

1           **Degradation of seventeen contaminants of emerging concern in**  
2           **municipal wastewater effluents by sonochemical advanced oxidation**  
3                                   **processes**

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22 **Abstract**

23 The simultaneous degradation of seventeen emerging concern pollutants in effluent  
24 from the municipal wastewater treatment plant (MWTP) of Bogotá-Colombia was  
25 studied using high frequency ultrasound (375 kHz). The considered compounds in the  
26 effluent corresponded to pharmaceuticals (diclofenac, carbamazepine, venlafaxine,  
27 ciprofloxacin, norfloxacin, valsartan, losartan, irbesartan, sulfamethoxazole,  
28 clarithromycin, azithromycin, erythromycin, metronidazole, trimethoprim and  
29 clindamycin); cocaine and its major metabolite benzoylecgonine. Due to limitation of the  
30 MWTP for the pollutants elimination, ultrasound was applied to remove these  
31 compounds. Interestingly, ultrasonic physical action led to releasing of ciprofloxacin,  
32 norfloxacin, diclofenac and sulfamethoxazole from suspended solids, whereas the  
33 chemical effects induced degradation of the rest of compounds. For the latter ones, an  
34 interesting correlation between the sonodegradation and arithmetic multiplication  
35 between hydrophobicity and concentration of pollutants was established. Afterwards,  
36 the sonochemical process was complemented with ferrous ions (sono-Fenton), ferrous  
37 ions plus light (sono-photo-Fenton) or ferrous ions plus light in presence of oxalic acid  
38 (sono-photo-Fenton/oxalic acid). Additionally, to clarify fundamental aspects of the  
39 different systems, individual treatments in distilled water of a model pollutant (valsartan)  
40 were performed. The complemented processes significantly enhanced all compounds  
41 degradation, following the order: sono-photo-Fenton/oxalic acid > sono-photo-Fenton ~  
42 sono-Fenton > sonochemistry. The Fe<sup>2+</sup> addition improved the pollutants elimination by  
43 generation of more hydroxyl radicals in the solution bulk. Meanwhile, oxalic acid  
44 avoided Fe<sup>3+</sup> precipitation favoring the iron catalytic cycle. Thus, the work demonstrates

45 the high potentiality of the sono-photo-Fenton/oxalic acid system for the pollutants  
46 elimination in real-world wastewater matrices.

47  
48 **Keywords:** Emerging pollutants; High frequency ultrasound; Advanced oxidation  
49 processes; Wastewater treatment; Sono-photo-Fenton, Sono-photo-Fenton/oxalic acid.

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## 52 **1. Introduction**

53 It is worldwide recognized that municipal wastewater treatment plants (MWTP) are not  
54 designed to deal with emerging concern pollutants (Verlicchi et al., 2012), which are  
55 commonly at very low concentrations in these matrices. Nowadays, both,  
56 pharmaceuticals and illicit substances are considered as emerging concern pollutants,  
57 they generally have cell membrane penetration easiness, favoring their toxic effects  
58 (Brausch et al., 2012). Pharmaceuticals as analgesics, psychiatric products,  
59 antihypertensives and antibiotics are frequently found in wastewaters (Campanha et al.,  
60 2015; Fatta-Kassinos et al., 2011; Ghoshdastidar et al., 2015; Gracia-Lor et al., 2012;  
61 Gros et al., 2010; Hernández et al., 2015a; Verlicchi et al., 2012), and such substances  
62 reach the aquatic environment even in pristine areas as the Antarctic (González-Alonso  
63 et al., 2017; Hernández et al., 2018). Also, illicit substances are commonly measured in  
64 MWTP effluents, as they are not completely removed with conventional treatments  
65 (Bijlsma et al., 2014; Parolini et al., 2018, 2017). Hence, due to the limitations of most  
66 treatments applied in MWTP, alternative and/or additional processes are required for

67 the elimination of these problematic compounds to decrease their negative impact on  
68 the environment.

69 Advanced oxidation processes (AOP), which are characterized by the formation and  
70 utilization of radical species (typically hydroxyl radical), have been used as effective and  
71 alternative treatments for complex wastewater, especially in the case of the non-  
72 biodegradable compounds (Boczkaj and Fernandes, 2017). Recently, it is gaining  
73 attention the application of AOP based on sulfate radical (Fernandes et al., 2018b;  
74 Serna-Galvis et al., 2017; Shah et al., 2018), AOP at alkaline pH (Boczkaj and  
75 Fernandes, 2017; Fernandes et al., 2018a) and treatments involving cavitation  
76 phenomena to degrade pollutants (Gagol et al., 2018a).

