

Review

Use of Ultrasound as an Advanced Oxidation Process for the Degradation of Emerging Pollutants in Water

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Abstract: Emerging pollutants are compounds of increased environmental importance and, as such there is interest among researchers in the evaluation of their presence, continuity and elimination in different environmental matrices. The present work reviews the available scientific data on the degradation of emerging pollutants, mainly pharmaceuticals, through ultrasound, as an advanced oxidation process (AOP). This study analyzes the influence of several parameters, such as the nature of the pollutant, the ultrasonic frequency, the electrical power, the pH, the constituents of the matrix and the temperature of the solution on the efficiency of this AOP through researches previously reported in the literature. Additionally, it informs on the application of the referred process alone and/or in combination with other AOPs focusing on the treatment of domestic and industrial wastewaters containing emerging pollutants, mainly pharmaceuticals, as well as on the economic costs associated with and the future perspectives that make ultrasound a possible candidate to solve the problem of water pollution by these emerging pollutants.

Keywords: emerging pollutants; advanced oxidation process; water pollution; ultrasound

1. Introduction

Emerging contaminants (ECs) are chemical products, both natural and synthetic ones, that comprise a wide range of chemical compounds, including medical and recreational drugs, personal care products, steroids, hormones, surfactants, perfluorinated compounds, flame retardants, dyes, plasticizers and industrial additives [1–3]. The presence of ECs in the environment was not measured or controlled in the past because they did not cause concern and, in general terms, there were no studies demonstrating a health risk to humankind and living beings. Additionally, the use of ECs was not as high as it is currently; and they were not detected in water, since advances in instrumental analytical chemistry have only recently permitted their quantification at ultra-trace and trace concentrations [4,5], i.e., at concentrations from ng L^{-1} to $\mu\text{g L}^{-1}$ [3,6]. Indeed, in the last years, ECs have been identified and quantified in effluents from wastewater treatment plant effluents, surface water, groundwater and even drinking water [3,5,7,8].

It is important to note that ECs can have harmful effects both on the environment where they are located and on human health. Nowadays, the toxicity ascribed to the presence of these pollutants on the environment has not been fully evaluated [8]; nevertheless, more and more eco-toxicological studies are being conducted [9]. In fact, the presence of ECs has been reported to represent a serious risk to both the environment and human health due to direct and/or indirect exposure [3,10], since they

can negatively influence algae, invertebrates and fish, as well as ecosystem dynamics and community structure [11,12]. It has been found that ECs can act as endocrine disruptors and alter the reproduction cycles, water transport and osmoregulation processes of biota [13,14]. Other emerging pollutants have antimicrobial activity, leading to bacteria resistance to commonly used antibiotics [5] and, subsequently, resulting in worldwide spread of diseases. Additionally, ECs can be bioaccumulated [8], changing cellular reactions in vital organs, such as liver, kidney and gills [15]. Other studies have reported gene expression changes in organisms exposed to ECs [16].

It has been proven that some ECs are persistent pollutants that are hardly degraded by conventional processes [8,17,18]. For this reason, the implementation of new technologies to guarantee their removal is proposed [3,7,17,19].

Advanced Oxidation Processes (AOPs) have been evaluated as an option for the degradation of a variety of organic pollutants in waters [1,20]. These processes are characterized by a wide number of radical reactions, most of which involve chemical agents along with a source of ultraviolet (UV) radiation [21]. These radicals attack a large number of recalcitrant organic compounds such as ECs and, since they are not very selective, they become an excellent precursor to the conversion of a wide range of pollutants.

Several works have been carried out assisted by AOPs in order to evaluate their efficiency in degrading CEs. AOPs consist of the formation of the free hydroxyl radicals (HO•), which are capable of oxidizing toxic and/or recalcitrant organic compounds into more biodegradable and less dangerous products, such as oxidized species and short chain hydrocarbons of low molecular weight like formaldehyde and aliphatic acids [22], among other innocuous products; thus, they provide an improvement to the treatability of AOP effluents [17]. In fact, photocatalytic degradation has been conducted in the presence of UV radiation and photosensitizers including TiO₂, H₂O₂ and persulfate, among other chemical agents, obtaining very positive results [23–25]. Likewise, photo-Fenton and ozonation at basic pH have been proven to be highly efficient in the degradation of this type of pollutants [26,27]. These advanced systems, therefore, offer a solution to the problem of EC environmental accumulation and resistance to biological degradation, in contrast to other processes, such as conventional physical or chemical processes [17,25].

Nevertheless, it should be noted that, among the different AOPs used in the treatment of ECs present in water, the use of ultrasound (US) has been reported to be a highly efficient process, not only in the removal of this kind of contaminants, but also in their degradation [28,29] and the conversion of other recalcitrant pollutants [26] and microbial load [30] in water. Likewise, the use of US, as an advanced oxidation process, is environmentally “clean” since it does not require the addition of chemicals to the aqueous medium in order to achieve its EC degradation target, and does not generate waste [31] like Fenton and photo-Fenton. Consequently, the use of US waves is an alternative option for the conversion of recalcitrant ECs.

Considering the above, this article reviews and discusses the contributions of researches on the degradation of ECs, especially pharmaceuticals, due to their potential risks to human and other living beings, in aqueous media through US, as an advanced oxidation technology, considering the presence or absence of catalysts or dissolved gases, among other parameters, influencing the efficiency of the aforementioned process. Additionally, the application of this process is described focusing on domestic and industrial wastewater containing ECs, as well as the economic cost estimation associated with the future perspectives related to its implementation alone or in combination with other AOPs.

2. Ultrasound Process

The US process has been reported as a very efficient AOP for the degradation of ECs present in water [32–36]. Additionally, it can overcome the limitations ascribed to the use of other AOPs commonly used for water treatment. It is noteworthy to mention that, by using the US process, mass transfer within the reaction medium is improved, as well as the EC degradation reaction rates.

Additionally, the consumption of chemicals, such as oxidizing and catalyzing agents, is reduced and no sludge is generated [22,37].

As part of this review, the state-of-the-art of the implementation of US, as an advanced oxidation process, is analyzed based on several works reported in the literature. First of all, the fundamentals of the process are described to continue with the factors mainly influencing the efficiency of the process. Afterwards, a number of examples are provided in order to have a general idea of the versatility of the advanced oxidation technology alone and/or in combination with other AOPs to efficiently degrade persistent compounds such as ECs. Finally, the capital and operation and maintenance costs are mentioned, and the future perspectives related to the application of the process are highlighted.

2.1. Operation Fundamentals

Aqueous medium sonolysis involves the production of waves through sound at a specific frequency, with compression and expansion cycles, leading to the formation of cavitation bubbles. These bubbles grow by the diffusion of vapor or gas from the liquid medium, reaching an unstable size that provokes their violent implosion, which in turn generates very high temperatures and pressures, approximately 4200 degrees K and 975 bar, producing the so-called “hot spots” that allow the decomposition of the water molecule to generate HO• [9], which is capable of oxidizing recalcitrant pollutants such as ECs with its high oxidation potential (2.8 V) [38], leading to the degradation of the toxic compounds and producing innocuous products, such as H₂O, carbon dioxide (CO₂) and inorganic ions.

Equations (1)–(4) show the decomposition of water and other molecules commonly dissolved in water by sonochemical waves [9,39], being the HO•, as well as the hydroperoxyl radicals (HO₂•), the main species that oxidizes the organic compounds present in the aqueous medium.

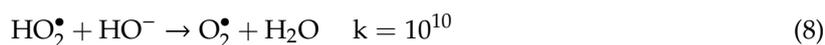
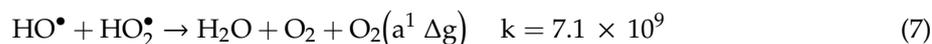
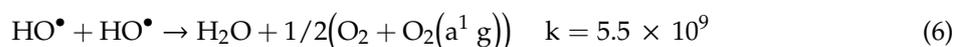
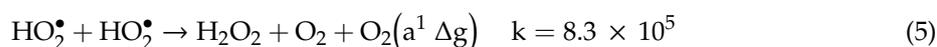


The cavitation bubbles are produced in two ways, symmetrically and asymmetrically. The difference between these is the support provided by a rigid surface (for instance, the surface of the reactor) for the bubbles to be formed. This difference has a direct influence on the way in which the bubbles implode, and thus on the release of pressure and temperature into the medium, resulting in the rupture of the water molecule and the formation of HO• [9]. The symmetrical bubbles release energy in all directions around their surface, while the asymmetrical ones generate an eruption of the liquid, mainly on the parts of the bubbles that are far away from the surfaces, forming long-range “micro-jets” that go to the solid surfaces [28].

