/or stirred tank reactors with stationary catalytic baskets is that they need to be pelletized or immobilized in opened macrostructures [27,28]. In this sense, some examples of continuous fixed-bed reactors filled with heterogeneous catalysts have been proposed to Fenton-like oxidation processes based on packing metallic-based catalyst pellets [27–31]. In recent years, reticulated porous ceramics (RPCs) have been also investigated using the polymeric sponge replication method, which is a simple and effective procedure to make reticulated ceramic foams, also known as open-cell cellular ceramics. In this method, a porous polymeric sponge used as scaffold is impregnated with a slurry of ceramic precursors to form a macroporous structure with a high mechanical strength after burning out the organic polymer and sintering of the ceramic precursors at high temperature [32]. The application of heterogeneous catalyst conformed as RPCs for AOPs has been hardly reported in literature. Some examples can be found in photocatalytic systems for water or air purification using RPCs of different materials (alumina, alumina/mullite, cordierite or polysiloxane-polyurethane foams) as support of the active TiO_2 photo catalyst [33–35]. Kocakuşakoğlu et al. demonstrated a remarkable performance an open three-dimensional network structure of a reticulated porous ZnO ceramic material with a high interconnected porosity in the photocatalytic degradation of the azo dye Reactive Red 180 [36].

This work will be focused on the preparation of a reticulated porous perovskite (RPP) material based on $LaCu_{0.5}Mn_{0.5}O_3$ as heterogeneous Fenton-like catalyst for the removal of emerging pharmaceutical micropollutants in HWW under continuous operation in a fixed bed reactor. The RPP material will be prepared following the sponge replication method. The catalytic activity

and stability will be assessed at different initial pH values, temperatures and hydrogen peroxide dosages using a hospital wastewater fortified with carbamazepine (CZP) as model pollutant. CZP is a common antiepileptic drug with important endocrine disrupting effects in water bodies [37] which is not effectively removed in wastewater treatment plants [3,6,38]. Finally, the efficiency of the RPP material will be tested for the removal of the pharmaceutical micropollutants contained in the hospital wastewater in the real range of concentration of μg/L.

2. EXPERIMENTAL

2.1. Materials

The reagents for the synthesis of the powder perovskite material were purchased from Sigma Aldrich ($Cu(CH_3COO)_2{\cdot}2H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$, $La(NO_3)_3{\cdot}6H_2O$ and citric acid). Commercial Dolapix CE 64, Optapix PA 4G, Contraspum KWE and polyurethane foams (PUS) for the preparation of the reticulated porous perovskite (RPP) material were kindly provided by Zschimmer & Schwarz España, S.A. Additionally, bentonite and ethanol used in the manufacturing method were provided by Süd-chemie and Scharlau S.L., respectively. Carbamazepine and sulphuric acid to adjust the pH of the catalytic experiments were obtained from Sigma-Aldrich.

2.2. Preparation and characterization of reticulated porous perovskite materials

Synthesis of powder $LaCu_{0.5}Mn_{0.5}O_3$ perovskite. It was performed using the method described by Carrasco-Diaz et al. [26]. Typically, $Cu(CH_3COO)_2{\cdot}2H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ as metallic sources were completely dissolved in 100 mL of ultrapure water. Then, citric acid was added until achieving a pH of 2.5 ± 0.3, and the resultant mixture was stirred for 3 h. Thereafter, the solution was dried at 70 ˚C for 12 hours to form the sol-gel, and then at 110 ˚C for 16 hours to obtain the amorphous solid. After that, it was crushed and sieved until a particle size between 236 and 254 nm, and finally calcined at 700 ˚C for 5 h in air atmosphere to obtain the powdered $LaCu_{0.5}Mn_{0.5}O_3$ perovskite material.

Preparation of reticulated porous perovskite material. It was prepared following the sponge replica method commonly used for the manufacturing of TiO_2 and other ceramic foams [32,39]. In this case, the powdered perovskite and additional inorganic binder (bentonite) were dispersed in ethanol (1 perovskite: 0.25 bentonite: 0.6 ethanol in wt.). Thereafter, a deflocculating agent (Dolapix CE 64; 65 wt. % respect to perovskite mass) was added to avoid the agglomeration of the powder particles. After a good dispersion, Optapix RA 4G (polyvinyl alcohol, 4 wt. % respect to perovskite mass) as organic binder and drops of non-ionic anti-foaming agent (Contraspum KWE) were added to the slurry suspension. The mixture was

maintained under vigorous stirring for 10 minutes. After that, a polyurethane foam of 40 ppi (pores per linear inch) with a cylindrical form (15 mm-diameter and 40 mm-height) was immersed in the perovskite-containing slurry suspension. After 30 min, the soaked foam was taken out and dried for 24 hours at ambient temperature. This procedure was performed twice. Finally, the organic polymer used as scaffold of the reticulated porous perovskite material was removed by calcination at 700 °C for 2 hours using a ramp of 5 °C/min and sintered at 1000 and 1200 °C for 2 hours with a heating rate of 5 °C/min.

Characterization techniques. X-ray diffraction (XRD) patterns of powder samples were carried out in an XPert Pro Diffractometer (Philips PW0340/00) using the CuKα radiation. Data were recorded at the 2θ angle ranging from 10° to 90° with steps of 0.04˚ and 2 s of accumulation each step. The composition of the synthetized perovskite material was determined by ICP-AES using a Vista AX Pro-720ES equipment, being the samples were previously digested under strong acid medium (HNO_3/HCl). Mechanical strength under compression of the reticulated porous perovskite materials was determined using a standardized mechanical test in a dynamometer Chatillon Force Measurement LTCM Series from AMETEK GmbH, according to ASTM D 4179/2011. In this test, probes of 1 cm^3 are subjected to a controlled compression program until failure. Finally, porosity of the reticulated samples (ε) were determined by the dislodged water known volume after its immersion in water.