77 There are diverse ways of cavitation; e.g., hydrodynamic cavitation or vibrational  
78 cavitation (also called acoustic cavitation or sonochemistry (Gagol et al., 2018a)). The  
79 combination of cavitation (hydrodynamic or acoustic) with external oxidizing agents  
80 (e.g., hydrogen peroxide, ozone, peroxone) is a potent way to generate extra radicals  
81 and remove diverse organic compounds (Gagol et al., 2018; Gagol et al., 2018b). Also,  
82 the sonochemical process has been found to be efficient for the degradation of  
83 recalcitrant pollutants in water (Serna-Galvis et al., 2016, 2015; Torres-Palma and  
84 Serna-Galvis, 2018; Villaroel et al., 2014; Xiao et al., 2014).

85 Sonochemistry uses high-frequency ultrasound waves to produce hydroxyl radical. The  
86 process implies formation and growth of micro-bubbles until reaching a critical size, at  
87 which they violently collapse (i.e., acoustic cavitation). The collapse of the micro-  
88 bubbles induces hot spots generation with singular conditions of pressure (~1000 atm)  
89 and temperature (~5000 K) (Adewuyi, 2001), producing hydroxyl radicals from

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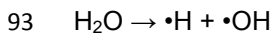
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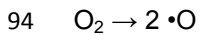
90 dissociation of water molecules and oxygen (Eq. 1-4). Furthermore, in sonochemistry,  
91 hydrogen peroxide is formed through hydroxyl radicals combination (Eq. 5).

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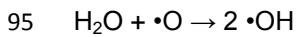
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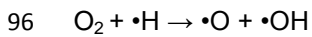
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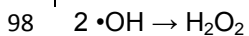
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99 The most works about sonochemical degradation of pollutants are typically focused on  
100 individual compounds in synthetic water (Serna-Galvis et al., 2015; Villaroel et al., 2014;  
101 Villegas-Guzman et al., 2015), and only few papers deal with sono-treatment of real-  
102 world municipal wastewaters (Naddeo et al., 2013; Xiao et al., 2014). Even more scarce  
103 is the information regarding high-frequency ultrasound improved with other AOPs for the  
104 treatment of wastewater containing pollutants at realistic low concentrations, i.e.,  
105 (sub)ppb (i.e.,  $\mu\text{g L}^{-1}$  to  $\text{ng L}^{-1}$ ).

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106 Considering the absence of relevant studies on this issue, the present work evaluates  
107 the simultaneous degradation of seventeen emerging concern pollutants (fifteen  
108 representative pharmaceuticals, an illicit drug and its main metabolite) at actual low  
109 concentrations ( $\mu\text{g L}^{-1}$  to  $\text{ng L}^{-1}$  levels) in real effluents from Bogotá-Colombia by high-  
110 frequency ultrasound and its complementation with iron and UVA light. After proving  
111 that most of the considered pollutants were not completely removed by the MWTP, the

112 ultrasonic system was applied to effluents from the plant. Sonochemical processes  
113 showed degrading action on the pollutants. Then, a possible correlation of sono-  
114 degradation rates with hydrophobicity and concentration of pollutants was studied.  
115 Afterwards, the addition of iron, UVA light and oxalic acid to ultrasound (i.e., sono-  
116 Fenton, sono-photo-Fenton and sono-photo-Fenton/oxalic acid) to enhance the  
117 pollutants elimination was evaluated. Furthermore, to better understand the  
118 fundamental aspects of these systems, valsartan (representative pollutant in the  
119 effluent) was selected as model compound and treated in distilled water.

120

## 121 **2. Experimental**

### 122 **2.1 Reagents**

123 Reference standards of pharmaceuticals and illicit drugs for LC-MS/MS analysis were  
124 acquired from Sigma-Aldrich, LGC Promochem and Toronto Research Chemicals. More  
125 details on reagents and chemicals used in analysis can be found in Text SM1  
126 (Supplementary material) and the reference (Botero-Coy et al., 2018).

127 Valsartan for individual experiments was purchased from Tecnoquímicas S.A. Oxalic  
128 acid and iron sulfate heptahydrate were obtained from Panreac and Merck, respectively.

129 Potassium iodide, ammonium heptamolybdate, acetonitrile and methanol were provided  
130 by Merck. Formic acid was purchased from Carlo-Erba.

131

### 132 **2.2 MWTP sampling and sonochemical reaction system**

133 Wastewater effluent samples (24-h composite) were taken from El salitre MWTP in  
134 Bogotá-Colombia using a volume-proportional sampling mode (every 2500 m<sup>3</sup>)

135 approximately every 10 min, during seven days using an auto-sampler Endress-Hauser.  
136 Then, the daily 24-h composites were mixed and such homogenized mixture was  
137 considered as the whole sample for the treatments.