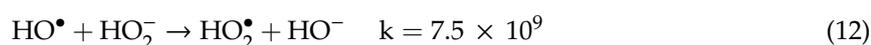
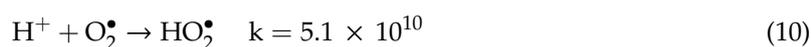
There are three reaction zones in the solution during the ultrasonic treatment process: (a) inside the cavitation bubble, (b) the bubble/water interface and (c) within the bulk solution [28,32,40]. In each of these zones, different reactions occur that favor the decomposition of pollutants. Hydrophobic, non-polar and/or volatile compounds react inside the cavitation bubbles and at the bubble/water interface, while hydrophilic and/or non-volatile pollutants react within the bulk solution [28,41–43].

Inside the cavitation bubbles, the reaction of the pollutant can occur in two ways: pyrolysis of the highly volatile compounds, or chemical reaction with the free HO• formed. At the bubble/water interface, the reaction occurs by pyrolysis and, fundamentally, by a reaction with the HO• that are formed from implosion and tend to diffuse throughout the solution medium, reacting with the compounds that are present at the interface. Within the solution, decomposition occurs only by reaction with HO•, which are released into the aqueous medium through implosion of the cavitation bubbles [9].

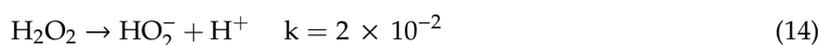
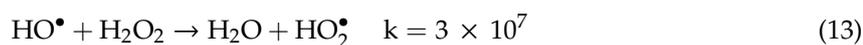
When free radicals reach the aqueous solution, they can recombine, as expressed in Equations (5)–(7), or react with hydroxyl ions (HO^-) (Equation (8)), resulting in a decrease of the system oxidation potential.



However, from Equation (8), superoxide radicals ($\text{O}_2^{\bullet-}$) are formed, as well as from the decomposition of HO_2^\bullet , as described by Equation (9), which also contribute to the degradation of emerging organic compounds, although in a smaller proportion than by HO^\bullet [38]. Additionally, in acidic medium, $\text{O}_2^{\bullet-}$ can react with protons (H^+) to form HO_2^\bullet (Equation (10)). Both of the free radicals can recombine, as represented in Equation (11), resulting in the production of HO_2^- , which in turn can be involved in HO^\bullet quenching (Equation (12)).



Hydrogen peroxide (H_2O_2) can also be formed in the US process, as described in Equation (5). In spite of the fact that H_2O_2 can scavenge HO^\bullet or be decomposed (Equations (13)–(15), respectively), it can be involved in the oxidation of ECs, as well as on the production of a higher amount of HO^\bullet , when US process is combined with UV radiation.



The reaction rate constants for the reactions expressed in Equations (5)–(15) were taken from Pavlovna et al. [44], demonstrating that, in general terms and according to the values of the reaction rate constants, the free radicals are easily formed through the US waves. As mentioned previously, these free radicals can react with the target pollutant; however, they can also recombine or be quenched by other compounds found in water such as the natural constituents of the matrix, making the reaction of the hydrophilic compounds within the solution less efficient and slower [45]. In this regard, in order to avoid side reactions of the US oxidation system, the optimization of the operating parameters or factors influencing the most the oxidation potential of the system must be conducted. This would subsequently allow the reduction of the economic costs associated with the studied advanced oxidation process for a more efficient degradation of the ECs of interest.

2.2. Efficiency of the Ultrasound Process

The US process must consider the control and variation of the different operating parameters, including the ultrasonic frequency, the electrical power and the pH and temperature of the solution [46,47], in order to be optimized with the subsequent reduction in the costs associated with the process performance. The nature of the contaminant of interest and the constituents of the water matrix must also be considered during the US-assisted AOP optimization procedure since they

are involved in the efficiency of the process. In addition to these factors, the type and the geometry of the sonochemical reactor must be considered.

2.2.1. Reaction Zones—The Nature of the Emerging Pollutant

In the ultrasonic radiation process, as indicated above, three reaction zones are recognized for the degradation of compounds: the cavitation bubble, the bubble–water interface and the bulk solution [28,43,48]. The process by which degradation occurs differs from zone to zone. Hydrophilic substances are located within the solution, non-volatile hydrophobic compounds are mainly housed in the bubble–water interface, and volatile substances are commonly located within the cavitation bubble [22].

Inside the cavitation bubble, the degradation reaction of the contaminant occurs by pyrolysis; on the other hand, in the bubble–water interface, the main reaction mechanism is by the attack of free radicals, such as HO•, which are immediately formed by the implosion of the cavitation bubbles; finally, in the bulk solution the reaction occurs directly with the free radicals that reach this zone [28].

According to different investigations, in the US process, the degradation of volatile compounds occur in two zones: in the bubble–liquid interface, through the reaction with the HO• released from the implosion, and/or inside the bubble, directly by pyrolysis [22,41]. The rates of destruction of volatile contaminants depend on the physical and chemical conditions within the bubble, specifically the hydrophobic and volatile nature of these compounds [31,41]. On the other hand, it has been shown that the reaction rate constant of US degradation of volatile compounds decreases with increasing initial concentration, indicating that the relationship between the concentration of a volatile compound in the cavitation bubble and its concentration in the solution will influence the rate of ultrasonic reaction, considering that the collapse temperature depends on the specific heat ratio of the gas mixture [41,48–51].

Hydrophobic compounds such as carbamazepine (CBZ), which has a Henry's constant of approximately 1.08×10^{-10} atm. $\text{m}^3 \text{mol}^{-1}$ and a moderate solubility in water [9], can be mainly housed in the bubble–water interface, but it is also found within the solution, allowing the protagonist of its degradation to be the HO•, which are immediately formed from the implosion both of the cavitation bubbles and the bubbles that travel within the solution [9].

To evaluate the zone and the way in which a compound is degraded, Nie et al. [28] have implemented the so-called “scavengers” of the HO•. In an experiment where the US process was used to degrade the pharmaceutical diclofenac (DCF), isopropyl alcohol and terephthalic acid were used to inhibit the reaction of the target compound with HO•, functioning as quenchers. The acid was considered to react with free radicals in the bulk solution, while the alcohol reacted both at the bubble–water interface and in the bulk solution. In this regard, the authors verified that when only the acid was added, the degradation of the compound was inhibited. However, when the alcohol was used exclusively as an inhibitor, degradation of the target EC was considerably reduced. It was, therefore, concluded that oxidation of DCF occurred mainly by HO• in the supercritical interface, especially when water was saturated with air and oxygen (O₂). Nonetheless, under argon (Ar)- and nitrogen (N₂)- saturated conditions, DCF degradation occurred within the cavitation bubbles and/or the bulk solution.

In a study carried out by Kidak and Dogan [52], where the degradation of alachlor through the US process was evaluated, it was concluded that due to the physical properties of the compound, such as the water solubility limit (140 mg L⁻¹ at 20 °C), vapor pressure (negligible), Henry's constant (3.2×10^{-8} to 1.2×10^{-10} atm·m³ mol⁻¹), octanol–water partition coefficient (Log K_{ow} = 2.63–3.53) and its positive ionization, the compound was housed in the bubble–liquid interface, indicating that the degradation was due to the HO• recently formed from the implosion of the cavitation bubbles. The degradation obtained of the target compound was near 100% with a frequency of 575 kHz and an electrical power of 90 W.

Adityosulindro et al. [53] evaluated the degradation of ibuprofen (IBU) in order to ascertain the reaction zone in which the degradation of IBU was established, and whether it was due exclusively to HO•. For this purpose, they tested the sequestration of these radicals through two compounds, n-butanol, which is a short chain alcohol with partial solubility in water that is expected to react with the radicals housed in the bubble–liquid interface; and acetic acid, which should react with the free radicals in the bulk solution due to it is a completely miscible compound. The results obtained indicated that, indisputably, IBU reacted with the HO• recently formed during the implosion of the cavitation bubbles, which means that it is a compound housed in the interfacial zone [53]. The same conclusion was reached by Méndez-Arriaga et al. [42], who attributed the degradation of IBU to the HO• recently produced, since IBU is considered to be housed at the bubble–water interface due to its Henry's constant (1.5×10^{-7} atm m³ mol⁻¹), low solubility in water (21 mg L⁻¹) and octanol–water partition coefficient (3.9).

