Sonozonation (sonication/ozonation) for the degradation of organic contaminants – A review

Published version:

DOI:10.1016/j.ultsonch.2020.105195

[Sonozonation (sonication/ozonation) for the degradation of organic contaminants – A review, Zhilin Wu, Anna Abramova, Roman Nikonov, Giancarlo Cravotto, Ultrasonics - Sonochemistry 68 (2020) 10519, https://doi.org/10.1016/j.ultsonch.2020.105195]

Sonozonation (sonication/ozonation) for the degradation of organic contaminants – A review

Zhilin Wu a,b, Anna Abramova c, Roman Nikonov c, Giancarlo Cravotto a,d,⁎
a *Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin, Via P. Giuria 9, I-10125 Turin, Italy*
b *Nanjing Institute of Environmental Science of the Ministry of Environmental Protection of China, Jiangwangmiaostr.8, 210042 Nanjing, China*
c *Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
d *Sechenov First Moscow State Medical University, 8 Trubetskaya ul, 119991 Moscow, Russia*

⁎ Corresponding author at: Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin, Via P. Giuria 9, I-10125 Turin, Italy.
E-mail address: giancarlo.cravotto@unito.it (G. Cravotto).

ABSTRACT

Ozonation (OZ) is an important advanced oxidation process to purify water and wastewater. Because of the lower solubility and instability of ozone (O_3), selective oxidation and dependence on pH value, the industrial applications of OZ have been hindered by the following disadvantages: incomplete removal of pollutants, lower mineralization efficiency and the formation of toxic by-products. Meanwhile, OZ seems to have higher processing costs than other technologies. To improve the treatment efficiency and O_3 utilization, several combinedprocesses, such as H_2O_2/O_3, UV/O_3, and Cavitation/O_3, have been explored, while the combined method of ultrasonication (US) with OZ is a promising treatment technology with a complex physicochemical mechanism.

In US alone, the sonolysis of water molecules can produce more powerful unselective oxidant hydroxyl radicals (%OH), and directly cause the sonochemical pyrolysis of volatile pollutants. In US/OZ, US can promote the mass transfer of O_3, and also drive the chemical conversion of O_3 to enhance the formation of %OH. Various layouts of US/OZ devices and the interactive effects of US/OZ (synergism or antagonism) on the degradation of various organics are illustrated in this review. The main factors, including US frequency, pH value, and radical scavengers, significantly affect the mass transfer and decomposition of O_3, the formation of %OH and H_2O_2, the degradation rates of organics and the removal efficiencies of COD and TOC (mineralization). As a result, US can significantly increase the yield of %OH, thereby improving the degradation efficiency and mineralization of refractory organics. However, US also enhances the decomposition of ozone, thereby reducing the concentration of O_3 in water and impairing the efficiency of selective oxidation with O_3 molecules.

Keywords:

Sonication, Ozonation, Sonozonation, Synergism, Degradation

1. Introduction

With rapid industrial development, a wide variety of organic compounds, such as dyes, pesticides, pharmaceuticals and their intermediates (phenols, substituted aromatics, etc.) are produced, used and discharged into our environment [1]. Many organics are toxic, chemically and biologically stable and difficult to remove using conventional treatments [2,3]. These harmful organics, which can occur and even remain in our environment for several years, are thus named persistent organic pollutants (POPs) [4,5].

Advanced oxidation processes (AOPs), which exploit highly reactive and unselective oxidant species, such as the hydroxyl radical (%OH), have been widely demonstrated to be efficient in the degradation and mineralization of refractory pollutants [6‑8]. Fenton's reagent for the generation of %OH, and possibly others via hydrogen peroxide (H_2O_2) in the presence of Fe^{2+}, are known to be very effective in the destruction of many hazardous organic pollutants in water [9,10]. The semiconductor photocatalytic process is another low-cost, environmentally friendly and sustainable treatment technology [8]. Besides, electrochemical oxidation [11], wet-air oxidation [12], non-thermal plasma [13,14], and combined technologies that use various AOPs [15] have also been investigated for their oxidative decomposition of organic contaminants in wastewater.

Ozonation (OZ) is a process that provides treatment with ozone (O3), often as one of the traditional AOPs [15‑20], while ultrasonication (US) has been quickly developing for the degradation of organic pollutants since about 1990 [21,22]. Ozone is a powerful oxidant, behind %OH, and more powerful than other common oxidants, such as chlorine dioxide (ClO_2), free chlorine (Cl_2) and H_2O_2 [23]. Ozone has been extensively used in the disinfection of water and for wastewater treatment [24]. OZ can occur directly via molecular O_3, or indirectly by %OH formed *in-situ* in water. Ozone is an electrophile with high selectivity toward olefins (double bonds), activated aromatic systems and non-protonated amines. In general, electron-donating groups (activating groups, $-NH_2$, -OH, etc.) enhance OZ, whereas electron-withdrawing groups (deactivating groups, $-NO_2$, $-SO_3H$, -halogen, etc.) reduce the OZ rates [25,26]. Meanwhile, ozone molecules partly decompose in water, leading to the formation of %OH, which easily oxidizes even inert types of organics [26]. In particular, %OH is formed upon the hydroxide-ion catalyzed decomposition of O_3 under alkaline conditions. Up to 0.55 mol of %OH can be produced from 1 mol O_3 at pH 10.5 [16]. In addition, H_2O_2 is another catalyst for the decomposition of O3, while O_3 is not a catalyst for the decomposition of H_2O_2 [27].

In general, US is the act of sonochemistry applying sound energy to process solutions, suspensions, and solid materials in liquids for various applications, such as medicine, biochemistry, biomaterial, biofuels, nanomaterial, organic and environmental chemistry, pharmaceutics and food processing [28‑30]. When the sound frequency used is over 20 kHz, sonication is also named ultrasonication. The terms sonication and ultrasonication are often used indiscriminately as “sonication”. Ultrasound causes high-energy chemistry and does so through the process of acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid. During the cavitation collapse, intense heating of the bubbles occurs. These localized hot spots have temperatures of roughly 5000 °C, pressures of about 500 atmospheres and lifetimes of a few microseconds [31,32]. Shock waves and microjets from collapsing cavitation in liquid‑solid slurries produce high-velocity interparticle collisions, the impacts of which are sufficient to melt most metals [28]. Ultrasound has also been used in the initiation and enhancement of degradation and catalytic reactions in both homogeneous and heterogeneous cases [33‑39].