138 The treatments were carried out in a Meinhardt ultrasound batch reactor with capacity of  
139 500 mL and 88 W L<sup>-1</sup> of actual ultrasonic power density (measured by calorimetric  
140 method (Kimura et al., 1996)). The reactor was operated at 375 kHz of frequency. The  
141 transduction efficiency of the reactor was 13%. In each experiment, a sample of 300 mL  
142 was treated. Reactor temperature was controlled at 20°C using a Huber Minichiller. In  
143 the light-complemented systems was used a Sylvania® UVA-lamp (BLB) of 4 W placed  
144 on a quartz sleeve and submerged in the ultrasonic reactor (Figure SM1, in  
145 Supplementary material). All ~~treatments experiments by sonochemistry and~~  
146 ~~sonochemistry/Fenton based processes of the samples~~ were performed at least by  
147 duplicate.

148

### 149 **2.3 Analyses**

150 The seventeen compounds were selected based on the previous studies on their  
151 occurrence in wastewaters from Bogotá-Colombia (Bijlsma et al., 2016; Botero-Coy et  
152 al., 2018). The determination of pharmaceuticals, cocaine and benzoylecgonine in  
153 wastewater was performed by liquid chromatography coupled to tandem mass  
154 spectrometry (LC-MS/MS) with triple quadrupole. Analyses to obtain the concentration  
155 of pollutants in the sample were carried out before and during each experiment.  
156 Quantification of compounds was made using the quantification transition (Q), external  
157 calibration with standards in solvent and relative peak areas with isotope-labeled

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158 internal standard (ILIS) (up to 12 ILIS were available for the compounds under study).  
159 The reliable identification of compounds in the samples was ensured by the ion ratios  
160 between the quantification (Q) and confirmation ( $q_1$  and  $q_2$ ) transitions, and by  
161 chromatographic retention time (tolerance ranges  $\pm 30\%$  for ion ratio,  $\pm 0.1$  min for  
162 retention time, in comparison with the reference standards injected in the calibration).  
163 Quality control samples (QCs) were included in every sample sequence to ensure  
164 reliability of concentration data. QCs consisted on real-world wastewater samples  
165 spiked at two concentrations, 0.1 and 1.0  $\mu\text{g/L}$ , which were analyzed within the batch  
166 following the same analytical procedure than for the samples. Most of QCs recoveries  
167 were satisfactory, with the wide majority within the range 70-120%, at the two levels  
168 tested. More details on the analytical methodology applied can be found in (Botero-Coy  
169 et al., 2018).

170 Chemical oxygen demand (COD) of the effluent was established following to the  
171 Standard Methods for Examination of Water and Wastewater (5220); according to the  
172 reported previously (Serna-Galvis et al., 2015). The pH of the effluent was measured  
173 using a pH93 pH-meter.

174 Total organic carbon (TOC) of the effluent was measured using a Shimadzu LCSH TOC  
175 analyzer. This was determined by combustion with catalytic oxidation at 680 °C using  
176 high-purity oxygen gas at a flow rate of 190 mL/min. The apparatus had a non-  
177 dispersive infrared detector. Calibration of the analyzer was attained with standard  
178 potassium hydrogen phthalate (99.5%) solution. The injection sample volume was 50  
179  $\mu\text{L}$ . Total suspended solids were determined by sewerage and Sanitation Company of  
180 Bogotá (EAAB-ESP) and taken from its monthly report of activities (EAB-ESP, 2018).

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181 Soluble iron was determined through the phenanthroline method by adding 80  $\mu\text{L}$  of the  
182 hydroxylamine hydrochloride solution and 200  $\mu\text{L}$  of the 1,10-phenanthroline solution  
183 were added to 1320  $\mu\text{L}$  of the sample. The pH of each cell was regulated with 400  $\mu\text{L}$  of  
184 the sodium acetate solution. The sample was homogenized and after 15 min of reaction  
185 in dark, the absorbance reading at 510 nm was carried out.

186 The evolution of valsartan (the model pollutant for the individual degradation) in distilled  
187 water was followed using a UHPLC Thermoscientific Dionex UltiMate 3000 instrument  
188 equipped with an Acclaim™ 120 RP C18 column (5  $\mu\text{m}$ , 4.6 x150 mm) and a diode  
189 array detector. The mobile phase was 10/46/44 % (v/v/v) methanol/acetonitrile/formic  
190 acid 10 mM at pH 3.0, the chromatograph was run in isocratic mode at 0.4  $\text{mL min}^{-1}$   
191 and the pollutant detected at 254 nm.

192 The accumulation of sonogenerated hydrogen peroxide was estimated by iodometry  
193 method (Text SM2) as reported by Serna-Galvis *et al.* (Serna-Galvis *et al.*, 2015). The  
194 possible primary products of valsartan sonodegradation were identified by LC coupled  
195 to high resolution MS (LC-HRMS) using a hybrid quadrupole-time of flight (QTOF)  
196 analyzer. For this purpose, an approach based on common fragmentation pathway was  
197 applied assuming that most degradation products share the fragmentation pathway with  
198 the parent compound. More details about the instrumental conditions as well as the  
199 elucidation strategy can be found in the following references (Ibáñez *et al.*, 2016;  
200 Martínez-Pachón *et al.*, 2018) and Supplementary material.