In the case of acetaminophen (ACP), a polar compound with high solubility (12.5 mg mL⁻¹), Villaroel et al. [54] reported that this contaminant was degraded in a greater proportion within the bulk, estimating that its behavior would be that of a hydrophilic substrate. Nonetheless, in this investigation, it was concluded that ACP can be housed both in the bulk solution and in the bubble–water interface, attributing its degradation to the HO• formed during the implosion of the cavitation bubbles. Based on the aforementioned authors' estimations, the hydrophilic or hydrophobic behavior of the target compound was more related to the initial pH value of the solution at which the study was carried out.

2.2.2. Ultrasonic Frequency

The frequency with which ultrasonic waves are produced can range from 20 to 10,000 kHz, and the US process is divided into three regions: low, high and very high frequency [22]. In Table 1, the frequency ranges used in the ultrasonic oxidation process are listed.

Table 1. Frequency ranges used in the ultrasonic process. Taken from [22].

Name	Ultrasound Range (kHz)
Very high	5000–10,000
High	200–1000
Low	20–100

Ultrasonic frequency is a fundamental parameter in the performance of US process, since the size and duration of the cavitation bubble, the violence of the implosion and, therefore, the production of HO• depend considerably on it [9,55].

The number of cavitation bubbles and bubble collapses increases with rising frequency. However, it is important to note that the bubbles generated at high frequencies are small, and release less energy than low frequency bubbles generated by a single pulse [6,56,57]. In addition, the escape of more HO• is inferred, before recombining, when faster collapses occur [9,58]. In this sense, the optimal frequency is determined by the integral efficiency of the energy discharge, which depends on the quantity, size and lifetime of the bubbles. It is noteworthy to mention that the optimal frequency varies according to the different compound to be treated [52,59].

Rao et al. [9] chose two frequency values (200 and 400 kHz) to determine the optimal one for the degradation of CBZ. The first of these values was more effective for the degradation of the target compound. This result was ascribed to the differences in calorimetric powers obtained for both frequencies under the same electrical power (100 W), resulting in a higher calorimetric power for the 200 kHz frequency. This can be attributed to what was previously explained, i.e., each EC requires an optimal frequency at which its degradation will be favored, which depends on its physicochemical properties. This optimal frequency will also be influenced by the geometry of the reactor since, as mentioned above, it will depend on the formation of symmetrical or asymmetrical cavitation bubbles.

On the other hand, in the research carried out by Güyer and Ince [23], different levels of ultrasonic frequency were evaluated in the US process of the DCF. The results obtained allowed the conclusion that the maximal rates of DCF degradation were reached at a frequency of 861 kHz and the minimal ones at 1145 kHz (carrying out tests with values of 577, 861 and 1145 kHz). The improvement between the 577 and 861 kHz was due to the fact that the latter reduced the size of the bubbles, leading to a greater number of bubbles and active oscillations, which contributed to the generation of HO• improvement. However, the highest frequency evaluated this efficiency was reduced due to the fact that the “optimal” frequency related to the reactor configuration was surpassed [53,56].

2.2.3. Electrical Power

The electrical power supplied to the ultrasonic transducer is a critical parameter that can largely determine the performance of the US process [9].

For Jiang et al. [41], the increase in ultrasonic power in the degradation of volatile compounds such as chlorobenzene, 1, 4-dichlorobenzene and 1-chloronaphthalene caused an increase in the cavitation energy, decreasing the cavitation limit and increasing the amount of bubbles produced. This resulted in a rise in the rate of degradation of this type of compounds, considering that the bubbles formed had enough energy to pyrolyze the tested pollutants. This is justified by the fact that volatile compounds are pyrolyzed within the cavitation bubbles, so the more bubbles formed, the more spaces for these compounds to react.

In a study carried out by Tran et al. [18], sonochemical efficiency was evaluated by means of calorimetric tests to determine the optimal power and to propose an experimental design in order to degrade the drug CBZ. It was determined that powers between 20 and 40 W favored sonochemical efficiencies, unlike what happened with powers of 10 W. This finding was attributed to the fact that as the power increased, so did the ultrasonic energy of the reactor, which caused the pulsation and collapse of the bubbles to be generated at a faster rate, resulting in a greater number of cavitation bubbles.

It is important to note that the effect of ultrasonic power and oxidizing species can be influenced by bubble dynamics [18]. The results reported by Gogate et al. [60] indicated that the size, number, lifetime and pressure of the bubbles were a complex function of the power dissipation rate. The research conducted by these authors explains the results obtained by Tran et al. [18], since they found that by increasing the power, the number of cavitation bubbles rose and, consequently, the production of HO• increased. In this way, the degradation of the target compound, CBZ in this case, was directly increased. Similar results were observed in the work carried out by Madhavan et al. [61] for DCF, who studied the degradation of this compound under a frequency of 213 kHz, a temperature of 25 °C, a variation of power density between 16–55 mW mL⁻¹ and a concentration of the pharmaceutical compound of interest of 0.07 mM. The same conclusion was also reached by Rao et al. [9], who studied the degradation of CBZ at pH 6, a frequency of 200 kHz and a power variation between 20 and 100 W, obtaining a higher degradation of CBZ at 100 W.

In the work carried out by Naddeo et al. [6], the degradation of DCF during the US process was evaluated. It was determined that, by increasing the power density from 100 to 400 W L⁻¹, the concentration of the contaminant decreased, making US the most efficient process. This result supports the theory developed in the work described above, i.e., the greater the potency, the greater the degradation percentage of the compound under study.

On the other hand, the combination of different levels of the parameters that influence the degradation of a compound in the US process must be considered. In this context, when the response surface methodology was used to determine the optimal operating levels of CBZ ultrasonic treatment, [18] it was observed that the treatment time had a more statistically significant impact on the efficiency of CBZ removal in comparison with the electrical power, as efficient degradation of the contaminant at lesser powers (10–40 W) required more treatment time. This fact is ultimately reflected in the use of electricity and, therefore, in higher operating costs associated with the application of the oxidation process.

Meanwhile, Kidak and Dogan [52] stated that increasing electrical power also increased the number of the bubbles formed, and that better results were expected in the degradation of the pollutants of interest. This assertion was supported by the results obtained in the experimentation with alachlor, where near 100% degradation was obtained through the US process (initial concentration of alachlor $100 \mu\text{g L}^{-1}$, frequency of 575 kHz and powers of 45, 60 and 90 W). In addition, they observed an increase in the reaction rate constants as the ultrasonic power increased.

However, in the work carried out by Ince [62], it was evidenced that the degradation of paracetamol (PCT), also known as ACP, DCF and IBU was reduced when operating with a high frequency (861 kHz). The author attributed that fact to the formation of clouds of bubbles when exceeding the threshold power (optimal), which increased the sound waves and, as a result, decreased the cavitation activity. The same author pointed out that below the power threshold, when the power was increased, the efficiency of the process rose.

Adityosulindro et al. [48] evaluated the degradation of IBU by the US process and the influence of the power density in the conversion of the target pharmaceutical. It was determined that increasing the power in a range between 25–100 W L^{-1} , over 180 min of treatment, contributed to a greater formation of $\text{HO}\bullet$. However, the authors stated that above a critical or optimal power density value, a cloud of bubbles would be formed, dispersing the formation of sound waves, which would in turn decrease the efficiency of the process [53].

2.2.4. Solution pH

The pH of the solution is a fundamental parameter in oxidation-reduction reactions. In the US process, the pH indicates the hydrophobic or hydrophilic nature of the target compound behavior, depending on whether the structure in which the pollutant is found is ionic or molecular. This property will allow the position to be determined in which the contaminant is housed in the US process, i.e., in the bulk solution (hydrophilic, non-volatile compounds), in the bubble–water interface (semi-volatile hydrophobic compounds), or within the cavitation bubble (hydrophobic, volatile compounds) [9]. This position, in turn, will determine whether the degradation pathway of the contaminant is by pyrolysis or by reaction with the $\text{HO}\bullet$ formed by implosion of the cavitation bubbles.