Overall, ozone is a powerful oxidant that can directly oxidize unsaturated organic compounds, especially with C = C double bonds in water. Ozone is spontaneously converted into a more powerful unselective species in water, %OH. However, ozone is difficult to disperse or dissolve into water, leading to lower gas‑liquid mass transfer. US and other mixing technologies, such as hydrodynamic cavitation, have thus been extensively used to enhance OZ and reduce the contact time for complete disinfection and degradation of hazardous contaminants in effluents [40‑45]. For example, the simultaneous treatment of US and OZ reduced the sterilization dose of ozone by 50% and increased the rate constant of the decolorization of rhodamine B (RB) by 55% [41]. It was suggested that US promotes the mass transfer and formation of %OH to cause higher OZ activity and higher O_3 utilization [41,46]. Fig. 1 hows the reaction pathway of sonozonation (US/OZ).

In general, the degradation of organic pollutants follows pseudofirst-order kinetics. The effects of some factors on the degradation kinetics have been demonstrated, almost without controversy. For example, a higher O_3 dose, gas flowrate, and O_3 content favor the degradation of organics [47–51], and the effect of the O_3 dose on dye decolorization was much greater than that of sonolysis density [52].

The rate constant decreases with increases in the initial concentration of organics [52–55]. Increases in ultrasonic power significantly enhance the destruction rate of different organic species [49,55–58], etc. This review summarizes recent publications on the setups of US/OZ and the synergism of US/OZ for the degradation of organic contaminants in aqueous solutions, as well as outlining critical issues, including synergistic mechanisms, US-improved O_3 mass transfer, USenhanced O_3 decomposition and the formation of %OH, as well as describing the roles of pH and ultrasonic frequency on US/OZ processes.

2. Sonozonation setups

In earlier studies, ozone-saturated water (O_3 solution) was used to investigate the role of US on O_3 decomposition, %OH and H_2O_2 formation, disinfection and organic degradation by O_3 [53,55,59]. In general, water was placed in a gas dispersion bottle and bubbled with O_3-containing gas at certain flowrates. Over recent decades, US batch reactors have been widely used with the continuous bubbling of O_3/O_2 or O_3/ air. The batch configuration of US/OZ setup depends on the structure of the ultrasonic transducer, which usually includes an ultrasonic horn or an ultrasonic bath. The ultrasonic horn or bath can also be connected with a pump and pipes in series to configure a closed or open flow system [60].

2.1. Sonozonation with the ultrasonic horn

Typically, US with an ultrasonic titanium horn (around 1–2 cm of tip diameter) is often performed with a low frequency and high power ultrasonic generator (20 kHz, 250–550 W). The horn transducer is placed 1–3 cm into 180–1200 mL of solution. US can be processed in pulses or continuously. The reactor was a doubled-wall glass chamber equipped with cooling media [56], or a flask immersed in a water bath to control the temperature, at room temperature, as shown in Fig. 2 [61]. If agitation is necessary, a magnetic stirrer provides the mixing of the solution in the reactor.

Ozone that originates from the O_3 generator with dry O_2 is continuously bubbled into aqueous solution via a gas diffuser. The flowrate of O_3 gas is determined with a flowmeter. The O_3 concentration in the gas is quite lower (0.6–2.0 wt%) monitored using the iodometric method with a KI solution [54,60,62,63]. When the reactor is a closed system, the ozone in the tail gas can be trapped by a KI solution so that the O_3 concentration in the tail gas can be detected and the utilization efficiency of O_3 can be evaluated [56].

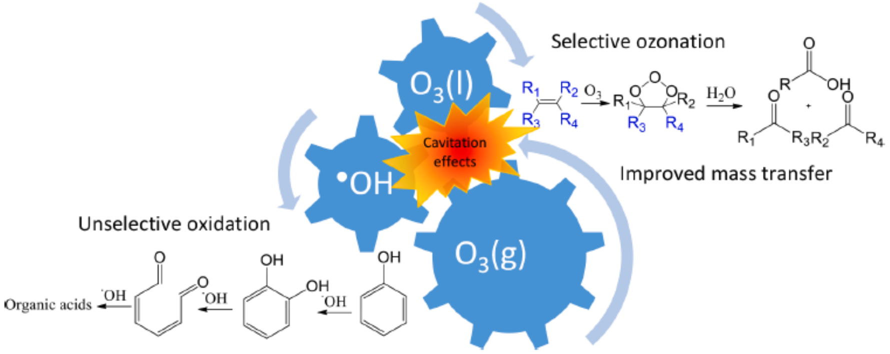

Fig. 1. Reaction pathway of organic degradation by sonozonation.

2.2. Sonozonation with ultrasonic bath

A more common type of US/OZ setup adapts the ultrasonic bath (up to 1200 mL at lab-scale). An ultrasonic transducer with a higher frequency (300–1141 kHz) and lower power (20–100 W) is located on the bottom of the reactor equipped with a water jacket [48,64,65], as shown in Fig. 3. The temperature of the reaction solution is controlled by a cooling medium. The ultrasonic power intensity has been determined to be below 2 W cm^{-2} in 150–800 mL of air-saturated distilled water by calorimetry [32,34,48,64,66]. Similarly, ozone gas is continuously bubbled into the reactor by a gas diffuser. Furthermore, several special configurations for US/OZ setup, based on ultrasonic baths, have been developed further. For example, Yang et al. have established a three-necked round flask reactor (1000 mL) within an ultrasonic cleaner (50 kHz, 120 W). Ozone gas was introduced into the bottom of the round flask via a neck [50]. With this reactor, the degradation of phenol was carried out in 800 mL of aqueous solutions with the chosen OZ and/or US.