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### 202 **3. Results and Discussion**

#### 203 **3.1. Inability of the MWTP for complete pollutants removal**

204 El salitre MWTP has a pre-treatment step (screening unit) and a primary treatment  
205 circuit (coagulation, flocculation and sedimentation units). The pre-treatment uses a bar  
206 to filter large solids and objects, which are collected in dumpsters and disposed in  
207 landfills. The primary treatment circuit conducts to removal of suspended solids and  
208 organic matter. El salitre plant normally operates at 4 m<sup>3</sup>/s (~350,000 m<sup>3</sup>/day), with a  
209 removal efficiency of 40% biological oxygen demand and 60% of suspended solids  
210 (EAB-ESP, 2018).

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211 Table SM1 presents the basic global parameters of the considered effluent (the mixture  
212 of seven days effluent samples). It can be noted that the effluent has a medium organic  
213 charge due to the moderate removal efficiency of the plant as above reported.  
214 Meanwhile, the target pollutants are contained at the concentrations reported in Figure  
215 1. In the effluent, the valsartan and losartan antihypertensives are at the highest  
216 concentrations followed by benzoylecgonine (cocaine metabolite), the anti-inflammatory  
217 diclofenac and the fluoroquinolone antibiotics (ciprofloxacin and norfloxacin). Due to the  
218 very high consumption, such substances (or their parent compounds) are vastly  
219 concentrated in wastewater and the treatment plant is unable to completely remove  
220 them (Botero-Coy et al., 2018). For example, losartan is an antihypertensive widely  
221 used in Colombia; indeed, problems about its improper use (related to over-dose) in  
222 daily practice have been found (Portilla et al., 2017). Ciprofloxacin is among the top 5  
223 most common antibiotics in Colombian hospitals of third generation (Alvarez et al.,  
224 2016), and its presence in Colombian hospital wastewater has been reported (Botero-  
225 Coy et al., 2018). Meanwhile, cocaine is a highly consumed illicit drug in populated

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226 Colombian cities such as Bogotá; consequently, its main metabolite (benzoylecgonine)  
227 has a high prevalence in wastewaters (Bijlsma et al., 2016; Hernández et al., 2015b).

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228 In our previous work, we studied the ability of conventional processes applied in El  
229 salitre MWTP to eliminate the emerging concern pollutants (Figure SM2) (Botero-Coy et

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230 al., 2018). A limited efficiency of the treatment plant for the pollutants removal was  
231 observed. In fact, some pharmaceuticals concentration in the effluent were higher than  
232 in influent (e.g., erythromycin, metronidazole, sulfamethoxazole and trimethoprim; which  
233 presented negative removal efficiencies). In some cases, MWTP can act as pollutants  
234 concentrators. This situation is not exclusive for El salitre MWTP, similar facts have  
235 been reported by Lacey *et al.*, Gros *et al.* and Jelic *et al.* (Gros et al., 2010; Jelic et al.,  
236 2010). Thus, the incomplete removals, even the increasing of pollutants concentration  
237 by conventional processes in MWTP, evidence the need of alternative/complementary  
238 treatment technologies.

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### 240 **3.2 Degradation of the 17 emergent pollutants by ultrasound**

241 Sonochemistry was applied to the effluent during 90 min to evaluate its degrading ability  
242 on the selected pollutants in the complex water. Therefore, the evolution of each  
243 contaminant under study was followed (Figure 2). It is worthy to note that for a few  
244 compounds, such as diclofenac, sulfamethoxazole, ciprofloxacin and norfloxacin, the  
245 ultrasound action increased their concentrations, whereas for the rest of pollutants the  
246 concentration decreased with the treatment time.

247 Due to the effluent contains suspended solids (Table SM1), some pollutants are sorbed  
248 on such solids. It is reported that non-ionic compounds tend to be highly sorbed onto

249 organic matter through van der Waals interactions; whereas for those pollutants with  
250 polar and/or charged functional groups, their sorption is governed by the combination of  
251 electrostatic interactions and van der Waals forces (Hyland et al., 2012). In fact,  
252 electrostatic interactions are determinant for the sorption of fluoroquinolone  
253 pharmaceuticals (e.g., ciprofloxacin and norfloxacin) on sewage solids (Ternes et al.,  
254 2004; Wu et al., 2009). Meanwhile, diclofenac presents a medium affinity towards  
255 sewage solids (Berthod et al., 2014; Ternes et al., 2004). In the case of the antibiotic  
256 sulfamethoxazole, although this pollutant has weak interactions, it can experiment some  
257 sorption on such solids (Yang et al., 2011).