2.3. Catalytic performance of perovskite materials for the removal of emerging micropollutants in hospital wastewater

Origin of the hospital wastewater (HWW). The hospital wastewater was taken directly from the main collector of a hospital located in the South of Madrid (Spain). In this central collector, three catch basins discharged their effluents from different activities carried out in the hospital. One of them correspond to general areas, X- rays and digestive areas. Whereas, the other two are from laboratories and ICU, anatomic, sterilization and pharmacology. The hospital wastewater used in this work is a mixture of the three effluents. In order to collect representative samples of the hospital daily discharge, three automatic auto-samplers of each collector basin were used to take 330 mL (110 mL each) of wastewater every 10 min through 7 days and mixed together, collecting up to 1000 L. The wastewater stored at 4 ˚C showed a COD and TOC concentrations of 179 mg/L and 130 mg/L, respectively. The nitrogen content was 41 mg/L of $N\text{-}NH_4^+$ and 69 mg/L of Total Kjedahl Nitrogen (TKN). Finally, the phosphorus content was ca. 3 mg/L $P\text{-}PO_4^{3-}$.

Preliminary catalytic tests of the powdered perovskite material. These experiments were performed in a stirred tank reactor in batch-wise operation. In a typical experiment, 600 mL of the HWW was spiked with 15 mg/L of carbamazepine (CZP) and placed in the reactor under

continuous stirring (700 rpm). The pH was adjusted, if necessary, by addition of H_2SO_4 2 N. Once the desired temperature was achieved, 0.6 g/L of the powder catalyst and 700 mg/L of H_2O_2 (stoichiometric concentration for total TOC consumption according to reaction R1) were added into the reactor, starting the reaction.

$$C + 2H_2O_2 \rightarrow CO_2 + 2H_2O \quad \text{(R1)}$$

The time of each experiment was extended until the hydrogen peroxide was completely consumed. The temperature (30, 50 and 70 ˚C) and the pH value (3, 5.5 and 7.5, corresponding to the natural pH of the HWW) were studied in batch experiments for the powdered perovskite catalyst.

Catalytic runs of reticulated porous perovskite material. These experiments were evaluated in a continuous up-flow fixed bed reactor (FBR) at atmospheric pressure. The FBR consists of a jacketed cylindrical tube of 1.5 cm of inner diameter and 25 cm of length. The catalytic bed was formed by 3 g of the reticulated porous perovskite catalyst. Spherical inert glass particles were located upper and lower to the catalyst bed in order to maintain it stable on place. The hospital wastewater was pumped by means of a ProMinent GUGAL S.A. pump, model DULCO®flex at 1 mL/min, giving a residence time of 3 minutes, according to equation 1 [40], where ε and V_{bed} are the porosity and volume of the reticulated porous perovskite material in the FBR.

$$t_{R=\frac{\varepsilon V_{bed}}{Q}} \quad (1)$$

The temperature of the catalytic runs was controlled using an external heating device of silicon oil that it is recirculated through the jacket of the reactor. Initially, the HWW was spiked with 15 mg/L of carbamazepine (CZP) and the activity and stability of the reticulated porous perovskite material in continuous operation was evaluated at different temperatures (50, 70 and 90 ˚C) and hydrogen peroxide dosages (700 mg/L and 350 mg/L). Finally, the performance of the catalyst was assessed for the removal of the emerging pharmaceutical micropollutants of the hospital wastewater at their real concentration.

Analytical techniques. Total Organic Carbon (TOC) was determined in a combustion/non-dispersive infrared gas analyser model TOC-V Shimadzu. Carbamazepine in the range of 0.15-15 mg/L was determined by a HPLC (Varian ProStar) equipped with a Phenomenex C18 (3 x 150 mm) column coupled to a pre-column Phenomenex HPLC Guard Cartridge System using a UV detector at 254 nm. A solution composed by HPLC quality methanol (49.5 %), ultrapure water (49.5 %) and glacial acetic acid (1 %) with a final pH value of 2-2.5 was used as mobile phase with a flowrate of 0.30 mL/min. Hydrogen peroxide was determined by a colorimetric method (DEV

(H15)) according to DIN 38 409 based on the measurement of the chromophore formed at 410 nm after the addition of a standard commercial solution of titanium oxysulfate ($TiOSO_4$ 1.9-2.1 %). The concentration of dissolved metals from the perovskite after treatment in the aqueous samples were measured by ICP-AES (Varian, Vista AX Pro-720ES). The emerging pharmaceutical micropollutants detected in the hospital wastewater and samples after treatment were analysed by ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-ESI-MS/MS) using vortex electrospray ionization interface (Bruker UHPLC/MSMS EVOQ™ QUBE). The method includes 22 pharmaceutical micropollutants of 7 different therapeutic groups (Table 1_SM). The samples were filtered through a dura-pore hydrophilic filter (PVDF, 0.65 µm) and extracted by solid phase extraction (SPE) using a polymeric cartridge (TELOS C18(EC), 200 mg/6 mL) from Kinesis. Chromatographic separation was achieved with a Bruker Intensity Solo 2 C18 column (100 x 2.1 mm and 2µm). The mobile phase (flow rate 400 µL/min) consisted of a gradient program of water with 0.04 % acetic acid and acetonitrile at 40 ˚C [41].

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization of the reticulated porous perovskite catalyst

According to the method used for the preparation of the reticulated porous ceramics, several preliminary experiments were needed to determine the optimal composition of the slurry suspension for a successful conformation of the final reticulated porous perovskite material. In these experiments, the dosage of bentonite and Optapix PA 4G as inorganic and organic binders was carefully studied in order to find an optimal viscosity of the slurry suspension for a complete soaking of the macroporous structure of the polyurethane sponge. Experimentally, it was determined that amounts of 25 wt. % (bentonite) and 4 wt. % (Optapix PA 4G) in basis to the mass of powdered perovskite, enables a good penetration of the slurry solution into the sponge structure to form final stable reticulated porous materials after removal of the organic polymer scaffold by calcination.