Faryadi et al. have reported that a microreactor immersed within a container (with a diameter of 9 cm and height of 11 cm) equipped with a high-frequency ultrasonic transducer (1.7 MHz, 9.5 W) was used to evaluate the effect of US on the micromixing and mass-transfer-rate performance inside the microreactor [67]. The actual power dissipated into the bulk liquid (in the container) and microchannel was 8.5 W and 4.45×10^{-4} W, respectively. The microreactor was made of glass tubes with an inner diameter of 0.8 mm, and 15, 25 and 35 cm lengths. The O3 stream from the O3 generator was introduced into channel A and the RB solution was introduced into channel B by a peristaltic pump at room temperature. The improved decolorization of the RB solutions using the OZ/US combination in this microreactor in an ultrasonic bath was examined and compared to the individual process.

Another example is an ultrasonic bath equipped with multiple ultrasonic fields [68]. Zhao et al. have reported a cuboid ultrasonic reactor with four walls mounted with four identical piezoelectric transducers (28 kHz). The total power input was controlled at 120 W either individually or in various combinations of transducers, leading to 0.39 W cm−2 of power intensity and 38.5 W L^{-1} of power density in any case. Using this reactor, the degradation of nitrobenzene (NB) in aqueous solution by US/OZ was observed with the increasing amount of ultrasonic transducers.

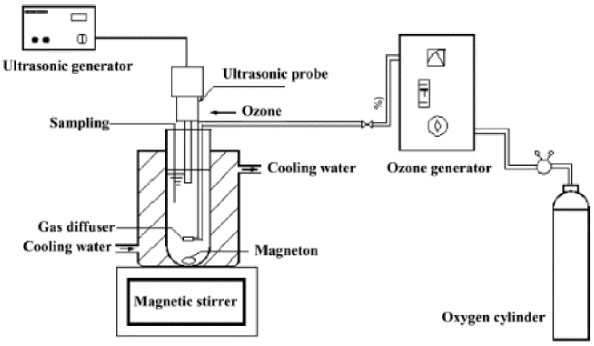

Fig. 2. The sonozonation set up with an ultrasonic horn, magnetic stirrer, O_3 gas diffuser, and cooling water. Reprinted from ref. [61] Copyright (2006), withpermission from Elsevier.

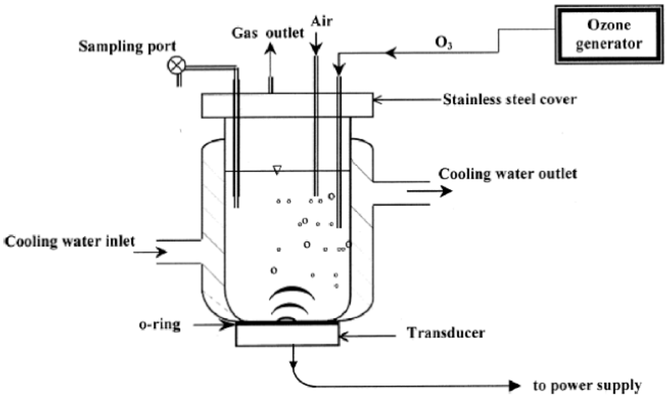

Fig. 3. The sonozonation set up with an ultrasonic bath and cooling water. Reprinted from ref. [64] Copyright (2001) with permission from Elsevier.

3. Synergistic effects of sonication and ozonation

The synergistic effect (SE) of the two factors is the most significant feature and advantage of the joint process. This synergism in US/OZ systems is principally caused by enhanced ozone dissolution, the excess decomposition of O_3 and enhanced *in-situ* formation of radical and peroxide [64]. The SE has been defined as the optimal rate constant of a combined system divided by the sum of rate constants of each independent system at optimal conditions, as shown in Eq. (1) [57,69]:

$$\mathrm{SE} = \frac{k_{US/OZ}}{k_{US} + k_{OZ}} \quad (1)$$

where *kUS/OZ*, *kUS* and *kOZ* are the degradation rate constants of a pollutant by US/OZ, US and OZ at optimal conditions, respectively.

A SE value over 1.0 indicates that the synergism of two factors exists. By contrast, antagonism appears if the SE value is below 1.0.

3.1. Degradation of volatile organic compounds in aqueous solution

Some volatile organic compounds (VOCs), such as carbon tetrachloride (CCl_4), are inert to O_3, but quite easy to degrade by sonolysis. It has been demonstrated that the presence of O3 during the sonolysis of CCl_4 at 20 kHz failed to enhance the rate of CCl_4 destruction [59].

However, methyl *tert*-butyl ether (MTBE) can be slowly oxidized by OZ. The pseudo-first-order rate constants (*kUS/OZ*, *kUS* and *kOZ*) of MTBE degradation by US (205 kHz, 200 W L^{-1}), OZ (20 mM O_3), and their combination (US/OZ) are 0.0522, 0.0036, and 0.188 min^{-1}, respectively, and the corresponding SE value was calculated to be 3.37 [53].

The degradation of MTBE was greatly accelerated in the US/OZ system. It was speculated that US enhanced mass transfer and O_3 decomposition; which allows the formation of more %OH. Meanwhile, Kang and Hoffmann have suggested that the major reaction site for MTBE with % OH is in the vapor phase of the cavitation bubbles and within the superhot interfacial region between the vapor and surrounding liquid phases, but not in the bulk aqueous phase [53].

Likewise, Lifka and Ondruschka have reported the similar synergism of US/OZ toward the degradation of MTBE, ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME). The SE values, 2.1 for TAME, 2.0 for MTBE and 1.5 for ETBE, were attained in an US/OZ system

(1 L of 0.1 mM solutions, 850 kHz, 50 W, bubbling with 1.5 wt% O_3 at 2 L h^{-1} for 60 min at 20 °C) [54]. Also, Park et al. have reported that the calculated SE values of US/OZ toward the degradation of dichloroacetonitrile (DCAN) were 2.56 and 2.15 at 35 and 283 kHz, respectively [57]. This remarkable synergism was also suggested to be attributed to the thermal decomposition of O_3 in the collapse of cavitation bubbles, and the resulting formation of %OH and H_2O_2 by US/OZ [57].