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258 Considering the sorption phenomena, the results in Figure 2 can be rationalized based  
259 on the physical and chemical effects of ultrasound. The physical action of ultrasound  
260 (i.e., turbulence and high shearing in the liquid medium by cavitation phenomena)  
261 induces size reduction of solids and release sorbed pollutants (Gunduz, 2009; Torres-  
262 Palma et al., 2017; Zorba and Sanin, 2013). Consequently, the concentration of  
263 released substances (i.e., ciprofloxacin, norfloxacin, diclofenac and sulfamethoxazole)  
264 is increased. It should be indicated that suspended solids can also induce the formation  
265 of cavitation bubbles (Mason and Pétrier, 2004), which can favor the sonochemical  
266 process application.

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267 The removal of the pollutants can be associated to the chemical effects of the process.  
268 As indicated in the introduction, high frequency ultrasound produces radical species.  
269 Radicals can attack the pollutants decreasing their concentration (Figure 2). Also, it can  
270 be mentioned that the sorption on solids hiders the direct attack of radicals to sorbed

271 compounds. However, when they are released, such compounds are more available for  
272 sonodegradation.

273 In ultrasound, degradation by pyrolysis as well as the interaction between pollutants and  
274 hydroxyl radical, depends on their proximity to the cavitation bubbles. Such proximity is  
275 determined by the initial concentration and the hydrophobic character of the compounds

276 (Torres-Palma and Serna-Galvis, 2018). Then, to evaluate the concentration feature,  
277 the initial molarity of pollutants was calculated and the sonochemical degradation rate  
278 for each pollutant was measured (Table 1). Interestingly, upon ultrasound action, the  
279 substances with the highest initial molar concentrations (e.g., losartan, valsartan and  
280 benzoylecgonine) had faster degradation (Table 1). This is because a higher  
281 concentration favors the pollutant diffusion toward the cavitation bubble increasing the  
282 probability of contact with hydroxyl radicals (Torres-Palma and Serna-Galvis, 2018).

283 For the evaluation of the hydrophobicity effect, pairs of substances with close molar  
284 concentration (valsartan-benzoylecgonine, clarithromycin-irbesartan (also azithromycin)  
285 and carbamazepine-cocaine) were considered; then, their Log Kow values (which are  
286 hydrophobicity indicators) and degradation were compared (Table 1). From each pair,  
287 the compound having the higher Log Kow (i.e., the more hydrophobic) presented larger  
288 degradation rate. This means that the more hydrophobic pollutants in the effluent are  
289 faster degraded because they are nearer the cavitation bubbles; and consequently,  
290 more susceptible to experiment reaction with hydroxyl radicals.

291 A possible way to conjugate concentration and hydrophobicity is the arithmetic  
292 multiplication between these two factors (which would denote the closeness to  
293 cavitation bubble in the sonochemical system). Indeed, the plot of degradation rate vs.

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294 C\*Log Kow (i.e., concentration multiplied by hydrophobicity) shows a very good  
295 correlation ( $R = 0.985$ , Figure 3). This means that among a set of pollutants,  
296 hydrophobic compounds and highly concentrated are faster degraded; whereas the  
297 lowly concentrated and hydrophilic substances have very slow degradation rates.  
298 Additionally, from groups of pollutants with similar hydrophobicity the more concentrated  
299 compounds will experiment high degradation rates. Meanwhile, for compounds at  
300 similar concentration, the degradation was higher with the increasing of the hydrophobic  
301 character of the substance. Regarding the pollutants released from solids by the  
302 physical action of ultrasound, their degradation by hydroxyl radicals or pyrolysis could  
303 be plausible after a more prolonged action of the sonochemical process (i.e., at  
304 treatment times higher than 90 min).

305 To better understand the chemical effects of ultrasonic process on pollutants, the  
306 treatment of the model compound (valsartan) under controlled conditions was carried  
307 out. Such substance was selected considering its high hydrophobicity and concentration  
308 in the effluent sample (Table 1). Furthermore, valsartan represents a risk in the  
309 environment because it can be transformed into valsartan acid, which is a very mobile  
310 and persistent compound (Berkner and Thierbach, 2014). Thus, valsartan degradation  
311 was initially performed in distilled water to avoid matrix interferences. Afterwards, the  
312 role of suspended solids was also tested by means of valsartan spiking in effluent with  
313 and without solids (Text SM3).

314 Figure 4 presents the evolution of valsartan submitted to high frequency ultrasound in  
315 distilled water. The process degraded ~ 60% of the compound after 30 min of treatment.  
316 In addition to the pollutant degradation, the accumulation rate ( $R_a$ ) of hydrogen

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317 peroxide (which is an indirect indicator of hydroxyl radical production ability of  
318 ultrasound, Eq. 5) in both presence (VAL) and absence of valsartan (BK) was also  
319 measured (Figure 4). The Ra in the presence of the pollutant is lower than in the  
320 absence, indicating that the reaction of valsartan with sonogenerated radicals limits the  
321 H<sub>2</sub>O<sub>2</sub> accumulation.