In the research carried out by Tran et al. [18], CBZ was degraded through the US process, considering the effects of the electric power, initial drug concentration, treatment time and pH of the solution (7–10). In this work, no significant influence on the part of pH was evidenced through an experimental factorial design, as a response surface methodology. This can be attributed to the fact that no tests were performed with acid pH values, which influence the structural form in which the compound is found in the aqueous medium and, therefore, the reaction zone in which it is found. Specifically, the pH values will favor or disfavor the hydrophobicity of the compound, with more hydrophobic compounds that are closer to the bubble–water interface reacting with the $\text{HO}\bullet$ that have just been formed from the implosion of the cavitation bubbles, whereas those compounds further away from the bubble–liquid (hydrophilic) interface possibly reacting with the $\text{HO}\bullet$ that reach the solution.

On the other hand, in the work carried out by Rao et al. [9], the influence of pH on the degradation of CBZ was evaluated, using levels between 2.0 and 11.0. The results showed that, at pH values between 4.5 and 11.0, the degradation remained constant and decreased in equal proportion, but with pH values close to 2.0 there was a small decrease in the degradation efficiency. This was ascribed to the fact that CBZ reacts at the bubble–water interface whenever hydrophobicity is favored—a result that was achieved with pH values between 4.5 and 11.0—whereas with pH values close to 2.0 the ionic structure of the compound, and thus its hydrophilicity, was favored. The compounds that can lodge very close to the cavitation bubbles can react with a greater amount of $\text{HO}\bullet$ than those ones that are in the bulk solution, which must wait for these oxidizing agents to reach them, being able to react with another compound along the way, such as the natural constituents of the aqueous matrix tested.

Meanwhile, Huang et al. [46] evaluated the degradation of DCF through US process in the presence of Zn^0 , performing an analysis of the influence of pH on this type of process. It was found that at pH

higher than 2 the degradation of DCF was very small, while at equal or lower values, the degradation of the tested compound reached percentages higher than 80%. The authors attributed this behavior to the fact that the pKa of DCF is 4.15, considering that aqueous media with a pH lower than this value will manage to maintain the molecular structure of this compound, and concluded that this form favored the absorption reaction of DCF by Zn^0 .

In the degradation of IBU through the US process, the influence of pH was evaluated, experimenting with values higher and lower than the pKa of the compound (4.9). It was found that, at lower values (2.6 and 4.3), the compound remained unprotonated and its degradation slightly increased, while the opposite occurred with an alkaline pH value (8.0), where IBU degradation was affected. However, the authors argued that under its ionic form, IBU should accumulate less at the bubble–water interface, which is where the $HO\bullet$ attack mainly occurs [53].

Al-Hamadani et al. [31] evaluated the degradation of sulfamethoxazole (SFX) and IBU under three pH conditions: acid (3.5), below the pKa values of the target compounds; basic (7), above the pKa values; alkaline (9.5), well above these values. The results showed degradations near 100% of the compounds in 1 h of treatment for a pH below pKa, while degradation was significantly affected above these values. This is attributed to the molecular form of the compounds, i.e., when the pH of the solution was below pKa, the hydrophobicity of the drugs and, therefore, their position in the bubble–water interface is improved, favoring a rapid reaction with the $HO\bullet$ recently formed during the implosion of the cavitation bubbles.

2.2.5. Constituents of the Water Matrix

Various investigations related to the degradation of ECs in water through AOPs have been carried out in aqueous matrices with different constituents. On one hand, some researches have been developed with synthetic waters which, in general, involve the use of distilled water doped with the chemical components offering the specific characteristics with which the researcher wishes to work. On the other hand, there are works operating with real wastewater or in which the efficiency of the process for natural surface and drinking water is evaluated.

The research carried out by Tran et al. [27] identified the levels of the operating parameters at which IBU could be degraded by 65% through a sono-electrolytic process under controlled conditions in synthetic water, using a statistical optimization procedure. These same conditions were evaluated with sewage from a municipal treatment plant, with organic and inorganic compounds, as well as microbial load, which was doped with a specific concentration of IBU. The result obtained was a greater degradation of the compound of interest (90%) than that statistically estimated with synthetic water. This result was ascribed to the apparent presence of the chloride ion (Cl^-), which favored electrolysis, and might also favor the formation of hypochlorous acid (HClO), which can improve IBU oxidation. This demonstrates the importance of studying the organic and inorganic content of the water to be treated, as this may favor or limit the degradation of the target compounds.

It has been reported that Cl^- have different effects on the elimination of ECs present in water treated by means of AOPs [63,64]. Rao et al. [9] evaluated the degradation of CBZ (0.025 mM) using 200 kHz 100 W US. These authors investigated the presence of different inorganic anions to determine their influence on the process. The anions evaluated were Cl^- , SO_4^{2-} and NO_3^- , and it was found that Cl^- slightly restricted the degradation of the investigated drug, while the others did not have a significant impact on the degradation of the compound of interest. This slight inhibition in CBZ degradation due to the presence of Cl^- can be attributed to the reaction of this ion with the $HO\bullet$ dispersed in the solution, resulting in the formation of $ClOH\bullet^-$.

In the work reported by Adityosulindro et al. [53] on the Fenton, US oxidation system and US-Fenton process, the efficiency of the degradation of IBU in distilled water and in wastewater from a municipal treatment plant was compared. The results showed a negligible difference between the degradation capabilities of all the evaluated processes in both distilled water and wastewater. In this context, the authors stated that the organic and inorganic content of the sewage effluent did not

compete with IBU for $\text{HO}\bullet$ and that the latter was capable of reacting first with the oxidizing agent. It is important to highlight that the experimentation was carried out at acid pH, which could favor the location of IBU in the interface zone, making it more competitive when reacting with the $\text{HO}\bullet$ formed from the implosion of the cavitation bubbles.

Rao et al. [9] compared the degradation of CBZ contained in synthetic water with that of an effluent from a municipal wastewater treatment plant, evaluating the efficiency of two processes: ultrasonic irradiation alone, and in combination with photolysis using UV radiation emitting at a wavelength of 254 nm. The results showed that, for the US process, the constituents of the real wastewater matrix had no influence on the degradation of CBZ when compared with the results for distilled water. On the other hand, in the combined process, the wastewater matrix increased the efficiency of the studied drug degradation. This can be attributed to the photolysis of certain compounds contained in the wastewater that provide the oxidizing agent and favor the degradation of CBZ. As a matter of fact, the referred authors gave the example of nitrate ions (NO_3^-).

In the research conducted by Villaroel et al. [54], the influence of ionic constituents of water on the degradation of ACP ($82.69 \mu\text{mol L}^{-1}$ and $1.65 \mu\text{mol L}^{-1}$), at a power of 60 W and ultrasonic frequency of 600 kHz, was evaluated. The results obtained in distilled water and in synthetic water containing calcium ions (Ca^{2+}), magnesium ions (Mg^{2+}), sulphates ions (SO_4^{2-}), bicarbonates ions (HCO_3^-), Cl^- , potassium ions (K^+) and fluorides ions (F^-) were compared. The results indicated that, for the lowest concentration of ACP, a more pronounced acceleration of degradation was observed when this occurred in water with similar ion content than in distilled water. The authors attributed this to the high content of HCO_3^- , which was likely to be the protagonist in the formation of the carbonate radical ($\text{HCO}_3\bullet$) when reacting with $\text{HO}\bullet$ radicals, being $\text{HCO}_3\bullet$, a contributor to the degradation of the target EC.

With regard to the use of dissolved gases and their influence on the degradation of organic ECs, in the work conducted by Nie et al. [28], whose objective was to degrade DCF through the US process, it was observed that under saturated air, O_2 and Ar, a complete mineralization of nitrogen and a partial mineralization of carbon was achieved. When oxygenation was added to the reaction solution, $\text{HO}_2\bullet$ was formed. Although these radicals do not have an oxidation potential as high as $\text{HO}\bullet$, as mentioned previously, $\text{HO}_2\bullet$ can contribute to the degradation of the compounds of interest [6].

