Degradation of seventeen contaminants of emerging concern in municipal wastewater effluents by sonochemical advanced oxidation processes

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Abstract

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

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

1. Introduction

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

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

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

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

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

$$H_2O \rightarrow \bullet H + \bullet OH \qquad (1)$$

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$$O_2 \rightarrow 2\, \bullet O \qquad (2)$$

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$$H_2O + \bullet O \rightarrow 2\, \bullet OH \qquad (3)$$

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$$O_2 + \bullet H \rightarrow \bullet O + \bullet OH$$

(4~~4~~)

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$$2\, \bullet OH \rightarrow H_2O_2 \qquad (5)$$

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

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Considering the absence of relevant studies on this issue, the present work evaluates the simultaneous degradation of seventeen emerging concern pollutants (fifteen representative pharmaceuticals, an illicit drug and its main metabolite) at actual low concentrations (µg L^{-1} to ng L^{-1} levels) in real effluents from Bogotá-Colombia by high-frequency ultrasound and its complementation with iron and UVA light. After proving that most of the considered pollutants were not completely removed by the MWTP, the ultrasonic system was applied to effluents from the plant. Sonochemical processes showed degrading action on the pollutants. Then, a possible correlation of sono-degradation rates with hydrophobicity and concentration of pollutants was studied. Afterwards, the addition of iron, UVA light and oxalic acid to ultrasound (i.e., sono-Fenton, sono-photo-Fenton and sono-photo-Fenton/oxalic acid) to enhance the pollutants elimination was evaluated. Furthermore, to better understand the fundamental aspects of these systems, valsartan (representative pollutant in the effluent) was selected as model compound and treated in distilled water.

2. Experimental

2.1 Reagents

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

Valsartan for individual experiments was purchased from Tecnoquímicas S.A. Oxalic acid and iron sulfate heptahydrate were obtained from Panreac and Merck, respectively. Potassium iodide, ammonium heptamolybdate, acetonitrile and methanol were provided by Merck. Formic acid was purchased from Carlo-Erba.

2.2 MWTP sampling and sonochemical reaction system

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

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

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

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2.3 Analyses

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

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

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

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

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Soluble iron was determined through the phenanthroline method by adding 80 µL of the hydroxylamine hydrochloride solution and 200 µL of the 1,10-phenanthroline solution were added to 1320 µL of the sample. The pH of each cell was regulated with 400 µL of the sodium acetate solution. The sample was homogenized and after 15 min of reaction in dark, the absorbance reading at 510 nm was carried out.

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

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

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3. Results and Discussion

3.1. Inability of the MWTP for complete pollutants removal

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

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

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

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In our previous work, we studied the ability of conventional processes applied in El salitre MWTP to eliminate the emerging concern pollutants (Figure SM2) (Botero-Coy et al., 2018). A limited efficiency of the treatment plant for the pollutants removal was observed. In fact, some pharmaceuticals concentration in the effluent were higher than in influent (e.g., erythromycin, metronidazole, sulfamethoxazole and trimethoprim; which presented negative removal efficiencies). In some cases, MWTP can act as pollutants concentrators. This situation is not exclusive for El salitre MWTP, similar facts have been reported by Lacey *et al.*, Gros *et al.* and Jelic *et al.* (Gros et al., 2010; Jelic et al., 2010). Thus, the incomplete removals, even the increasing of pollutants concentration by conventional processes in MWTP, evidence the need of alternative/complementary treatment technologies.

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3.2 Degradation of the 17 emergent pollutants by ultrasound

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

Due to the effluent contains suspended solids (Table SM1), some pollutants are sorbed on such solids. It is reported that non-ionic compounds tend to be highly sorbed onto organic matter through van der Waals interactions; whereas for those pollutants with polar and/or charged functional groups, their sorption is governed by the combination of electrostatic interactions and van der Waals forces (Hyland et al., 2012). In fact, electrostatic interactions are determinant for the sorption of fluoroquinolone pharmaceuticals (e.g., ciprofloxacin and norfloxacin) on sewage solids (Ternes et al., 2004; Wu et al., 2009). Meanwhile, diclofenac presents a medium affinity towards sewage solids (Berthod et al., 2014; Ternes et al., 2004). In the case of the antibiotic sulfamethoxazole, although this pollutant has weak interactions, it can experiment some sorption on such solids (Yang et al., 2011).

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

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

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

In ultrasound, degradation by pyrolysis as well as the interaction between pollutants and hydroxyl radical, depends on their proximity to the cavitation bubbles. Such proximity is determined by the initial concentration and the hydrophobic character of the compounds (Torres-Palma and Serna-Galvis, 2018). Then, to evaluate the concentration feature, the initial molarity of pollutants was calculated and the sonochemical degradation rate for each pollutant was measured (Table 1). Interestingly, upon ultrasound action, the substances with the highest initial molar concentrations (e.g., losartan, valsartan and benzoylecgonine) had faster degradation (Table 1). This is because a higher concentration favors the pollutant diffusion toward the cavitation bubble increasing the probability of contact with hydroxyl radicals (Torres-Palma and Serna-Galvis, 2018).