322 The structure of the degradation products, elucidated by QTOF MS, indicates that they  
323 are formed from the attack of •OH to tetrazole ring (DP1), biphenyl moiety (DP2) and  
324 pentanamide group (DP3, DP4 and DP5) (Table 2). This indicates the high reactivity of  
325 such functional groups on valsartan toward the sonogenerated hydroxyl radical. The  
326 attacks to tetrazole ring and biphenyl moiety are additions to pi-systems, which are  
327 typical pathways of •OH (Martínez-Pachón et al., 2018). Meanwhile, the action on  
328 pentanamide can be described as an initial hydrogen abstraction by hydroxyl radical (a  
329 common pathway reported for alkyl-amides (Doan et al., 2010; Hayon et al., 1970)) and  
330 the posterior evolution to the oxidized forms of carbon on the alkyl-chain. Consequently,  
331 if valsartan, a hydrophobic and highly concentrated pollutant in the MWTP, is degraded  
332 by hydroxyl radical action, it can be proposed that the other substances (which are less  
333 concentrated and/or more hydrophilic) are also eliminated by the •OH attacks.

334 Regarding the role of suspended solids, it must be indicated that they may have a dual  
335 effect. Extra cavitation bubbles can be formed thought trapped air inside of the solids  
336 (Mason and Pétrier, 2004). However, solids can also provoke cavitation attenuation  
337 (Larrarte and François, 2012). Then, to evaluate the effect of suspended solids in the  
338 sonochemical process, degradation of spiked valsartan in the effluent with and without  
339 solids was tested. As seen in Figure SM3, under work conditions, the valsartan

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340 degradation is slightly favored in absence of solids. Nevertheless, it is remarkable the  
341 ability of ultrasound to remove pollutants even in the presence of suspended solids  
342 (Figure 2 and Figure SM3).

343 On the other hand, considering that the sonochemical reactor operation at  $88 \text{ W L}^{-1}$   
344 represents high consumption of electrical energy, degradation times longer than 90 min  
345 were not evaluated. Additionally, taking into account that the hydrogen peroxide (a sub-  
346 product of ultrasonic process) can be used to produce more radicals by addition of iron  
347 ions and light (i.e., photo/Fenton based processes) as an interesting option to achieve  
348 higher and faster elimination of pollutants and decrease the energy consumption  
349 respect to the sonochemical or photochemical processes acting alone (Torres et al.,  
350 2007, 2008a, 2008b). Hence, the addition of iron and light to the sonochemical process  
351 for the effluent treatment was evaluated.

352

### 353 **3.3 Improvement of sonochemical degradation by addition of iron, UVA light and** 354 **oxalic acid**

355 The pollutants removal by sonochemical process with addition of ferrous ions (sono-  
356 Fenton), ferrous ions plus light (sono-photo-Fenton) or ferrous ions plus light in  
357 presence of oxalic acid (sono-photo-Fenton/oxalic acid) was tested. Figure 5 shows the  
358 behavior of pollutants under the different systems. It can be noted that in these  
359 processes the concentrations of diclofenac, ciprofloxacin and norfloxacin (the supposed  
360 sorbed compounds) decreased as the treatment time increased. Under sono-Fenton  
361 and sono-photo-Fenton treatments, sulfamethoxazole concentration increased initially,  
362 but it decreased as the processes was progressing. Remarkably, in the sono-photo-

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363 Fenton/oxalic acid system, after the first 30 min of treatment, the concentration of  
364 sulfamethoxazole notably diminished from 0.37 to 0.14  $\mu\text{g L}^{-1}$ .

365 To determine the differences among the treatments, the elimination of pollutants after  
366 90 min was evaluated using two measures (percentage of degradation (PD) and  
367 removed amount (RA in ng), Table 3). Thus, three comparison criteria were applied:  
368 total summation (i.e., arithmetic addition of PD or RA values), average (i.e., arithmetic  
369 average of PD or RA) and pondered elimination percentage (calculated using Eq. 6).

370

371 
$$\text{Pondered elimination} = \frac{\sum_{i=1}^{17} (C_o \times PD)_i}{\sum_{i=1}^{17} C_{o,i}} \quad (6)$$

372 Where  $C_o$  represents the initial concentration (in  $\mu\text{g L}^{-1}$ ).

373

374 Table 3 shows that sonochemistry has negative values for the three criteria. Therefore,  
375 from a general point of view, such system had a predominance of the releasing effect  
376 over the degrading action. In fact, it has been reported that physical effects of  
377 ultrasound are able to break suspended solids from secondary effluents (Torres-Palma  
378 et al., 2017), which is an advantage of ultrasound over other AOPs because it makes  
379 more available the released compounds for radicals attacks.

380 In contrast to ultrasound alone, the other three systems exhibited positive values of the  
381 total summation, average and pondered elimination percentage, indicating the  
382 prevalence of degrading effects in these processes. Moreover, for sono-Fenton and  
383 sono-photo-Fenton, the pollutant elimination criteria had close values, whereas sono-  
384 photo-Fenton/oxalic acid exhibited higher numbers.