On the other hand, it must be highlighted that when chlorine atoms are part of the target EC structure, they are transformed to Cl^- through the reaction of the pollutant of interest with $\text{HO}\bullet$ or by pyrolysis in the US process [41,49]. Therefore, the release of Cl^- occurs during the sonochemical degradation of chlorinated compounds, which was attributed to the rapid excision of the carbon–chlorine bonds by high temperature combustion occurring within the cavitation bubbles or at the bubble–liquid interface. Cl^- , as indicated above, can reduce the oxidation potential of the process.

Under this scenario, studies aiming at examining the efficiency of the US process are required to be conducted by using real matrices due to the natural constituents of the water matrices can positively or negatively influence the degradation percentages and reaction rates of the ECs of interest.

2.2.6. Temperature of the Solution

According to some authors, temperature variation in the US process directly influences cavitation intensity due to the changes in the physicochemical properties of the compound and the type of cavities formed, which can affect the kinetic velocity constant of the degradation reaction [65].

Al-Hamadani et al. [31] indicated that certain parameters were affected by increasing the temperature in the US process. First, it was found that cavitation energy decreased, as well as the threshold limit of the energy required to produce cavitation. In addition, it was found that the amount of dissolved gas was reduced, leading to the transfer of organic molecules from the bulk solution to the bubble–water interfacial region. Finally, the vapor pressure increased, causing the cavitation bubbles to contain more water vapor. Furthermore, the aforementioned authors, who evaluated the degradation of SFX and IBU through US, evidenced the temperature influence on the

oxidation process. Temperatures between 15 and 55 °C were tested and it was concluded that, when this parameter was increased, the degradation of the studied compounds rose, as a rise in the temperature of the bulk caused the cavitation threshold to lower, which contributed to the formation of a greater number of cavitation bubbles and, therefore, to a greater amount of HO•. However, these authors pointed out that other works have shown an adverse effect of temperature on the degradation of the contaminant. These findings can be attributed to the fact that the surface tension and viscosity of the solution increase, generating cavitation bubbles with less intensity due to a rise in the vapor pressure of the liquid.

2.3. Application of Ultrasound Process to Water Treatment

Table 2 compiles several relevant research works related to the treatment of ECs through ultrasound as an AOP alone or in combination with other physical-chemical and advanced oxidation technologies.

Table 2. Summary of works related to the removal of emerging pollutants through the ultrasound process and its combination with other physical-chemical and advanced oxidation processes.

Process	Ref.	Pollutant/Type of Water	Operating Conditions	Found Results
US	[28]	DCF/Synthetic water	Co DCF: 0.05 mM. Frequency: 585 kHz. Power intensity 160 W L ⁻¹ pH: 7 Situations: air saturation, argon, oxygen and nitrogen. Temperature: 4 °C Glass cylindrical reactor of 750 mL connected to transducer Working volume: 500 mL. Treatment time: 60 min. HO• scavenger agents: Isopropyl alcohol and terephthalic acid. Co H ₂ O ₂ : 0.5 and 5 mM.	The elimination of DCF (without scavenger) and the formation of chloride ions were established as first-order reactions. Dichlorination rates, under all gas saturation conditions, were 1 to 2 times higher than DCF degradation rates. Dichlorination was a major reaction pathway during ultrasonic degradation of DCF; it developed within the solution by HO• attacks. There was only a partial mineralization in the 4 gas saturation conditions. The lowest peroxide concentration allowed a higher rate of degradation of the DCF.
US	[52]	Alachlor/ Synthetic water	Co Alachlor: 100 µg L ⁻¹ Frequency: 575, 861 y 1141 kHz. Electric power: 45, 60 and 90 W. Reactor: Glass cylindrical reactor of 500 mL Temperature: 25 °C. Treatment time: 90 min. pH: 7	Alachlor degradation was a pseudo-first order kinetics. A 100% degradation of alachlor and a mineralization of 25% was achieved, in 60 minutes of treatment, with a frequency of 575 kHz and a power of 90 W. The intermediate products from degradation of each tested power were analyzed, identifying their abundance in the samples.
US	[66]	Rosaniline (PRA) and ethyl violet (EV)	[PRA] and [EV]: 10 ppm Frequency: 350 kHz Electrical Power: 60 W. Treatment time: 30 min. Presence of ions: Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ .	A complete degradation of EV and PRA was observed with a first order pseudo velocity constant. A good COD removal of 97% and 92%, respectively, was observed for EV and PRA after 3 h. The rate constants were higher with the addition of chloride ions in the case of EV and were not altered in the case of PRA. The improved degradation of EV in the presence of chloride is probably due to the salting effect and the reaction of the secondary radicals. EV degradation decreased from 100% to 80% with an increase in carbonate ion concentration from 0 to 100 ppm. In the case of PRA, a significant improvement in degradation was observed with the addition of CO ₃ ²⁻ .

Table 2. Cont.

Process	Ref.	Pollutant/Type of Water	Operating Conditions	Found Results
US	[33]	Benzophenone-3 (BP-3)/ Synthetic water	Treatment time: 10 min Frequency: 574, 856 and 1134 kHz. Electrical Power: 100–200 W L ⁻¹ . [BP-3]: 1 ppm. Temperature: 25 ± 2 °C. Relationship of pulse time and silence time: PT/ST.	574 kHz or a lower frequency value is optimal for degradation of BP-3. The optimum power density level was 200 W L ⁻¹ . A maximum degradation level of 79.2% was obtained for EP = 200 W L ⁻¹ , a PT/ST ratio of 10 and frequency 574 kHz. The degradation was almost the same for all PT/ST ratios from 3 to 12.
US	[34]	Triclosan (TCS)/ Synthetic water	Treatment time: 60 min. Frequency: 215, 373, 574, 856 and 1134 kHz. Electrical Power: 40, 76, 140 and 200 W L ⁻¹ . [TCS]: 1 mg L ⁻¹ . Temperature: 25 ± 2 °C. Treatment volume: 300 mL.	The 574 kHz frequency had the highest degradation rates. With 574 kHz, at 40 W L ⁻¹ , 88% of TCS degraded in 60 min, while at 140 W L ⁻¹ , TCS degraded completely in less than 25 min. The highest TCS degradation rate was obtained at the highest power density level of the equipment, 200 W L ⁻¹ . It was shown that the only variable that had statistical significance and an effect on degradation after 10 min was the power density.
US	[35]	Bisphenol-A/ Synthetic water	Frequency: 300 kHz. Electrical Power: 80 W. Treatment volume: 300 mL. [BPA]: 0.12 and 300 µM. pH: 8.3 [HCO ₃ ⁻]: 12–500 mg L ⁻¹ Temperature: 21 °C. Addition: Cl ⁻ , SO ₄ ²⁻ and HPO ₄ ²⁻ [6 mM].	The addition of HCO ₃ ⁻ , in the range of 12–500 mg L ⁻¹ did not have a significant effect on the BPA degradation rate. The bicarbonate concentration had a significant effect for the 0.12 BPA concentration: a higher bicarbonate concentration produced higher initial decomposition rates. Solutions containing ions other than bicarbonate showed significantly lower degradation rates. The bicarbonate/carbonate solution produced a significantly improved degradation rate of BPA.
US	[54]	Acetaminophen (ACP)/ Synthetic water and mineral water	Frequency: 600 kHz. Electrical Power: 20–60 W. Treatment volume: 300 mL. [ACP]: 82.69 µM. pH: 3–12. Temperature: 20 ± 1 °C. Addition: glucose, oxalic acid, propan-2-ol and hexan-1-ol.	The ultrasonic degradation in acidic medium (pH 3.0–5.6) is greater than that obtained in basic aqueous solutions (pH 9.5–12.0). The degradation of ACP would increase if its hydrophobicity is favored. The degradation rate increases with increasing acoustic power. The substrate degradation rate increases with increasing initial substrate concentration to a plateau. The presence of organic compounds negatively affects the sonochemical degradation efficiency of ACP, except glucose. A positive effect of mineral water was observed when the ACP concentration decreased 50 times (1.65 µM).
US	[36]	1-H- Benzotriazole (1HB)	[1HB]: 41.97–167.88 µM. Presence of oxygen, nitrogen, ozone and radical scavengers	With the increase in concentration, the degradation rate of 1HB also increased by 40%. A high applied ultrasonic power improved the degree of elimination of 1HB. The initial degradation rate accelerated in the presence of ozone and oxygen, but was inhibited by nitrogen. The most favorable pH for degradation was an acid medium. The removal of more than 90% of the contaminant was achieved

Table 2. Cont.