After optimization of the binders´ composition of the slurry suspension that contains the active perovskite material for the dip-coating of a polyurethane sponge, the slow removal of the organic skeleton by calcination with a controlled heating rate is a key variable for obtaining a consistent reticulated porous material. According to the thermogravimetric analysis of the polyurethane sponge (Figure 1_SM), a temperature of 700 °C and a heating rate of 2.5 °C/min was established for achieving a slow and complete decomposition of the organic polyurethane. Likewise, a further thermal treatment for sintering of the reticulated porous material was

studied at 1000 and 1200 °C. Table 1 shows the porosity (ε) and the mechanical strength of the reticulated porous perovskite (RPP) materials after primary calcination at 700 °C and secondary calcination at 1000 and 1200 °C. At 1000 °C, a stable reticulated porous perovskite material was achieved with a mechanical strength of 14 N and porosity of 0.6. The increasing of temperature up to 1200 °C enhances the mechanical strength until 23 N, but the porosity significantly decreased to 0.3, probably due to the shrinkage and partial collapsing of the perovskite-based structure with the temperature. On the other hand, it was clearly evidenced that 700 °C was insufficient to obtain a reticulated porous material consistent enough. Figure 1 shows images of RPP materials calcined at 700, 1000 and 1200 °C.

Table 1. Properties of $LaCu_{0.5}Mn_{0.5}O_3$-RPPs prepared with different sintering temperatures.

Sample	T_{final} (˚C)	ε	Resistance (N)
RPP-700	700	Non-stable structure	
RPP-1000	1000	0.60	14 ± 3
RPP-1200	1200	0.30	23 ± 3

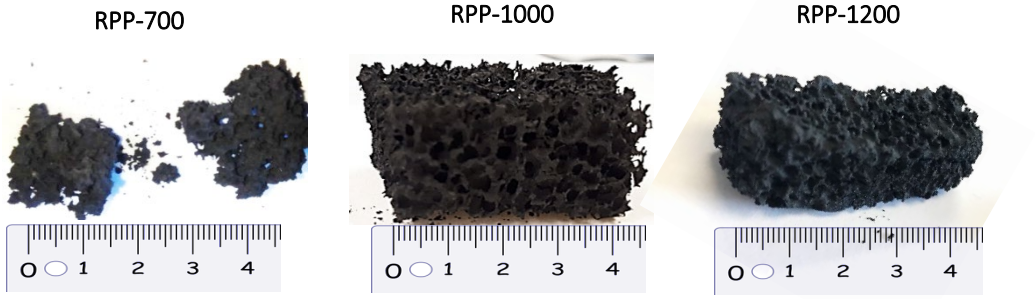


Figure 1. Images of calcined reticulated porous perovskite materials at 700, 1000 and 1200 °C

Additionally, XRD patterns of powder reticulated porous materials after crushing (RPP-700, RPP-1000 and RPP-1200) were assessed as compared to the powder $LaCu_{0.5}Mn_{0.5}O_3$ perovskite precursor (Figure 2). The RPP-700 material showed characteristic diffraction peaks at 22.6°, 32.2°, 39.8°, 46.2° and 57.4°, corresponding to (101), (121), (220), (202) and (240) lattice planes of the standard ABO_3 structure (JCPDS file: 37–1493). The RPP-1000 material retains the typical ABO_3 perovskite structure, although small diffraction peaks at 30 ° appeared, being attributed to the presence of bentonite. In the case of RPP-1200 material, the intensity of characteristic

signals of ABO_3 perovskite structure decreased and additional diffraction peaks were observed, which can be attributed to segregation of bentonite (montmorillonite, 28°- 30°), copper oxides (~35°) and manganese and lanthanum oxides (~43°-47°). These results evidenced a partial conversion of the perovskite structure to other crystalline phases at 1200 ºC.

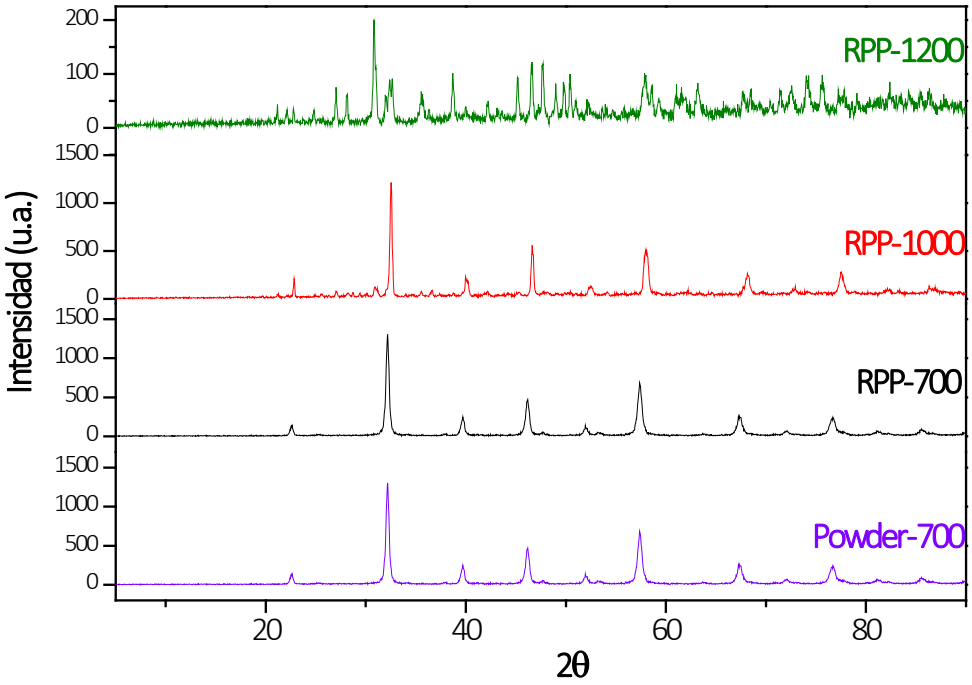


Figure 2. XRD patterns of RPP materials and powder $LaCu_{0.5}Mn_{0.5}O_3$ perovskite precursor

3.2. Preliminary catalytic tests of powder $LaCu_{0.5}Mn_{0.5}O_3$ perovskite material.

The influence of the initial pH (3, 5.5, 7.5) and temperature (30, 50 and 70 ˚C) was initially studied for the treatment of the hospital wastewater spiked with carbamazepine (CZP) as model pollutant for a better evaluation of the catalytic performance of the powder $LaCu_{0.5}Mn_{0.5}O_3$ perovskite.