Codi de camp canviat

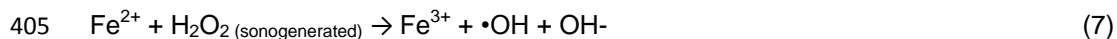
385 The addition of  $\text{Fe}^{2+}$  (i.e., sono-Fenton) improved the global pollutants elimination  
386 (Table 3) by the generation of more hydroxyl radicals (mainly in the bulk of solution) in  
387 the system through the Fenton reaction (Eq. 7) (Ammar, 2016; Torres et al., 2008b),  
388 contributing to the elimination of both the released pollutants from solids and hydrophilic  
389 ones. At the same time, organic matter components in the effluent have carboxylic and  
390 polycarboxylate groups, which can complex the produced  $\text{Fe}^{3+}$  (Eq. 8) (Fujii et al.,  
391 2014). Hence, a significant iron fraction can remain in a soluble form (see Figure SM4  
392 soluble iron in the systems).

Codi de camp canviat

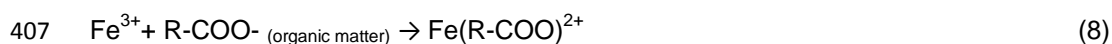
Codi de camp canviat

393 The UVA light used for the sono-photo-Fenton system had low interfering effects by the  
394 matrix components (e.g., suspended solids), as evidenced by the low absorbance of the  
395 water (Table SM1 and Text SM4). Thus, the illumination of water with the UVA lamp  
396 may photo-regenerate  $\text{Fe}^{2+}$  (Eq. 9), which in the oxidizing environment of ultrasound  
397 can be fastly returned to  $\text{Fe}^{3+}$  ( $k$ :  $63\text{-}76 \text{ M}^{-1}\text{s}^{-1}$ , Eq. 7) producing more radicals. Radical  
398 may also degrade the carboxylic moieties. Then, the depletion of carboxylic groups by  
399 action of UVA light (Eq. 9) and radical, plus the near neutral conditions (i.e.,  $\text{pH} \sim 7.5$   
400 during process, Table SM2) lead to the formation of insoluble  $\text{Fe}^{3+}$  species (Eq. 10), as  
401 evidenced by the decreasing of dissolved iron (Figure SM4). In the effluent case, such  
402 blocking of the iron availability can limit the photo-Fenton process efficiency. This would  
403 explain why sono-photo-Fenton had no improvements respect to sono-Fenton system.

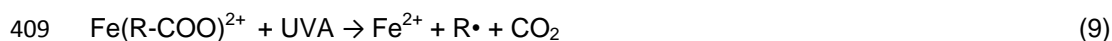
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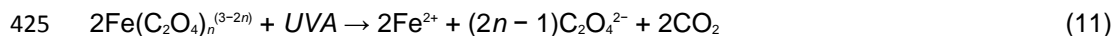
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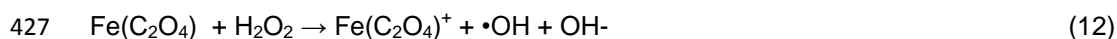
412

413 In the case of sono-photo-Fenton/oxalic acid process, the iron (III) precipitation is  
414 avoided by the carboxylic acid presence at considerable concentration (2 ppm). Oxalic  
415 acid is a strong complexing agent of iron, keeping it in a soluble form (as Figure SM4  
416 shown). Furthermore, ferric oxalate complexes, such as  $\text{Fe(C}_2\text{O}_4\text{)}^+$ ,  $\text{Fe(C}_2\text{O}_4\text{)}_2^-$  and  
417  $\text{Fe(C}_2\text{O}_4\text{)}_3^{3-}$ , are photoactive and promote the catalytic cycle of iron (Ammar, 2016;  
418 Pignatello et al., 2006). This favors the generation of additional radicals for the  
419 pollutants degradation (Eq. 11-12). Also, it is well-known that the reaction constant ( $k =$   
420  $3.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) of the ferrous oxalate complex with hydrogen peroxide (Eq. 12) is  
421 higher than that reported for classical Fenton reaction ( $k = 63\text{-}76 \text{ M}^{-1} \text{ s}^{-1}$ , Eq. 7)  
422 (Pignatello et al., 2006; Prato-Garcia et al., 2009). For these reasons the sono-photo-  
423 Fenton/oxalic acid presented the highest global removal of pollutants (Table 3).

424



426



428

429 To understand fundamental aspects of sono-Fenton, sono-photo-Fenton and sono-  
430 photo-Fenton/oxalic acid, the treatment of valsartan in distilled water was also studied.