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

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

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

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

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Figure 4 presents the evolution of valsartan submitted to high frequency ultrasound in distilled water. The process degraded ~ 60% of the compound after 30 min of treatment. In addition to the pollutant degradation, the accumulation rate (Ra) of hydrogen peroxide (which is an indirect indicator of hydroxyl radical production ability of ultrasound, Eq. 5) in both presence (VAL) and absence of valsartan (BK) was also measured (Figure 4). The Ra in the presence of the pollutant is lower than in the absence, indicating that the reaction of valsartan with sonogenerated radicals limits the H_2O_2 accumulation.

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

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

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

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

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3.3 Improvement of sonochemical degradation by addition of iron, UVA light and oxalic acid

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

Fenton/oxalic acid system, after the first 30 min of treatment, the concentration of sulfamethoxazole notably diminished from 0.37 to 0.14 µg L^{-1}.

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

$$Pondered\ elimination = \frac{\sum_{i:1}^{17}(C_o\ x\ PD)_i}{\sum_{i:1}^{17} C_{o,i}} \qquad (6)$$

Where Co represents the initial concentration (in µg L^{-1}).

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

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

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

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

$$Fe^{2+} + H_2O_{2\ (sonogenerated)} \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad (7)$$

$$Fe^{3+} + R\text{-}COO^-_{\ (organic\ matter)} \rightarrow Fe(R\text{-}COO)^{2+} \qquad (8)$$

$$Fe(R\text{-}COO)^{2+} + UVA \rightarrow Fe^{2+} + R\bullet + CO_2 \quad (9)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(s)} \quad (10)$$

In the case of sono-photo-Fenton/oxalic acid process, the iron (III) precipitation is avoided by the carboxylic acid presence at considerable concentration (2 ppm). Oxalic acid is a strong complexing agent of iron, keeping it in a soluble form (as Figure SM4 shown). Furthermore, ferric oxalate complexes, such as $Fe(C_2O_4)^+$, $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^{3-}$, are photoactive and promote the catalytic cycle of iron (Ammar, 2016; Pignatello et al., 2006). This favors the generation of additional radicals for the pollutants degradation (Eq. 11-12). Also, it is well-known that the reaction constant ($k = 3.1 \times 10^4\ M^{-1}\ s^{-1}$) of the ferrous oxalate complex with hydrogen peroxide (Eq. 12) is higher than that reported for classical Fenton reaction ($k = 63\text{-}76\ M^{-1}\ s^{-1}$, Eq. 7) (Pignatello et al., 2006; Prato-Garcia et al., 2009). For these reasons the sono-photo-Fenton/oxalic acid presented the highest global removal of pollutants (Table 3).

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$$2Fe(C_2O_4)_n^{(3-2n)} + UVA \rightarrow 2Fe^{2+} + (2n - 1)C_2O_4^{2-} + 2CO_2 \quad (11)$$

$$Fe(C_2O_4) + H_2O_2 \rightarrow Fe(C_2O_4)^+ + \bullet OH + OH^- \quad (12)$$

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

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

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$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \qquad (13)$$

$$Fe\,(OH)^{2+} + UVA \rightarrow Fe^{2+} + \bullet OH \qquad (14)$$

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

Besides the k^1 determination during the treatments of valsartan, the hydrogen peroxide accumulation rates (Ra) for the different systems (Figure 6B) were also established, following the order: sonochemistry > sono-Fenton ≥ sono-photo-Fenton > sono-photo-Fenton/oxalic acid. In sono-Fenton and sono-photo-Fenton, Ra was lower than in sonochemistry, indicating a higher Fe-H_2O_2 interaction (i.e., more production of •OH) and consequently an increasing in the valsartan degradation (i.e., a higher k^1 value, Figure 6A). Meanwhile, the lowest hydrogen peroxide accumulation rate in the sono-photo-Fenton/oxalic acid system could be associated to the highest formation of additional •OH (Eq.11-12) used to enhance the valsartan elimination and the possible reaction with oxalic acid. Finally, it should be mentioned that the k^1 and Ra values in Figure 6 are coherent with the results shown in Table 3 for the whole set of pollutants, confirming the improvement of degradation by the addition of iron (II), UVA light and oxalic acid to the sonochemical processes.

Conclusions

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

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

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

Acknowledgments

The authors thank Universidad de Antioquia UdeA for the support provided to their research group through “Programa de Sostenibilidad” and the financing from COLCIENCIAS through the projects No. 111577757323 (Convocatoria 777 de 2017) and No. 123371552034 (Convocatoria 715 de 2015). The authors from UJI acknowledge the financial support from Generalitat Valenciana (Research Group of Excellence, PrometeoII/2014/023). E.A. Serna-Galvis thanks COLCIENCIAS his doctoral scholarship (Convocatoria 647 de 2014).

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