Furthermore, ozone can directly oxidize unsaturated compounds,such as benzene and cyclohexene. As compared with the SE values for the degradation of MTBE, ETBE and TAME, a relatively lower SE value (1.16) toward the degradation of benzene was observed in an 850 kHz US/OZ system [54]. Due to the existence of C]C double bonds in alkene,cyclohexene reacts with O_3 more rapidly [68,70]. Weavers and Hoffmann reported that the value of *kUS*, *kOZ*, and *kUS/OZ* of 2.5 mM cyclohexene degradation in aqueous solutions by US (20 kHz, 263 W L^{-1}), OZ (20 mL min^{-1} of 0.66 wt% O_3 gas), and their combination (US/OZ) is 0.134, 0.057, and 0.204 min^{-1}, respectively, in an open ultrasonic reactor [60]. Thus, the SE value is calculated to be 1.07, suggesting the presence of very slight synergy between US and OZ toward cyclohexene degradation. By contrast, *kUS, kOZ and kUS/OZ* were observed to be 0.050, 0.019, and 0.065 min^{-1} in a 500 kHz closed reactor, and the SE value was 0.94, suggesting antagonism exists between US and OZ. It can be speculated that US promotes the decomposition of O_3 and diminishes the direct OZ of cyclohexene at 500 kHz US.

As discussed above, SE is dependent on the physicochemical propertiesof VOCs such as volatility, hydrophobicity, and especially reactivity with O_3. The degradation rate constants of various VOCs by US, OZ, US/OZ, and the SE values observed in previous studies have been summarized in Table 1, and the corresponding reaction conditions are shown in the references. The correlation between SE and *kOZ* as being well established is shown in Fig. 4. It appears that an optimal range of *kOZ* (2.53×10^{-3}–6.40×10^{-3} min^{-1}) exists, and that leads to higher SE values (2.00‐5.17). It suggests that the synergism of US/OZ can occur as VOCs are reactive to O_3 at proper degrees. No or very slight synergism, even antagonism was attained for inert or very highly reactive VOCs, such as CCl_4 or cyclohexene to O_3.

3.2. Degradation of semi-volatile organic compounds in aqueous solution

In general, the direct pyrolysis of semi-volatile (SVOCs) or non-volatile organic compounds, such as phenols and organic acids, is difficult to attain during the collapse of cavitation bubbles, and the sonolytic degradation of SVOCs is mainly attributed to the oxidation by %OH formed in the implosive cavities, and within the super-hot interfacial region between the cavities and surrounding liquid phases. Therefore, the sonolytic degradation rate of SVOCs is relatively slow compared with VOCs. He et al. have reported the degradation of succinic acid in aqueous solutions by US, OZ and US/OZ under alkaline conditions in separate experiments [51]. The typical results are illustrated in Fig. 5. As shown in Fig. 5, the sonolytic degradation of succinic acid is very slow, while OZ is quite fast due to oxidation by the %OH formed under alkaline conditions, rather than by molecular O_3 [71]. As a result, the pseudo-first-order rate constants were 0.0009, 0.0073 and 0.0180 min^{-1} for US, OZ and US/OZ treatment, respectively [51]. The SE value was thus calculated to be 2.20. Therefore, the major pathway of succinic-acid degradation by US/OZ was most likely due to the additional %OH formed from the decomposition of O_3 with US under alkaline conditions.

By contrast, phenols can react with both molecular O_3 (Electrophilic reactions) and %OH radicals [25]. The reaction of pentachlorophenol (PCP) with O3 was enhanced by audible-frequency sonication under alkaline conditions since the first-order rate constant of PCP degradation by the coupling method (2 L, 0.43 kHz, and 165 W L^{-1}) is more than 15 times higher than that with bubbling O_3 alone, while H_2O_2 was not generated and PCP was not degraded by audible-frequency sonication alone [72]. It indicates that the audible-frequency sonication greatly enhanced the mass transfer, dissolution of O_3 and %OH formation in aqueous solution. Under acidic conditions, O_3 auto-decomposition to produce %OH is suppressed [73]. Barbier and Petrier have reported that the pathway of the rapid degradation of 4-nitrophenol (4-NP) is a selective fast reaction with molecular O_3 by OZ alone at pH 2, while the coupling of US/OZ inhibits the degradation of 4-NP at 20 kHz by consuming a significant fraction of the O_3 transferred to solution in the cavitation bubbles [74]. However, the degradation of 4-NP in the 500 kHz US/OZ system was faster than those under 20 kHz US/OZ and OZ alone. This indicates that more %OH was formed at 500 kHz and that both molecular O_3 and the produced %OH accelerated the degradation rate together. By contrast, Weavers et al. have illustrated the synergism of US/OZ for the degradation of 4-NP, NB, and 4-chlorophenol (4-CP) at pH 2.4 in a 20 kHz system, while antagonism appeared in a 500 kHz system [75]. Nowadays, the combination of US/OZ has been extensively applied to the degradation of dyes, since O_3 is of special interest to decolorization. In general, the degradation of dyes by US alone can be neglected, compared with the degradation by OZ, while the remarkable synergistic effects of US/OZ have been mostly observed. For example, a SE value of 1.97 for C.I reactive black 5 (RB5) [64] and 1.42 for reactive red X-3B [69] have been attained. However, C.I. basic red 9 (pararosaniline) and malachite green are important exceptions [76,77], which were rapidly oxidized by molecular O3 due to the existence of C]C bond, leading to the antagonism of US/OZ, with an SE value of<1.0, or very slight enhancement under acidic conditions. This further suggests that US can enhance the decomposition of O_3, by reducing O_3 concentration and diminishing the direct reaction with molecular O_3 in the solutions.