Figure 3 a and 3 b shows the H_2O_2 conversion and CZP removal of the catalytic tests carried out at the initial pH of ca. 7.5 (natural pH of the hospital wastewater) and 30, 50 or 70 ˚C. The rate of the oxidant conversion increases with the temperature, achieving a complete conversion at 220 min, 180 min and 120 min for 30, 50 and 70 ºC, respectively. Likewise, the removal rates of CZP are significantly increased with the reaction temperature, reaching removals of 5 %, 75 % and 100 % at the end of each catalytic run at 30, 50 and 70 ºC, respectively. The low efficiency of the catalyst at 30 ºC could be attributed to a predominance of the ineffective decomposition of H_2O_2 in H_2O and ½ O_2 promoted by the oxygen vacancies of the perovskite structure [42]. In

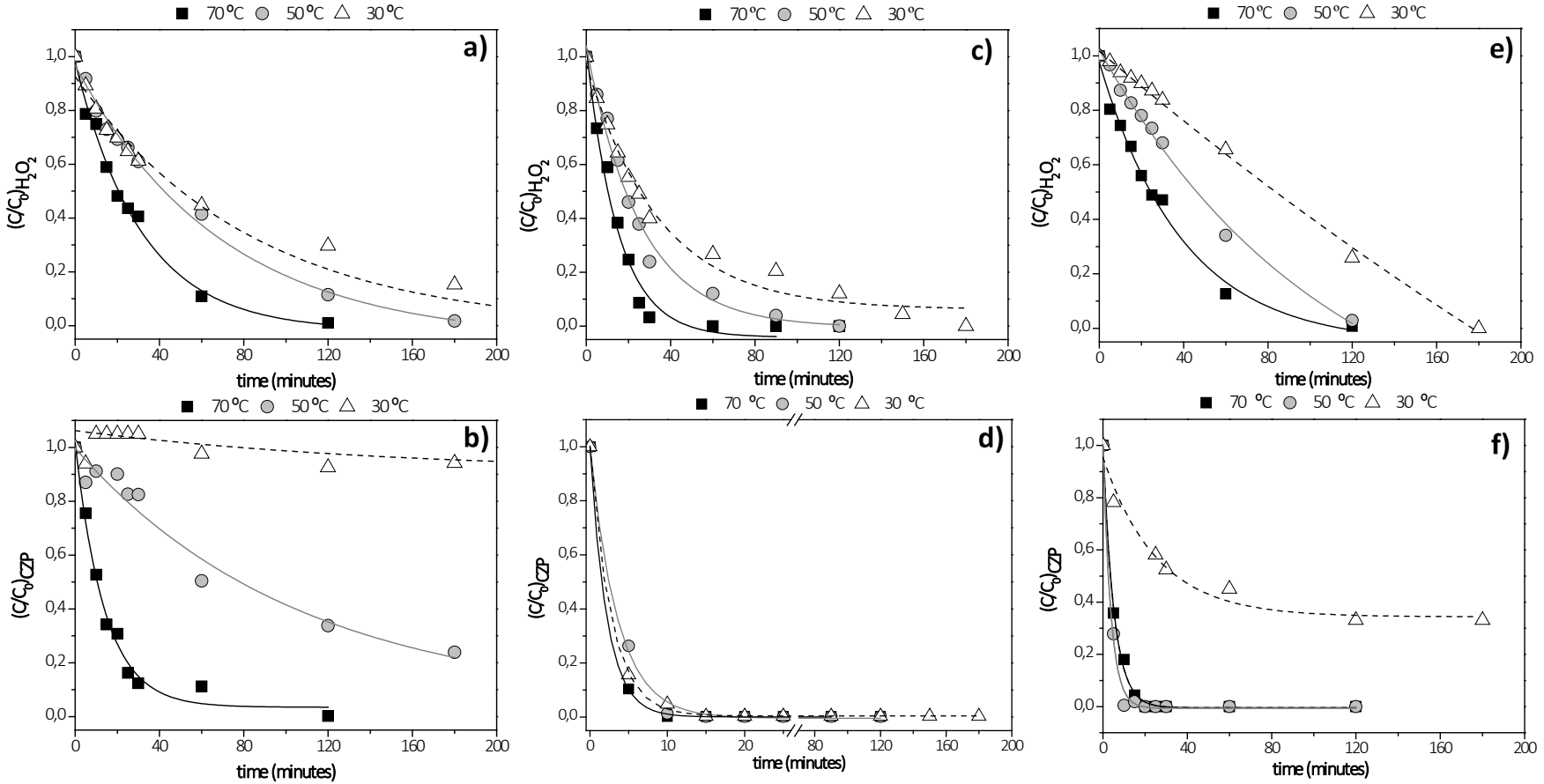
fact, the chemical composition of the synthetized powder perovskite ($LaCu_{0.5}Mn_{0.49}O_{2.79}$) evidence a slight defect of oxygen in comparison to the theoretical one ($LaCu_{0.5}Mn_{0.5}O_3$). Blank experiments performed at 70 ºC to determine the oxidative capacity of hydrogen peroxide in absence of catalyst and the adsorption capacity of perovskite in absence of oxidant (Figure 2_SM a and b, respectively), also revealed a low removal of CZP (25 %) by the action of H_2O_2 and a negligible adsorption of CZP. Concerning the TOC mineralization, a low TOC reduction was observed for all the studied temperatures in the catalytic experiments at the initial pH of 7.5. The complex composition of the HWW, accompanied with a relevant amount of urea, can be responsible for this low TOC mineralization [10]. The effect of the complex matrix was confirmed by repeating the catalytic test at 70 ºC with CZP in ultrapure water instead of the hospital wastewater matrix (Figure 3_SM). In this case, a remarkable TOC mineralization of ca. 40 % was achieved after 120 min. The stability of the metallic species of the $LaCu_{0.5}Mn_{0.5}O_3$ during the catalytic runs determined by the analysis of the metal ions dissolved in the reaction medium after reaction (Table 2), evidenced a negligible leaching of metallic species, with values of La and Mn concentrations below the detection limit (< 0.2 mg/L) and lower than 0.7 mg/L for Cu (less than 1 % of the Cu content of the solid catalyst).