Process	Ref.	Pollutant/Type of Water	Operating Conditions	Found Results
US/Electro-oxidation (EO)	[27]	IBU/ Synthetic water and sewage	<p>Co IBU Synthetic: 10 mg L⁻¹ Increase in conductivity Na₂SO₄ 0.01 mol L⁻¹. Co IBU Municipal: 20, 100 µg L⁻¹ and 10 mg L⁻¹. pH residual municipal: 6.6. Frequency: 520 kHz. Electric power: 10–40 W. Current densities: 3.6–35.7 mA cm⁻². Cylindrical reactor with a cathode and an anode immersed in the solution. Temperature: 5–40 °C. Working volume: 3 L. Treatment time: 30–180 min.</p>	<p>The best constant for speed and efficiency of degradation was obtained with the US/EO, process, followed by EO alone and then US alone. 84.74% elimination of the IBU was achieved with US/EO. In the EO process, HO• can be generated on the surface of the electrode, then the US increases the mass transfer between these and the contaminants. Between 10–40 °C there were no significant differences in the degradation of IBU. Intensity of the current and treatment time are the most influential factors. Optimum conditions are: 110 min treatment, 4.09 A and 20 W. In municipal sewage, 90% of IBU was removed.</p>
US O ₃ O ₃ /US US/UV O ₃ /UV US/O ₃ /UV	[62]	Azo dyes (AD), Endocrine Disrupting Compounds (EDC) and pharmaceuticals (PHAC)/ Synthetic water	<p>Reactor 1: horn-type sonicator. Capacity of 100 mL. Frequency 20 kHz. Power: 0.46 W mL⁻¹. Reactor 2: plate-type sonicator. Frequency: 577, 866, 1100 kHz. Power intensity: 0.23 w mL⁻¹. Use US + O₃. Reactor 3: Ultrasonic bath. Frequency: 200 kHz. Power: 0.07 W mL⁻¹. Reactor 4: tailor-made hexagonal glass reactor coupled with 3 UV lamps (254 nm). Frequency: 520 kHz. Power: 0.19 W mL⁻¹.</p>	<p>AD degradation is faster by O₃/US. The UV/US process was very effective in degrading AD. With the addition of H₂O₂ a better discoloration was obtained. The rate of AD decomposition is faster in the presence of solid particles. EDCs had better degradation at alkaline pH and low frequency. At acidic pH, degradation was improved by adding Fenton or O₃ processes. For PHAC, ultrasonic processes were more efficient at high frequencies and acid pH.</p>
US/Zn ⁰	[46]	DCF/Synthetic water	<p>Co DCF: 10 mg L⁻¹. Reactor: Beakers, ultrasound probe. Working volume: 100 mL. pH: 2–7. Frequency: 20 kHz Power: 30–300 W. Treatment time: 30 min. Addition of Zn⁰</p>	<p>At acid pH, the US process accompanied with Zn⁰ was more efficient, while adding Zn⁰ alone and experimenting with the US alone did not result in further degradation of DCF. At pH higher than 2 the DCF was not eliminated. At pH 2, degradation of 80.92% was achieved in 15 min. Process of US/Zn⁰. There were no significant differences in degradation at different Zn⁰ concentrations and different power densities. Dichlorination was the degradation pathway. The main aspect of this reaction, together with the Zn⁰ reduction, was the O₂•⁻.</p>
US Fenton/US	[53]	IBU/Synthetic water and municipal sewage	<p>Co IBU: 20 mg L⁻¹. pH: 2–8. Power density: 25–100 W L⁻¹. Frequency: 12–862 kHz. Addition of H₂O₂. Addition of Iron (Fe). HO scavenger agents: n-butanol and acetic acid. Reactor: 1 L glass. Ultrasound probe, cup horn type. Temperature: 25 °C.</p>	<p>At alkaline pH the degradation rate decreased significantly. The addition of H₂O₂ did not contribute to the degradation of IBU by the US process. The sono-Fenton process was more efficient in eliminating the IBU than both processes separately. In the sono-Fenton process no significant influence on the degradation of the IBU was achieved by varying the power density in the studied range. In the municipal sewage the degradation was more effective with the combined processes, with results similar to those obtained with synthetic water. However, the efficiency of the individual US process decreased.</p>

Table 2. Cont.

Process	Ref.	Pollutant/Type of Water	Operating Conditions	Found Results
US US/UV	[9]	CBZ/Synthetic water	Co CBZ: 0.00625–0.1 mM. Sonolytic Reactor: 500 mL Cylindrical glass beaker Frequency: 200 and 400 kHz. Power: 20–100 W. Temperature: 20 °C. pH: 2–11. Photolytic reactor: Camera with two low-pressure Hg lamps, 253.7 nm. Combined reactor: Assembly of the sonolytic reactor inside the photolytic reactor.	CBZ degradation follows a pseudo-first order kinetics. Faster degradation rate and greater removal with a frequency of 200 kHz. When methanol was applied as HO• sequestering agent, there was no significant drug removal. The HO• was the protagonist of the degradation. As electrical power increased, CBZ degradation increased. SO ₄ ²⁻ and NO ₃ ⁻ hindered the transfer of electrons during oxidation. The degradation of CBZ with UV radiation alone was negligible. The UV/US process achieved the highest CBZ removal. Twenty-one reaction intermediates were detected.
US/Single-walled carbon nanotubes	[31]	SFX and IBU/ Synthetic water	Co SFX and IBU: 10 µM. Single-walled carbon nanotubes (SCN). Stainless steel reactor. Frequency: 1000 kHz Power: 180 W pH: 3.5–7–9.5. Temperature: 15 to 55 °C. Reaction time: 60 min. Working volume: 1 L.	As the temperature increased, the cavitation threshold decreased, bubble formation increased together with the amount of HO•. At pH values below the pKa of the compounds, complete degradation was obtained within 50–60 minutes. At higher pH values, complete degradation was not achieved. In the presence of the SCN the degradation and the speed constant of the same was favored. The adsorption capacity of the SCN favored the removal of the compounds.
US/EO	[29]	CBZ/Synthetic water	Working volume: Reactor 1: 1 L and Reactor 2: 100 L. Cathode and anode in the form of expanded metal plates. Anode: Ti/PbO ₂ Cathode: Ti Electric current: 1–15 A. Type of water: Potable (from the tap). Co CBZ: 10 mg L ⁻¹ . Na ₂ SO ₄ : 0.01 mol L ⁻¹ Temperature: 20 °C. Ceramic transducer: diameter 4 cm. Frequency: 520 kHz. Power: between 10 and 40 W. Reaction time: between 90 and 180 min.	The combined US/EO process offered the best kinetic velocity constant. The degree of synergy, in the combination of the processes, rose with the increase in US power. As the current intensity increased, the depurative capacity rose. CBZ degradation was greater when the two processes (US and EO) were implemented simultaneously than separately. There was a 99.5% degradation of CBZ with the combined process.
US/O ₂ /Fe	[67]	Metazachlor (MTZ)/Synthetic water	Generator US: 20 kHz. Titanium alloy probe. Co: 10 µM MTZ. pH: 3.0. Temperature: 22 °C. Presence or absence of dissolved oxygen. Presence or absence of nitrogen. Treatment time: 120 min. Addition of powdered ferric oxyhydroxide 50 mg L ⁻¹ .	MTZ degradation followed a pseudo-first order kinetics. The saturation of water with oxygen favored the degradation of MTZ. Excess oxygen can capture H• and avoid recombination with HO•. With the addition of ferric oxide and the recombination of HO• to produce H ₂ O ₂ , the Fenton process is generated in the middle of sonolysis. The application of US made the iron leaching process three times faster than conventional mechanical agitation, allowing better contact between the liquid and solid phases. 97% of MTZ was degraded with the addition of ferric oxide. The velocity constant was twice than that of US process alone.

Table 2. Cont.