Similarly to the VOCs discussed above, the SE of US/OZ for the degradation of SVOCs is dependent on the physicochemical properties of the SVOCs and, especially, reactivity with O_3. Various correlations between SE and *kOZ* have been established for low and high ultrasonic frequency systems under acidic conditions, respectively, as shown in Fig. 6.

Fig. 6 shows that the antagonism or very slight synergism of US/OZ was attained for the degradation of most SVOCs, except for RB5 in high frequency (300‑520 kHz) systems. In general, both weaker mechanical turbulence and the rapid decomposition of O_3 caused by the high-frequency US diminish the reaction of SVOCs with molecular $O_{3,}$ whereas more %OH formed at high frequencies is favorable to mineralization. In low-frequency systems, however, stronger mechanical turbulence enhances the mass transfer and dissolution of O_3 in aqueous solutions.

Remarkable US/OZ synergism was thus observed for the degradation of most SVOCs, except for compounds with C]C bonds, such as malachite green.

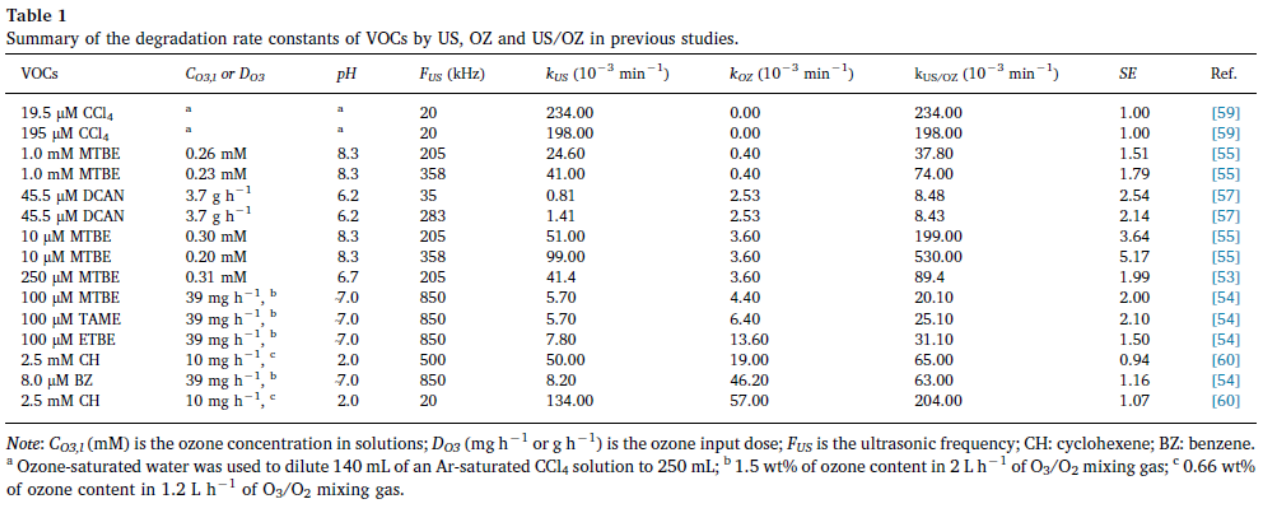

Table 1

Summary of the degradation rate constants of VOCs by US, OZ and US/OZ in previous studies.

VOCs	$C_{O3,l}$ or D_{O3}	pH	F_{US} (kHz)	k_{US} (10^{-3} min^{-1})	k_{OZ} (10^{-3} min^{-1})	$k_{US/OZ}$ (10^{-3} min^{-1})	SE	Ref.
19.5 μM CCl_4	[a]	[a]	20	234.00	0.00	234.00	1.00	[59]
195 μM CCl_4	[a]	[a]	20	198.00	0.00	198.00	1.00	[59]
1.0 mM MTBE	0.26 mM	8.3	205	24.60	0.40	37.80	1.51	[55]
1.0 mM MTBE	0.23 mM	8.3	358	41.00	0.40	74.00	1.79	[55]
45.5 μM DCAN	3.7 g h^{-1}	6.2	35	0.81	2.53	8.48	2.54	[57]
45.5 μM DCAN	3.7 g h^{-1}	6.2	283	1.41	2.53	8.43	2.14	[57]
10 μM MTBE	0.30 mM	8.3	205	51.00	3.60	199.00	3.64	[55]
10 μM MTBE	0.20 mM	8.3	358	99.00	3.60	530.00	5.17	[55]
250 μM MTBE	0.31 mM	6.7	205	41.4	3.60	89.4	1.99	[53]
100 μM MTBE	39 mg h^{-1}, [b]	~7.0	850	5.70	4.40	20.10	2.00	[54]
100 μM TAME	39 mg h^{-1}, [b]	~7.0	850	5.70	6.40	25.10	2.10	[54]
100 μM ETBE	39 mg h^{-1}, [b]	~7.0	850	7.80	13.60	31.10	1.50	[54]
2.5 mM CH	10 mg h^{-1}, [c]	2.0	500	50.00	19.00	65.00	0.94	[60]
8.0 μM BZ	39 mg h^{-1}, [b]	~7.0	850	8.20	46.20	63.00	1.16	[54]
2.5 mM CH	10 mg h^{-1}, [c]	2.0	20	134.00	57.00	204.00	1.07	[60]

Note: $C_{O3,l}$ (mM) is the ozone concentration in solutions; D_{O3} (mg h^{-1} or g h^{-1}) is the ozone input dose; F_{US} is the ultrasonic frequency; CH: cyclohexene; BZ: benzene.
[a] Ozone-saturated water was used to dilute 140 mL of an Ar-saturated CCl_4 solution to 250 mL; [b] 1.5 wt% of ozone content in 2 L h^{-1} of O_3/O_2 mixing gas; [c] 0.66 wt% of ozone content in 1.2 L h^{-1} of O_3/O_2 mixing gas.