The acidification of the initial pH of hospital wastewater up to 3 showed a significant increase of the conversion of hydrogen peroxide and the removal of CZP even at 30 ºC (Figure 3 c and 3 d). Thus, a complete elimination of CZP was reached in less than 20 minutes at this temperature, being necessary less than 10 minutes at 50 and 70 ºC. These results reveal a better efficiency of the oxidant, which is attributed to the higher oxidation potential of hydroxyl radicals at acid pH (2.7 V at pH 3 vs. 1.8 V at pH 7) [43]. The TOC removal was also improved at this pH, achieving values of ca. 19, 31 and 36 % for 30, 50 at 70 ˚C, respectively. However, it must be noteworthy that the metal leaching of the perovskite catalyst dramatically increased with the acid pH, obtaining concentrations of La, Cu and Mn after reaction between 87-113, 18-22 and 20-25 mg/L, respectively (Table 2). Thus, the acidification of pH at 3 significantly affects the stability of the $LaCu_{0.5}Mn_{0.5}O_3$ perovskite material, limiting its application as Fenton-like catalyst.

Catalytic experiments at pH of 5.5 (Figure 3 e and 3 f) also revealed a good catalytic performance of $LaCu_{0.5}Mn_{0.5}O_3$ perovskite with remarkable conversions of hydrogen peroxide and removal rates of carbamazepine. CZP removals higher than 95 % were achieved in less than 10 minutes at 50 and 70 ºC. At 30 ºC, the removal of CZP was significantly higher than that obtained at the pH of 7.5, but still low with only 65 % of removal after 180 min of reaction. Thus, a minimum temperature of 50 ˚C seems to be recommendable for a fast CZP degradation. Regarding the catalyst stability, the metal concentration of La, Cu and Mn after reaction were in the range of

0.6-1.1, 1.2-1.3 and 1.2-3.7 mg/L, respectively (Table 2). These concentrations correspond to percentages of metal leaching lower than 6 % in all the cases. Moreover, it was observed that the catalyst stability is not significantly depended on the reaction temperature in the studied interval (30 - 70 ºC). These results of the metal leaching demonstrate a higher stability of the Cu on the solid catalyst as compared to that obtained by other copper-containing catalysts operating in analogous reaction conditions, making $LaCu_{0.5}Mn_{0.5}O_3$ perovskite a promising heterogeneous Fenton-like catalyst [23,44,45].

Summarizing, the performance of $LaCu_{0.5}Mn_{0.5}O_3$ perovskite in terms of the CZP removal progressively increased with the decrease of pH, but in detriment of catalyst stability. The better compromise between activity and stability is obtained at pH values and temperatures equal or higher than 5.5 and 50 ºC, respectively. This pH is the minimum value in which the lixiviation of metallic species and consequently the loss of active phase is still negligible. At the same time, 50 ºC was the minimum temperature required in order to obtain a desirable catalyst activity in terms of CZP removal, hydrogen peroxide consumption and TOC mineralization. At 50 ˚C and initial pH of 5.5, it was reached a total CZP removal in hardly 10 minutes and a TOC mineralization of ca. 22 % after 120 min. Moreover, these results are obtained using a catalyst loading (0.6 g/L) and hydrogen peroxide concentration (0.7 g/L), amounts that are much lower than those used in other works reported in literature for the elimination of CZP through homogeneous and heterogeneous Fenton processes. So, Sun et al. hardly achieved a 3 % removal of a 15 mg/L solution of CZP after 180 min of reaction, using 5 mg/L of a homogeneous Fe(III) catalyst at neutral pH, room temperature and 0.6 g/L of H_2O_2 [46]. The use of a heterogeneous catalyst of Fe_3O_4 nanoparticles with a concentration of 1.84 g/L and 20 g/L of H_2O_2 achieved a CZP removal of 86 % at neutral pH and room temperature [47]. However, a decrease of the catalyst loading and the oxidant concentration up to 1 g/L and 3.4 g/L, respectively, dramatically reduced the effectivity of the catalyst, leading to a removal of CZP of only 6 %. $CuFeO_2$ micro-particles achieved a 31 % removal of CZP in 60 minutes at room temperature and neutral pH, but needing a H_2O_2 concentration and a catalyst loading of 7 g/L and 1 g/L respectively [48].



361 **Figure 3.** Normalized concentration of hydrogen peroxide and carbamazepine concentrations at initial pH of 7.5 (a) and (b), 3 (c) and (d), 5.5 (e) and (f) for
362 different reaction temperatures (30, 50, and 70 °C) in batch experiments with powder $LaCu_{0.5}Mn_{0.5}O_3$ perovskite at: $[H_2O_2]_0$ = 700 mg/L, [catalyst] = 0.6 g/L,
363 $[CZP]_{spiked}$= 15 mg/L in HWW and stirring =700 rpm

Table 2. Metal leaching of catalytic tests performed at different temperatures and initial pH values using $LaCu_{0.5}Mn_{0.5}O_3$. Values in brackets correspond to percentage of metal lost from the solid catalyst

pH	T (˚C)	[La]	[Cu]	[Mn]
			(mg/L)	
7.5	70	< 0.2 (0.06 %)	0.37 ± 0.06 (0.5 %)	< 0.2 (0.3 %)
	50	< 0.2 (0.06 %)	0.48 ± 0.07 (0.6 %)	< 0.2 (0.3 %)
	30	< 0.2 (0.06 %)	0.67 ± 0.06 (0.9 %)	< 0.2 (0.3 %)
5.5	70	0.60 ± 0.02 (0.2 %)	1.24 ± 0.90 (1.3 %)	1.39 ± 0.09 (2.1 %)
	50	1.10 ± 0.03 (0.3 %)	1.57 ± 0.91 (2 %)	3.66 ± 0.07 (5.5 %)
	30	0.97 ± 0.03 (0.3 %)	1.27 ± 0.90 (1.6 %)	1.11 ± 0.10 (1.7 %)
3	70	94 ± 1 (28 %)	19 ± 1 (25 %)	21 ± 1 (31 %)
	50	113 ± 3 (33 %)	22 ± 1 (28 %)	25 ± 1 (37 %)
	30	87 ± 1 (26 %)	18 ± 1 (23 %)	20 ± 1 (30 %)