Codi de camp canviat

Codi de camp canviat

431 Figure 6A presents the comparison among the pseudo-first order rate constant ( $k^1$ ) for  
432 valsartan degradation by these processes. Figure SM5 depicts the control experiments.  
433 From Figure 6A, it was evidenced an acceleration of the pollutant elimination by iron (II),  
434 UVA light and oxalic acid addition to ultrasound. Contrarily to the observed in  
435 wastewater, in distilled water the degradation by sono-photo-Fenton was higher than by  
436 sono-Fenton. Furthermore, the pH of the solution during treatments reached values  
437 below 4.0 (Table SM2). At pH range 2.0-4.0 predominates the soluble iron form  
438  $\text{Fe}(\text{OH})^{2+}$  (Eq. 13), which has strong UV absorption facilitating the photo-Fenton  
439 reaction (Loures et al., 2013). Indeed, when such iron (III) form is irradiated by UVA, a  
440 ligand-to-metal charge transfer occurs, involving the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and  
441 hydroxyl radical formation (Eq. 14). The  $\text{Fe}^{2+}$  regenerated during irradiation interacts  
442 with sonogenerated hydrogen peroxide (Eq. 7) producing more radicals, which  
443 accelerate the valsartan degradation (see sono-photo-Fenton in Figure 6A).



448

449 In the case of sono-photo-Fenton/oxalic acid system, the  $k^1$  value was 40 % higher than  
450 by sonolysis alone. Such result confirms the accelerating role of oxalic acid. Oxalate, as  
451 iron ligand, can increase the  $\bullet\text{OH}$  production in the bulk of solution according to Eq. 11-  
452 12, favoring in this way a faster and higher pollutant elimination.

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453 Besides the  $k^1$  determination during the treatments of valsartan, the hydrogen peroxide  
454 accumulation rates (Ra) for the different systems (Figure 6B) were also established,  
455 following the order: sonochemistry > sono-Fenton  $\geq$  sono-photo-Fenton > sono-photo-  
456 Fenton/oxalic acid. In sono-Fenton and sono-photo-Fenton, Ra was lower than in  
457 sonochemistry, indicating a higher Fe-H<sub>2</sub>O<sub>2</sub> interaction (i.e., more production of •OH)  
458 and consequently an increasing in the valsartan degradation (i.e., a higher  $k^1$  value,  
459 Figure 6A). Meanwhile, the lowest hydrogen peroxide accumulation rate in the sono-  
460 photo-Fenton/oxalic acid system could be associated to the highest formation of  
461 additional •OH (Eq.11-12) used to enhance the valsartan elimination and the possible  
462 reaction with oxalic acid. Finally, it should be mentioned that the  $k^1$  and Ra values in  
463 Figure 6 are coherent with the results shown in Table 3 for the whole set of pollutants,  
464 confirming the improvement of degradation by the addition of iron (II), UVA light and  
465 oxalic acid to the sonochemical processes.

466

## 467 **Conclusions**

468 This work showed that the conventional systems used in El salitre MWTP (Bogotá-  
469 Colombia) partially removed the emerging contaminants under study. In fact, such  
470 systems can promote, for some compounds, a simple transference of pollutants from  
471 aqueous medium to other phase (e.g., substances sorption on suspended solids). On  
472 the contrary, the sonochemical process led to the pollutants releasing from suspended  
473 solids; additionally, the interaction with the sonogenerated hydroxyl radical induced the  
474 degradation of both pharmaceuticals and illicit substances.

475 The ultrasonic elimination of pollutants seemed to be dependent on concentration and  
476 hydrophobicity parameters. In fact, the arithmetic multiplication between these two  
477 factors ( $C \cdot \log K_{ow}$ , which was used to denote the closeness to cavitation bubble)  
478 presented a good correlation with the contaminants degradation rate. This means that  
479 those hydrophobic compounds found at high concentrations in the effluent (e.g.,  
480 losartan or valsartan) are faster degraded; whereas the low concentrated hydrophilic  
481 substances (e.g., metronidazole or trimethoprim) have very slow degradation rates.

482 The addition of iron (II), UVA light and oxalic acid to the sonochemical process  
483 significantly increased the pondered removal of the pollutants in the effluent, thanks the  
484 production of extra hydroxyl radicals through reactions between iron and sonogenerated  
485 hydrogen peroxide. The presence of oxalic acid (or carboxylic groups in effluent organic  
486 matter) makes iron more available for extra radicals formation in the bulk of solution,  
487 with the subsequent improvement of pollutants elimination. It can be pointed out that the  
488 ultrasonic system complemented with iron (II), UVA light and oxalic acid presentd a  
489 strong potential for the pollutants elimination in real-world wastewater matrices. Finally,  
490 it is important to indicate that the feasibility of applying the high frequency ultrasound  
491 technique at wastewater treatment plant scale is hampered by its high electrical energy  
492 consumption and the low transduction efficiency. However, the fundamental aspects  
493 (e.g., pollutants degradation enhancement by iron (II), UVA light and oxalic acid  
494 addition) derived from sonochemistry are transferable to the other analogous systems  
495 based on the cavitation phenomena, such as hydrodynamic cavitation, which has lower  
496 costs for scaling up.

497

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505

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