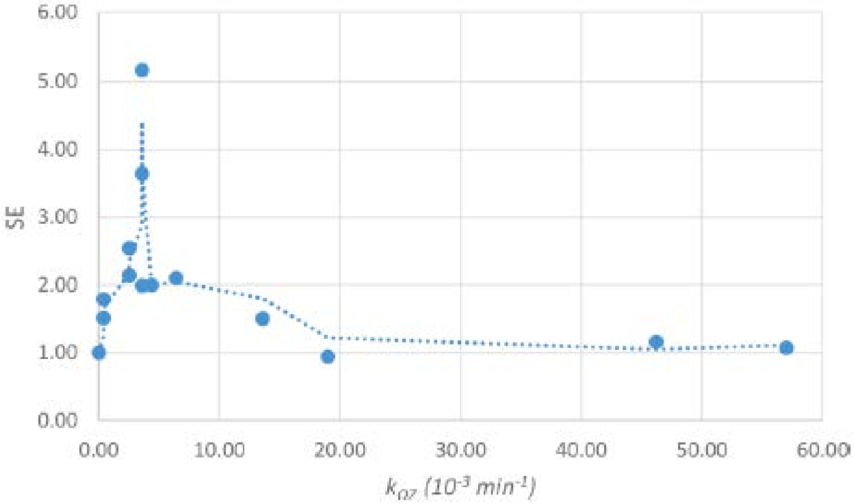

Fig. 4. The correlation between SE and *kOZ* for VOCs. (Data adopted from the references [53–55,57,59,60]).

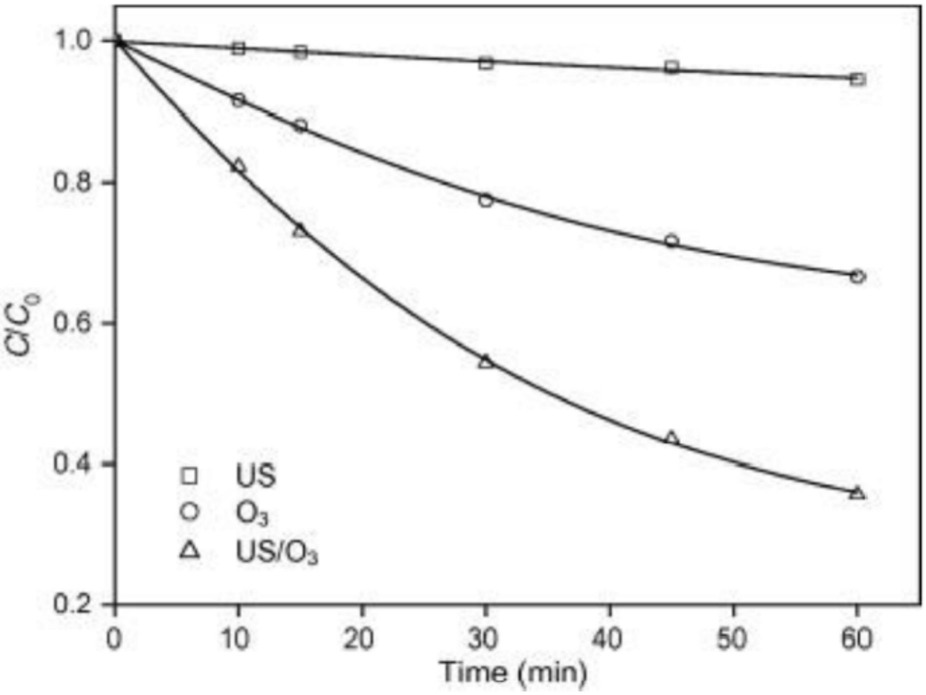

Fig. 5. Comparison of succinic acid degradation in aqueous solution by US, OZ (O_3) and US/OZ (US/O_3). Conditions: C0 100 mg L^{-1}; pH 10.0; ozone dose4.5 g h^{-1}; US frequency 20 kHz; US power density 44 W L^{-1}; temperature 25 °C. Reprinted from ref. [51] Copyright (2001) with permission from Elsevier.

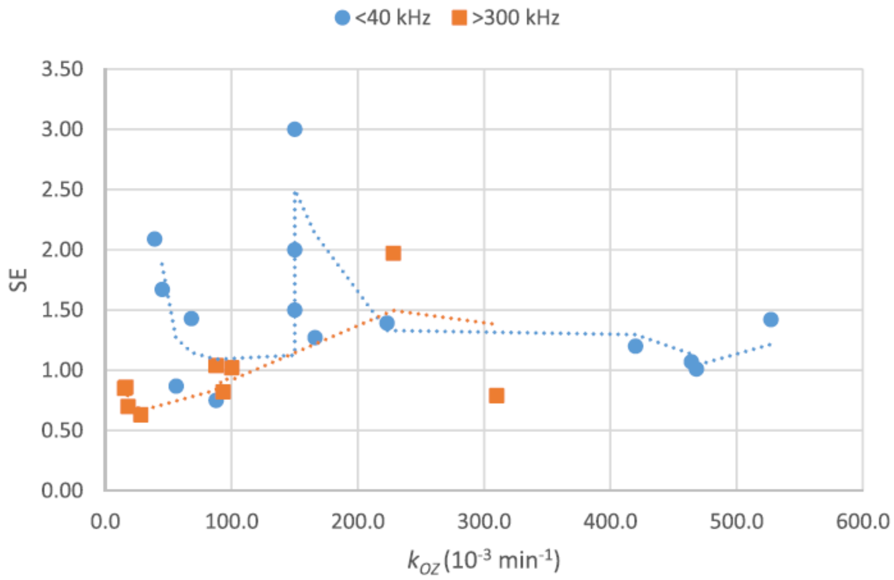

Fig. 6. The correlation between SE and kOZ for SVOCs in terms of ultrasonic frequency. (Data adopted from the references [47,48,56,58,64,69,74,75,77,78,79]).