3.3. Catalytic performance of reticulated porous perovskite materials in continuous up-flow fixed bed reactor

The two reticulated porous perovskite materials RPP-1000 and RPP-1200 were tested in a catalytic fixed bed reactor for the treatment of the HWW spiked with 15 mg/L of CZP. These catalytic runs were performed at 70 ºC, initial pH of 5.5, stoichiometric dosage of hydrogen peroxide (700 mg/L) and residence time of 3 min. The RPP-1200 was less active than RPP-1000 with a H_2O_2 conversion and CZP removal of ca. 20 and 70 %, respectively. On the contrary, the RPP-1000 achieved a total consumption of the oxidant and CZP removal higher than 90 %. The oxidant conversion and CZP removal of both experiments along the time on operation at steady-state conditions can be found in Figure 4_SM. The lower catalytic performance of RPP-1200 material is attributed to the loss of the perovskite active phase and porosity when the material was calcined at 1200 ºC for sintering of the reticulated porous material. On the other hand, it was very remarkable that both materials maintained their physical reticulated porous structure

after 5 hours on operation. Moreover, the leaching of the metal containing in the perovskite catalyst was almost negligible.

In order to assess the influence of the temperature in continuous operation of the up-flow fixed bed reactor using the reticulated porous perovskite material RPP-1000, additional catalytic runs were carried out at 50 and 90 ºC. These experiments were performed maintaining the acidification of the hospital wastewater up to 5.5, the stoichiometric amount of H_2O_2 (700 mg/L) and the residence time at 3 min. Figure 4 shows the hydrogen peroxide conversion and the CZP removal at steady-state conditions after 5 hours of continuous operation at 50, 70 and 90 ˚C. At 50 ˚C, 82 % of CZP was eliminated but not all the hydrogen peroxide was used (74 % of oxidant conversion). The increase of temperature up to 90 ˚C allows a total oxidant conversion with the increase of the CZP removal until 92 %. It must be noted that the stability of the reticulated porous perovskite material was not significantly affected by the increase of temperature, with concentrations of La, Cu and Mn in the outlet effluent ranging from 0.2-3.8 mg/L, 1.0-2.3 and 3.2-5.9, respectively. The overall metal leaching from the solid catalyst after 5 hours of operation was in all the cases lower than 8 %. These results indicate a high stability of the reticulated porous perovskite catalysts. Additionally, the initial H_2O_2 concentration was decreased from 700 to 350 mg/L at 70 ˚C in order to evaluate the performance of the RPP-1000 material at a lower oxidant dosage (Figure 4). It must be noted that the hydrogen peroxide is the most significant cost in Fenton operation process. The removal of carbamazepine significantly decreases at steady state (after 5 hours of operation) from 87 % to 40 %. Additional catalytic run in absence of hydrogen peroxide evidenced a negligible CZP removal (see Figure 4). These results indicates the important role of the oxidant in the production of hydroxyl radicals and consequently the oxidation of carbamazepine [49]. Thus, the catalytic performance is enhanced by the temperature and the catalyst was very stable even at 90 ºC. The intermediate temperature of 70 ˚C allowed a remarkable CZP removal (ca. 87 %) with an almost total oxidant conversion (93 %). Moreover, the results of a non-catalytic run with only hydrogen peroxide proved the active role of the catalyst. The run performed in absence of catalyst (RPP-1000 replaced by equivalent volume of glassy spheres of 1 mm diameter) achieved only a 30 % of CZP removal by the potential oxidation of hydrogen peroxide (Figure 4). The H_2O_2 conversion and CZP removal of the catalytic runs performed at different temperatures and hydrogen peroxide dosages along the time on operation are shown in Figure 5_SM and 6_SM, respectively.

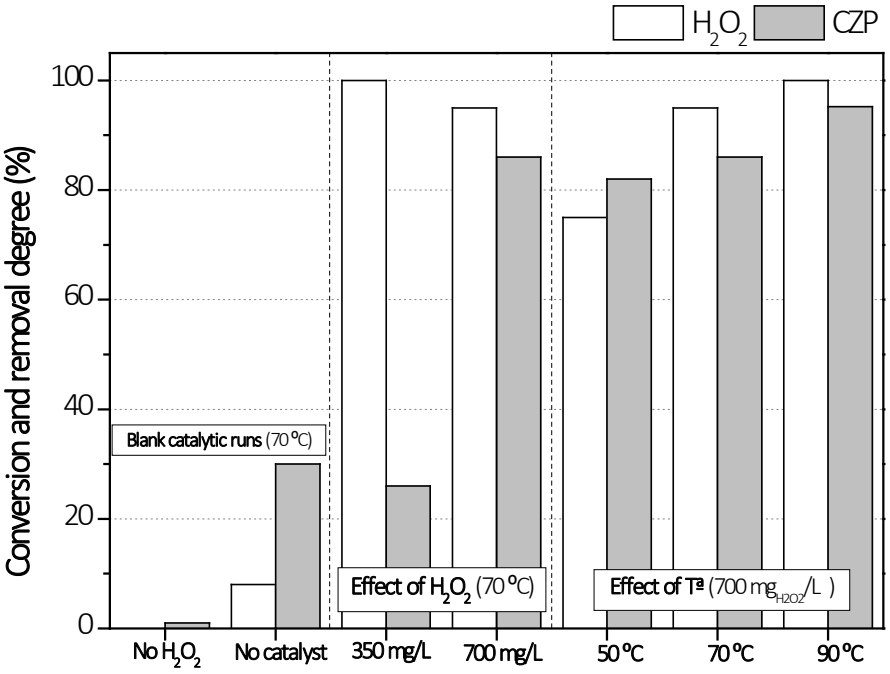


Figure 4. Influence of temperature and hydrogen peroxide dosage on the catalytic performance of reticulated porous perovskite material RPP-1000 in a catalytic fixed bed reactor. Operation conditions: HWW spiked with CZP (15 mg/L), acidification at pH of 5.5, residence time = 3 min.