Process	Ref.	Pollutant/Type of Water	Operating Conditions	Found Results
US/Additives [68]		Oxacillin (OXA)/ Synthetic water	Working volume: 250 mL Electrical power: 60 W. Frequency: 275 kHz. Temperature: 20 °C. Mannitol and calcium carbonate were used as additives	In the presence of additives, OXA was efficiently removed. The sonochemical process was able to completely degrade the antibiotic, generating solutions without Antimicrobial Activity. The contaminant did not mineralize even after 360 min.
US/O ₃	[32]	Benzophenone-3 (Bp3)/ Synthetic water	Frequency: 20 kHz. Electrical power: 55.9 W. Temperature: 25 °C. Working volume: 200 mL [Bp3]: 3.9 mg L ⁻¹ . pH: 2, 6.5 and 10. O ₃ : 0.5 mL min ⁻¹ . N ₂ y O ₂ : 800 mL min ⁻¹ . Presence of nitrate, chloride and bicarbonate ions [5 mmol L ⁻¹].	Increasing the electrical power also increases the degradation of Bp3. At a lower pH (2) a more effective degradation of Bp3 was observed. PKa Bp3: 8.06. The presence of O ₂ , O ₃ and the combined process of US/O ₃ improved the degradation of Bp3. Being faster US/O ₃ . Bicarbonate ions accelerated the degradation of Bp3.

Due to the demonstrated efficiency ascribed to the use of US-assisted AOPs in the degradation of ECs in water, it has been widely applied for tackling the problem of water pollution with these pollutants of growing concern [32,36,64]. As stated previously, it is highlighted that the water matrix is a topic of utmost importance when it comes to the evaluation of the pollutant removal capability through AOPs. In fact, in the literature, different works have been reported based on the elimination through US waves of various ECs commonly present in water matrices of different nature, from drinking water effluents to natural surface water, with domestic and industrial wastewaters being highly studied [40,69,70] due to the vast variety of compounds that can be found in these kinds of aqueous matrices.

For instance, Cetinkaya et al. [69] investigated the decolorization of textile waters using the sono-Fenton process, obtaining better results at pH 3, achieving 96% of color removal. The influence of ferrous ions (Fe²⁺) concentration was analyzed, testing its variation between 0.05 g L⁻¹ and 0.2 g L⁻¹. A color removal of 90% and 99% was observed with the lowest and the highest Fe²⁺ concentration, respectively. These results indicated that the sono-Fenton process required small amounts of Fe²⁺ to achieve high removals of the dyes. Additionally, H₂O₂ consumption was reduced by about 30% with the sono-Fenton process compared to the classic Fenton process. Furthermore, authors optimized operating parameters involved in the investigated AOP, achieving the highest removal of color at a frequency of 35 kHz, pH 3, 0.05 g L⁻¹ of Fe²⁺, 1.65 g L⁻¹ of H₂O₂ and a treatment time of 60 min.

The removal of tetracycline (TC) has also been evaluated by Nasserri et al. [40] in a wastewater effluent by applying the US process. Some of the natural characteristics of the studied wastewater were: pH 7.9, chemical organic demand (COD) of 25 mg L⁻¹, HCO₃⁻ content of 164 mg L⁻¹, Cl⁻ of 92 mg L⁻¹, NO₃⁻ of 24 mg L⁻¹ and Na⁺ of 50 mg L⁻¹. A lower removal rate of TC, but in the same order of magnitude, in wastewater (1.25 × 10⁻² min⁻¹) compared to that one obtained in ultrapure water (1.75 × 10⁻² min⁻¹) was observed. These results may be ascribed to the negative influence of the water constituents, as explained previously; in this case, due to the high levels of organic matter, in terms of COD, which can prevent the formation of OH• and, subsequently, reduce the rate of TC degradation.

In turn, Serna-Galvis et al. [71] experimented with wastewater from El Salitre Treatment Plant, located in Bogotá (Colombia), with the objective of applying the sono-photo-Fenton/Oxalic Acid AOP for the removal of the following pharmaceuticals: DCF, CBZ, venlafaxine, ciprofloxacin, norfloxacin, valsartan, losartan, irbesartan, SFX, clarithromycin, azithromycin, erythromycin, metronidazole, trimethoprimine and clinimetropimine, as well as cocaine and its main metabolite benzoylecgonine. The operating conditions were: 300 mL of working volume, 88 W L⁻¹ of power density, 375 kHz of frequency, 20 °C of temperature, a UVA lamp of 4 W, a Fe²⁺ content of 5 mg L⁻¹ and an oxalic acid concentration of 2 mg L⁻¹. It was observed that the application of the sonochemical process alone led

to the release of contaminants from suspended solids. The addition of Fe^{2+} , UVA light and oxalic acid to the US process significantly increased the elimination of the studied ECs in the effluent, thanks to the production of additional $\text{HO}\bullet$ through reactions between iron and the sonogenerated H_2O_2 . It is important to note that the presence of oxalic acid makes iron more available for the formation of additional free radicals within the solution, causing the improvement of EC degradation.

With the aim of comparing the findings of degradation reported by US in wastewater, the work conducted by Vilardi et al. [70], where the efficiency of conventional and heterogeneous Fenton for the degradation of contaminants present in the wastewater of a tannery in terms of COD, total phenolic compounds (TP) and Cr(VI), is presented. The authors carried out the experimentation at large laboratory scale using a reactor with a volume of 7.4 L. It was concluded that the heterogeneous Fenton process was significantly more efficient with respect to the conventional one for the elimination of COD and TP, once the optimal values of the operating parameters were found. The percentages of COD and TP removal for the heterogeneous Fenton were $75.5 \pm 2.1\%$ and $85.1 \pm 0.7\%$, respectively. Likewise, it was observed that a smaller amount of iron sludge was produced due to the heterogeneous Fenton process (17.5%) compared to that one achieved through the conventional Fenton process (21.6%), which is a key aspect for the feasible implementation of the process at industrial scale.

Although the heterogeneous Fenton process implemented above was demonstrated to produce relatively low amounts of sludge, a more environmentally safe process must be required to overcome the pollution of aqueous resources with recalcitrant contaminants. In this regard, the use of US as an AOP alone or in combination with other advanced oxidation technologies seem to be an attractive treatment option.

3. Future Perspectives

Although the application of US alone as an advanced oxidation technology to overcome the critical situation ascribed to ECs in aqueous environments has been demonstrated to be efficient, the coupling of US with other AOPs could improve the mineralization of emerging organic compounds [72,73] within a further reduced time of treatment. For this reason, the use of US hybrid techniques has been recently studied to improve EC mineralization results [6,23,45,73]. A clear example of this is the combination of sonolysis with the Fenton process. This combination, which is so-called sono-Fenton, could stimulate a faster conversion and/or mineralization of ECs. This is achieved through: firstly, higher generation of $\text{HO}\bullet$ [74]; secondly, an improved mixture and contact between $\text{HO}\bullet$ and the pollutants of interest [72,73], and thirdly, improved generation of Fe^{2+} [75].

Different strategies in addition to the combination of the Fenton process with sonolysis have been tested in the last years. An example of this is the work developed by Tran et al. [20], where the electro-oxidation (EO) process was combined with US. This combination was based on the fact that, initially, the formation of $\text{HO}\bullet$ is achieved on the wall of an electrode made up of a non-active material through the EO process, and the chemical exchange of these $\text{HO}\bullet$ with contaminants could then be improved due to the formation of the US waves and cavitation bubbles resulting from the US process. In this study, a higher kinetic velocity constant and a greater efficiency in the removal of IBU was obtained with the combined process of EO/US in comparison with the results obtained in each process independently. As a result, 90% of the IBU contained in samples of municipal sewage was removed using optimal parameter levels, such as the treatment time, the current intensity and the US power, which were determined through the response surface methodology. The beneficial results of the exposure of electrochemical cells to the effects of US power are related to the improved mass transport, increased current efficiencies, and continuous electrode surface activation [20,76,77]. These effects can be attributed to the rapid generation and collapse of the micro-bubbles within the electrolyte medium or near the electrode surface [20,77,78].