3.3. Mineralization of organic contaminants

The intermediates formed during the oxidation may be more harmful than the precursor compounds. The mineralization efficiency, namely, the removal efficiency of total organic carbon (TOC) is one practical means of estimating the overall process [64]. Vinodgopal et al. reported that 60% mineralization was achieved during the sonolysis of 33 μM RB5 in 6 h at 640 kHz and 240 W and the only remaining degradation product was oxalate, suggesting that RB5 was converted *via* sonochemical oxidation to stable and environmentally acceptable forms at 60% of the mineralization [80]. As a comparison, Ince and Tezcanlí reported that the removal efficiency of TOC during the oxidative degradation of 600 mL of 20 μM RB5 in 60 min by US (520 kHz, 1.63 W cm^{-2}), OZ (50 L h^{-1}) and their combined process of US/OZ was effective than US alone for achieving mineralization, while the synergies induced by the combination of US/OZ enhance the mineralization efficiency. To reach similar mineralization, thus the treatment time can be significantly shortened by the US/OZ process. Similarly, Gultekin and Ince also compared the mineralization efficiency during the oxidative degradation of 100 mL of 30 μM acid orange 7 (AO7) and acid orange 8 (AO8) in 60 min by US (300 kHz, 25 W), OZ (180 L h^{-1}) and their combined process of US/OZ. As a result, the mineralization by US lone is negligible, while the mineralization by OZ is more efficient, but not sufficient. The combination of US/OZ can significantly enhance the dye mineralization. The synergy may be attributed not only to more % OH generation and increased O_3 mass transfer, but also to the formation of secondary oxidative species (e.g. %O_2^{-} and %O_2H), which may oxidize the recalcitrant byproducts [48]. Likewise, He et al. reported the TOC removal efficiencies during the degradation of C.I. reactive yellow 84 (RY84) by US, OZ, and US/OZ in aqueous solutions [51]. The value of *kUS, kOZ, and kUS/OZ* of 95 mg L^{-1} TOC reduction was observed to be 1.7×10^{-3}, 1.1×10^{-2} and 1.5×10^{-2} min^{-1}, respectively, during the degradation of 500 mg L^{-1} RY84 at pH 10 for 60 min by US/OZ (20 kHz, 44 W L^{-1}, 4.5 g O_3 h^{-1}). The SE value was 1.18, indicating that the US/OZ combination is more efficient for TOC removal than US or OZ alone.

Olson and Barbier have demonstrated the role of %OH in TOC removal during the oxidation of natural organic matter (NOM) by US/OZ [81]. 91% TOC was removed from a 10 mg L^{-1} fulvic acid solution for 60 min with US/OZ (20 kHz, 55 W) and 87% of the original carbon was removed as CO_2 (g). With OZ alone, however, only 40% of the TOC was removed and only 28% of the original carbon was mineralized. When the US/OZ process was applied to a high-color groundwater sample, containing 2.8 mg L^{-1} TOC and 35 mg L^{-1} bicarbonate, TOC removal was completely inhibited. After the pretreatment of the groundwater sample to remove carbonate species, however, 90% of the TOC was removed in 40 min [81]. Thus all the examples indicate the critical role of %OH in the reaction pathway in US/OZ systems.

Furthermore, the toxicity of solutions decreased significantly with continuous mineralization by US/OZ treatment. EC50 value reached to 67% with a higher mineralization efficiency (45%) after US/OZ treatment in 90 min from 14% of initial EC50 of an amoxicillin solution (high toxicity), while EC50 value was achieved 11% by US alone and 14% with by OZ alone, respectively, indicating that US is not capable to obtain effective oxidation and the newly formed intermediate compounds increase the toxicity. In contrast, the US/OZ treated effluents contain fewer intermediate products due to higher mineralization; which can easily be interpreted as less toxic compounds released in the environment [65].

In addition, the removal efficiency of COD is also used to indicate the degree of mineralization. Wang et al. reported the mineralization of 120 mL of 400 mg L^{-1} tetracycline by US (20 kHz, 142.8 W L^{-1}), OZ ($C_{O_3,g}$ = 45.6 mg L^{-1}, Qg = 35 L h^{-1}) and the combined US/OZ [49].

Consequently, US slightly affects the COD removal, while 76% and 91% of COD removals are achieved by OZ alone and US/OZ, respectively. It demonstrates the existence of synergism between US and OZ for the mineralization of tetracycline. Yang et al. reported the degradation of 1679 mg/L phenol, corresponding to 4000 mg/L COD, in 800 mL aqueous solutions by US (50 kHz, 120 W), OZ (100 L h^{-1}) and their combination of US/OZ [50]. Due to the lower yield of %OH formed during phenol degradation by US alone, COD reduction is negligible.

However, 29.2% and 36.5% COD removal are achieved using OZ alone and US/OZ in 60 min, respectively. Furthermore, 75.7% and 79.8% of COD removal are achieved using OZ alone and US/OZ in 300 min, respectively. The pseudo-first-order rate constants of COD degradation were 4.8×10^{-3} and 5.4×10^{-3} min^{-1}, as observed for OZ and US/ OZ, respectively. Besides, the removal of COD increased with increased pH value in the pH range of 4‑12, and reached the maximum value (79.2%) for 240 min at pH 11. *n*-Butanol has frequently been used as an %OH scavenger to determine the role of %OH in pollutant degradation. Therefore, 250 mg of *n*-butanol was added to 800 mL of the above reaction system, leading to reduced COD removal (71.3%), all other things being equal. Therefore, it can be confirmed that %OH plays a critical role in the removal of COD during phenol degradation in aqueous solutions within US/OZ systems.