Few works have approached the study of continuous Fenton processes using heterogeneous catalytic systems for long periods of operation [50,51]. Iron nanoparticles embedded within ordered mesoporous carbon catalyst (Fe-OMC) showed a phenol conversion above 90 %, although the efficiency decreased during 39 h of long-term evaluation [50]. A Highly dispersed Fe^{3+}-Al_2O_3 catalyst (6 wt. % Fe) retained remarkable mineralization levels of phenol (X_{TOC}> 70%) with a cumulative iron loss of ca. 20 % of the initial Fe loaded in an up-flow fixed bed reactor (UFBR) after 70 hours on operation [51]. In this work, the catalytic performance of reticulated porous perovskite catalyst was tested for 70 hours at 70 ºC, slight acid pH (5.5) and moderate hydrogen peroxide concentration (700 mg/L) in order to assess the feasibility of the catalyst for long-term continuous treatment of the hospital wastewater. Figure 5 shows the results of oxidant conversion and CZP removal along the time on operation. Interestingly, the CZP elimination increases up to complete removal after 10 h on operation accompanied with a total hydrogen peroxide conversion. Moreover, the reticulated porous perovskite material keeps constant a total CZP removal and hydrogen peroxide conversion and maintains its mechanical integrity up to 70 h on operation. The TOC reduction was of hardly 10 % at steady-state

conditions, as consequence of the refractory behaviour of the complex HWW matrix. Therefore, this catalytic system is proposed as an alternative on-site pre-treatment for the removal of pharmaceutical micropollutants, prior to discharge of the HWW into the sewer system for final depuration of the water in a conventional WWTP [5]. These results make this reticulated porous perovskite catalyst a promising catalyst to be applied in continuous Fenton processes based on fixed bed reactors, in this case for the removal of pharmaceutical micropollutants in hospital wastewaters.

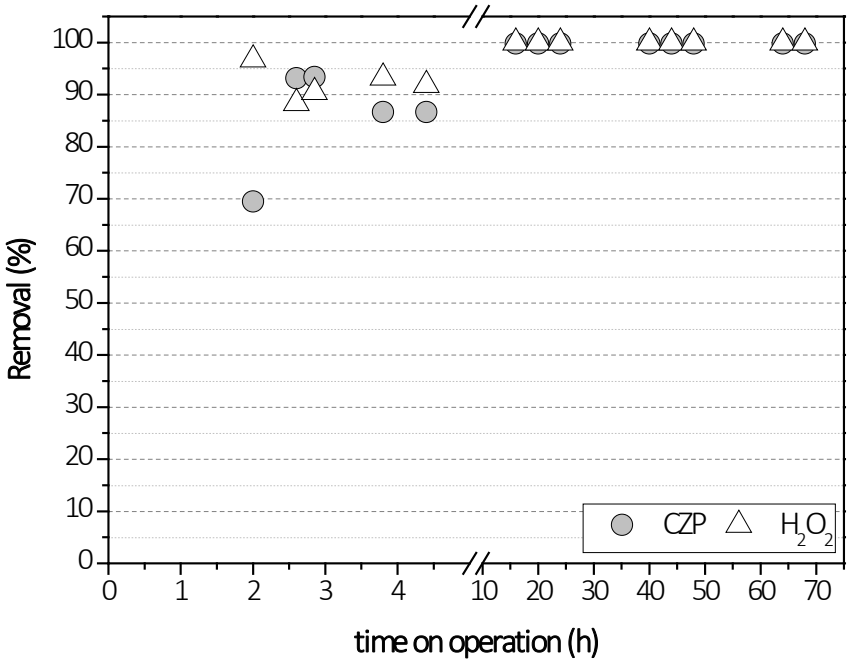


Figure 5. Long term catalytic run of reticulated porous perovskite material RPP-1000 in a catalytic fixed bed reactor. Operation conditions: HWW spiked with CZP (15 mg/L), acidification at pH of 5.5, 70 ºC, [H_2O_2] = 700 mg/L and residence time = 3 min.

3.4. Catalytic performance of reticulated porous perovskite material for the removal of emerging pharmaceutical micropollutants of hospital wastewater

The removal of the pharmaceutical micropollutants contained in the HWW at their original concentration was evaluated. In this case, additional carbamazepine was not spiked in the HWW. Figure 6 shows the concentration of the pharmaceutical micropollutants before and after the treatment and the removal efficiency using the reticulated porous perovskite material RPP-1000 in the fixed bed reactor. Eighteen pharmaceutical micropollutants were detected in the hospital wastewater (Table 1_SM). Antypirine (AAA), amoxicillin (AMZ), caffeine (CFN),