In turn, Ince's 2018 study [62] evaluated the degradation of toxic ECs through US in combination with other AOPs. In this study PCT, DCF and IBU were analyzed, finding that the degradation of the selected ECs was more efficient at high frequencies and acid pH. Degradation was further improved

with the presence of solid catalysts, which provided surfaces that enhanced the formation of cavitation bubbles and, therefore, the performance of the oxidation processes. In the referred research, the use of iron nano- and micro-particles resulted in a higher rate of DCF elimination by using nano-particles [62], which was attributed to the synergy of US with these particles through the enrichment of massive surfaces with excessive sorption sites and cavitation nuclei. In addition, reactions at the bubble–liquid interface were intensified by the distortion of asymmetric shapes, the degree of which increases as particle size decreases [62]. On the other hand, the coupling of an ozonation system with UV radiation and sonication, with the optional addition of FeSO_4 , completely degraded DCF [62]. Finally, this work compared the efficiency of the following AOPs: US, O_3/US , UV/US and $\text{O}_3/\text{US}/\text{UV}$. High removals of the drugs of interest were found in all the tested processes, reaching about 100% elimination accompanied by a mineralization between 40 and 60% of all the ECs with the combination of US, O_3 and UV radiation.

In the work developed by Rao et al. [9], sonolytic and photolytic AOPs were combined for the degradation of CBZ. The result was a significant improvement in the drug degradation compared to the results obtained when the processes were individually implemented. The reason for this fact was related to the formation of H_2O_2 resulting from the recombination of $\text{HO}\bullet$ from sonolysis. This oxidizing agent can be photolyzed by UV light and more $\text{HO}\bullet$ can be produced, which are the main contributors to CBZ degradation.

CBZ removal was also studied by Mohapatra et al. [79], through the US process, Fenton and ferro-sonication (a combination of FeSO_4 with the US process). It was found that the most efficient AOP was the Fenton process, with elimination percentages between 84–100%; this was followed by ferro-sonication, with values between 62–93%, while sonolysis only achieved CBZ elimination percentages between 22%–51%. The authors concluded that the higher the radiation intensity (5.8, 12.4 and 16 W cm^{-2}), the greater the elimination of the target drug. Moreover, according to their research, the resulting ranges of efficiency between one process and another were because FeSO_4 contributed to the formation of a greater amount of $\text{HO}\bullet$.

Although Fenton process has been proven to be an efficient technology for the degradation of some ECs [70,79], residual sludge is produced, especially when the homogeneous Fenton process is applied [70]. In this regard, further studies are needed to give an alternative use to such as sludge, contributing to the so-called principles of the circular economy. In this regard, Vilardi et al. [80] treated a tannery wastewater with mixed-iron coated olive stone bio-sorbent particles in combination with H_2O_2 . They found a COD removal efficiency of 58.4% and a TP removal of 59.2%, at $\text{H}_2\text{O}_2/\text{COD}$ (w/w) equal to 0.875. The coated olive stones were regenerated with sodium hydroxide (NaOH) and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) solutions after five cycles in order to enable their reuse.

In addition, considerate the circular economy principles, economic costs analysis must be carried out in order to discern whether an AOP tested at laboratory or pilot plant can be scale up for industrial application in real water effluents.

4. Cost Consideration

As reviewed, the efficiency of ultrasound has been demonstrated to degrade any kind of recalcitrant pollutants. However, there are limitations related to the economic costs associated with the use of this advance oxidation technology for the treatment of water containing toxic pollutants [39]. One such limitation is the cost, which can be divided into two groups: the capital or inversion costs, which consists of those costs associated with the manufacture of the sonochemical reactors and can be amortized over a span of years at a considered amortization rate [39], and the operation and maintenance costs. The economic cost estimation linked to the operation and maintenance labor include the part replacements, which mainly consists of the transducer element replacement and the tip or electronic circuit replacements. In fact, according to Mahamuni and Adewuyi [39], the part replacement costs are assumed to be 0.5% of the capital costs. Labor and analytical costs must also be considered when operation and maintenance costs are estimated. Labor costs include inspection,

repair and replacement based on hours of service life of control panels, leakages and pressure gauge, among others. In turn, analytical costs consist of the costs related to the analysis of samples and, subsequently, the costs associated with the reactants and chemicals used for the sample analysis. Additionally, electrical costs, which can be based on the power consumption of the referred AOP, are of utmost importance since they are usually very high, especially in those countries where the cost of each kWatt is high. Hence, the use of renewable resources for generating electrical energy is an attractive option that is emerging for the advanced oxidation system to be implemented. As a matter of fact, Rubio-Clemente et al. [81] assessed the efficiency of the UV/H₂O₂ system powered by a photovoltaic (PV) system in a photochemical reactor at laboratory scale. According to the results reported by the authors, similar efficiency was observed between the oxidation system powered with energy from the electrical grid and that one generated using the PV cells implemented.

Another alternative for reducing the economic costs related to the use of ultrasound for treating polluted water is utilizing hybrid oxidation techniques by combining US with other AOP, including the use of oxidizing or catalyzing agents, such as ozone (O₃), H₂O₂, iron, titanium dioxide (TiO₂), wolfram trioxide (WO₃), zinc oxide (ZnO), etc., and electrochemistry to name just a few. In this regard, Expósito et al. [25] evaluated the efficiencies of mineralization in terms of total organic carbon (TOC) and CBZ removal by using the US/UV/H₂O₂/Fe oxidation process at laboratory scale in a thin film UV reactor coupled to a 24 kHz 200 W direct immersion horn-type sonicator, obtaining efficiencies around 90%, which are higher than the efficiencies reached by the processes alone. In fact, a synergistic effect higher than 55% was found between the US process and UV irradiation.

However, although application of US hybrid techniques in some occasions can be more attractive for water treatment, Mahamuni and Adewuyi [39] reported that the costs associated with these treatment techniques are one to two orders of magnitude higher than when US is implemented alone. This can be ascribed to the costs linked to the additional chemicals used for the hybrid process to occur, i.e., the use of oxidizing agents such as O₃ and H₂O₂, or the catalyzing agents as iron salts, TiO₂, ZnO or WO₃, among others, as well as the adjustment of the pH of the solution if needed. Moreover, when US is used along with UV radiation, the costs associated with the replacements of the lamps and the electrical consumption of the lamps must be considered, as well as those ones related to the O₃ generator repair when O₃ is combined with US.

With this in mind, it can be concluded that the cost estimation studies based on pilot plants would be of high importance for to discern both the capital and the operation and maintenance costs related to the implementation of the US process. Furthermore, although high efficiencies can be obtained in a short period of time by using hybrid techniques with US, the economic costs associated with it are higher; therefore, further studies are needed to discern if the combination of US with another AOP is worth to be implemented under any circumstances. On the other hand, the type of pollutant plays a crucial role on the cost estimation procedures, since treating water containing hydrophobic pollutants has lower costs ascribed in comparison with those ones for treating compounds of hydrophilic nature [39].

5. Conclusions

After a critical review of the results found in the literature concerning the US process for the elimination of ECs, it is important to highlight the following conclusions:

- The US process is environmentally clean, as it does not produce chemical residues or sludge in comparison with other AOPs, such as Fenton and photo-Fenton processes, and other advanced oxidation technologies using catalysts, including TiO₂, ZnO and WO₃, among others.
- The nature of the pollutant is an issue of utmost concern when evaluating the efficiency of the ultrasound process, since hydrophobic, non-polar and/or volatile compounds react inside the cavitation bubbles and at the bubble/water interface, while hydrophilic and/or non-volatile pollutants react within the bulk solution.

- On the other hand, the operating parameters, such as the pH and the temperature of the solution, ultrasonic frequency, electrical power, dissolved gases and the nature and concentration of the pollutant, must be evaluated under a wide range, since the efficiency of the process depends on them. In this regard, the considered operating factors should be optimized in order to maximize the degradation of the pollutant of interest and minimize the operation and maintenance costs.
- The degradation efficiency of aqueous pollutants also depends, to a large extent, on the type of sonoreactor and the geometry of the system. Therefore, the optimization of the sonoreactor, in terms of geometry and type, is recommended to be carried out especially when scaling the US-assisted AOP up.
- Further researches are needed for evaluating the efficiency of the referred process in real water matrices since, as reviewed, aqueous matrix background can highly influence the efficiency of the oxidation system and, subsequently, the degradation of the pollutant to be studied.
- The combination of ultrasound with other advanced oxidation or conventional processes used for water treatment can offer a high percentage of removal and mineralization of the compound under study. However, the associated economic costs are commonly higher than when US is applied alone. Therefore, further studies based on the efficiency about the cost estimation of the US oxidation process alone and in combination with other AOPs are required, especially in pilot plants, to obtain a closer point of view for the advanced oxidation technology scale-up.

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