azithromycin (AZM), cyclophosphamide (CPD), iohexol (IHX) and sulpiride (SPD) were the most abundant compounds with concentrations ranging from 10 to 390 μg/L. These drugs are commonly used in hospitals as analgesic/anti-inflammatory, antibiotic, stimulating, antineoplastic, X-ray agent and psychiatric drugs. Gemfibrozil (GFZ), ibuprofen (IBU), ranitidine (RNT) and sulfamethoxazole (SMX) as lipid regulator, anti-inflammatory, antagonist receptor and antibiotic, respectively, were found in concentrations from 1 to 10 μg/L. The rest of compounds including bisphenol A (BPA), carbamazepine (CZP), diclofenac (DCF), hydrochlorothiazide (HCT), metoprolol (MTP), metrodinazole (MDZ) and progesterone (PGT), were detected in much lower concentrations (< 1 μg/L). The presence and concentrations of these pharmaceutical micropollutants in the HWW are in accordance to the typical characterization of these effluents with analgesics, antibiotics and contrast agents as some of the main contributing therapeutic groups [52]. The catalyst was extremely efficient for the removal of 9 micropollutants with concentrations after treatment below the detection limits. All the most abundant compounds (CFN, CPD, AZM, IHX, SPD, AMX and AAA) were eliminated with efficiencies above 95 % and 90 % for the case of HCT. Only two compounds detected at very low concentrations such as metropolol (MTP, 0.42 ± 0.45 μg/L) and carbamazepine (CZP, 0.13 ± 0.01 μg/L) showed lower removal degrees. The low removal efficiency of these two micropollutants can be due to the lower efficiency of hydroxyl radicals for oxidizing more diluted concentration. Moreover, very low concentrations are more susceptible to sampling and analytical error [53]. Nevertheless, it must be noted that the remaining CZP and MTP concentrations (ca. 0.09 μg/L and 0.13 μg/L, respectively) are quite lower than their predicted non-effect concentration (PNEC) (2.5 μg/L and 7.9 μg/L, for CZP and MTP, Table 1_SM). It also occurs for the remaining PCs' concentrations in the treated HWW (Table 1_SM), demonstrating that the risk for aquatic organisms can be ruled out after this Fenton heterogeneous treatment.

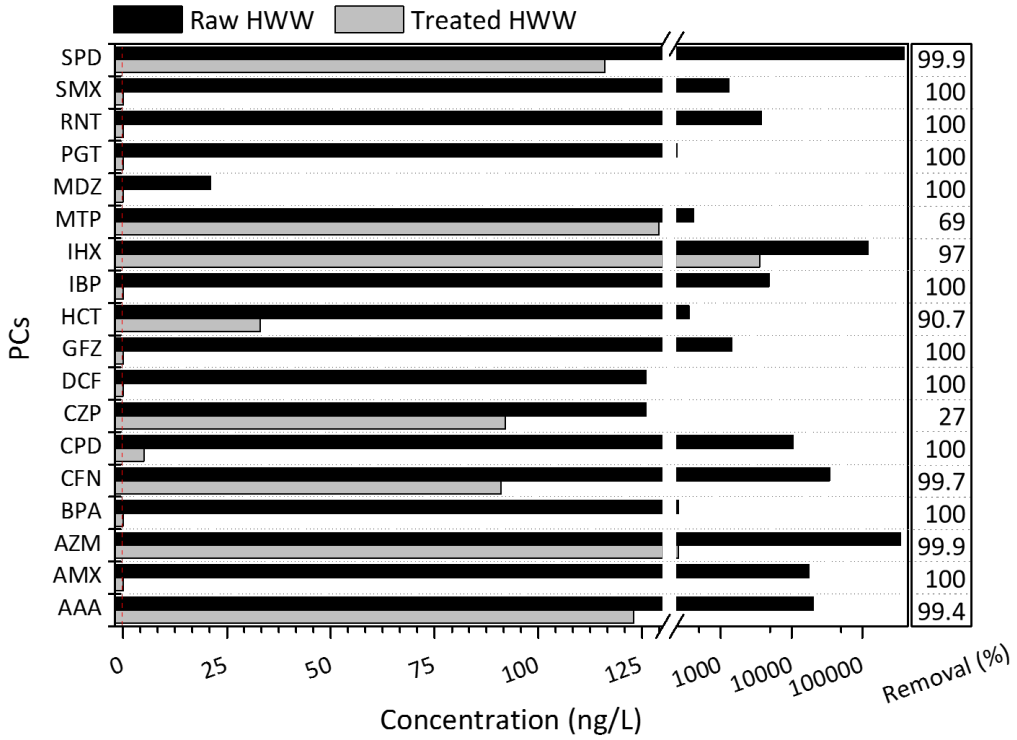


Figure 6. Concentration of pharmaceutical micropollutants in the raw and treated HWW after the Fenton treatment in the FBR and removal efficiencies achieving for each PC. Reaction conditions: T = 70 ˚C, pH = 5.5, $[H_2O_2]_0$ = 700 mg/L, $LaCu_{0.5}Mn_{0.5}O_3$-RPC = 3 g = 3 g and flow rate = 1 mL/min (t_R = 3 min).

4. CONCLUSIONS

Powdered $LaCu_{0.5}Mn_{0.5}O_3$ perovskite was successfully immobilized on a reticulated porous structure by double impregnation and calcination at 1000 ˚C, achieving a high mechanical resistance and non-alteration of its characteristic ABO_3 lattice. The activity and stability of $LaCu_{0.5}Mn_{0.5}O_3$ perovskite as heterogeneous Fenton-like catalyst was tested for the removal of carbamazepine spiked in a hospital wastewater matrix as model pollutant. The powdered $LaCu_{0.5}Mn_{0.5}O_3$ perovskite showed a complete CZP removal (120 minutes) and low values of metal leaching (< 1 mg/L) at the natural pH of the wastewater (7.5) and 70 °C. At pH of 3, the stability of the perovskite dramatically decreased. The acidification until pH of 5.5 allows a complete CZP removal in 20 minutes with a remarkable enhancement of the stability. The reticulated porous perovskite catalyst has achieved a complete removal of CZP at steady-state conditions in an up-flow fixed bed reactor for the continuous treatment of a wastewater fortified with CZP at weak acid pH (5.5), 70 ˚C and moderate dosage of hydrogen peroxide (700 mg/L).

494 This catalyst maintained its mechanical integrity and catalytic activity for 70 hours on operation.
495 Likewise, the most abundant compounds (CFN, CPD, AZM, IHX, SPD, AMX and 4-AAA) of the
496 hospital wastewater at the real concentrations of μg/L were eliminated with high efficiencies
497 between 95 and 100 %. Only some compounds detected at the lowest concentrations (< 1 μg/L)
498 showed lower removal degrees. The catalytic activity and the low leaching of the reticulated
499 porous $LaCu_{0.5}Mn_{0.5}O_3$ perovskite for operation at weak acid pH makes this material a promising
500 catalyst for application in Fenton-like processes using up-flow fixed bed reactors.

501

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507

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