4. Effect of sonication on mass transfer of ozone

The enhancement that US can provide to OZ efficiency is generally attributed to two physicochemical mechanisms: (1) decomposition of O_3 by US causes increased free-radical activity; (2) simultaneous US treatment enhances the liquid phase volumetric mass transfer coefficient (KLa). Both mechanisms improve O_3 transfer between gas and liquid, as well as the utilization of O_3 [41]. The dissolved ozone concentration (CO_3) in water is influenced by various parameters, such as temperature, pH, gas flowrate, O_3 partial pressure, mixing mode and speed, etc. [82]. CO_3 at a time (t) is usually dependent on the KLa value and the equilibrium ozone concentration (C^*O3), while C^*O_3 is dependent on Henry's law constant (KH), at a given temperature (T, °C), and the O_3 concentration (CO_3, g, mg $L{-}1$) in the gas leaving the reactor. The equations are given as follows [41,83]:

$$\frac{dC_{O3}}{dt} = k_L a (C_{O3}^* - C_{O3}) \quad (2)$$

$$ln \frac{C_{O3}^*}{C_{O3}^* - C_{O3}} = k_L a \bullet t \quad (3)$$

$$C^*_{O3} = \frac{C_{O3,g}}{K_H} \quad (4)$$

$$K_H = \frac{1}{10^{(-0.25-0.013T)}} \quad (5)$$

Mass transfer thus depends on the *KLa* value, on the concentration of saturation, and on the decomposition of O_3 (or reaction rate) [41]. Weavers and Hoffmann have demonstrated the sonolytic degradation of O_3 and enhancement of mass transfer by 20 and 500 kHz US in both closed and open continuous-flow systems [60]. It was reported that the *KLa* values (ca. 0.28‑0.41 min^{-1}) under 20 kHz US were much greater than those (ca.0.05‑0.10 min^{-1}) in the 500 kHz reactor over the power density range studied. At 20 kHz, the enhancement of US was suggested include the partial contribution of the turbulence induced by acoustic streaming. Meanwhile, the *KLa* values increased rapidly with US power density at both 20 kHz and 500 kHz. More importantly, the sonochemical degradation of O_3 reduced the aqueous O_3 concentration below the saturation value in the ultrasonic reactor, allowing more O_3 to diffuse into the solution. Zhao et al. have also verified the decrease of residual ozone concentration with identical O_3 input in multiple-ultrasonic fields [68]. The maximum O_3 concentration decreased from 0.82 mg L−1 under OZ alone to 0.75, 0.70, 0.59, and 0.50 mg L^{-1} with 1‑4 pieces of ultrasonic transducers at identical total US power, respectively, and the US time to reach the maximum O_3 concentration was sequentially reduced from 30 min to 25, 20, 15, and 10 min. Thus the maximum *KLa* value by US/ OZ reached 0.43 min^{-1} with 4 pieces of ultrasonic transducers compared to 0.20 min^{-1} by OZ alone.

Lall et al. have used Karman indigo tests to determine the O3 concentration in solution and the *KLa* value of O_3 at 20 kHz at various US power densities (40, 80, and 120 W L^{-1}) [56]. An increase in the *KLa* value and the corresponding increase in the apparent rate constants of dye degradation were achieved at higher ultrasonic powers. At the maximum ultrasonic power input for dye degradation, the ratio *kUS/OZ/kOZ* increased by 204%, whereas the ratio *KLa(US/OZ)*/*KLa(OZ)* increased by 90%, implying that the improving mass transfer of O_3 contributed partly to the dye degradation, but other factors such as the involvement of radical species also contribute. Moreover, Weavers and Hoffmann found that the *KLa* value increases linearly with flowrate in a 500 kHz reactor at 50.3 W L^{-1} US power density, while the *KLa* value rises rapidly and reaches an apparent saturation value in a 20 kHz reactor at 263 W L^{-1} [60]. Furthermore, increasing the flowrate leads to a larger net surface area for the mass transfer of O_3 to the solution. Over the past decade, the microreaction technology has been applied to mass transfer-limited gas‑liquid reactions thanks to process miniaturization [84‑86]. Faryadi et al. have demonstrated that US can still enhance the mass transfer significantly, even within a microreactor [67]. In 15 cm microchannel, *KLa* values of 6.47 and 7.382 min^{-1} were achieved at O_3 gas flowrates of 10 or 40 mL min^{-1} under US, as compared to *KLa* values of 3.38 and 4.1 min^{-1} without US. In summary, US not only increases turbulence but also decreases saturated O_3 concentration in aqueous solutions, which increases the rate of O_3 mass transfer to solutions.

5. Sonochemical enhancement of ozone decomposition and hydroxyl-radical formation.

Ozone can be spontaneously decomposed by hydroxide ions and converted into %OH in water, in particular, under alkaline conditions (Reaction (1) and (2)) [16,53,63,87]. Therefore, ozone decomposes rapidly at a pH above 7, while the rate is rather slow at pH=2. Barbier and Petrier reported that the first-order rate constant of O_3 decomposition is 0.038 min^{-1} [74]. In addition, the rate of O_3 self-decomposition, in the pH range above 8, was expressed as $-d[O_3]/dt = 374 \times [O_3][OH^-]0.88$ [88].

$$O_3 + OH^- \rightarrow HO_2^{\cdot} + {}^{\cdot}O_2^- \qquad (1)$$

$$O_2^- + O_3 + H^+ \rightarrow {}^{\cdot}OH + 2\,O_2 \qquad (2)$$

Ozone can undergo extremely rapid decomposition in water under US [46,53]. The sonochemical enhancement of O_3 decomposition is attributed to O_3 pyrolysis in the cavitation bubble or at the bubble interface, but does not occur significantly in bulk solution with US, and is not modified by the production of H_2O_2 [74,81]. Investigating the change in concentration of O_3, H_2O_2, and %OH in aqueous solutions can provide direct evidence. Whereas, the enhancement of O_3 decomposition and %OH formation can also be indirectly demonstrated by the increasing removal efficiency of TOC under US, as well as the effects of %OH scavengers.

5.1. Decomposition of ozone

The sonolytic decomposition of O_3 and the formation of %OH have been expressed as the following reactions [53,69,74]:

$$O_3 \rightarrow O_2 + O(^3p) \qquad (3)$$

$$O_3 + O(^3p) \rightarrow 2O_2 \qquad (4)$$

$$H_2O + O(^3p) \rightarrow 2^{\cdot}OH \qquad (5)$$

Reactions (3)‑(5) occur preferably in the implosive cavities. The active species formed migrate to the gas‑liquid interface of cavities and transfer into the bulk water [54]. A comparison of the O_3 decomposition kinetics in a batch reactor without and with 20 kHz US demonstrated that the observed first-order rate constant for O_3 decomposition dramatically increased from 0.032 min^{-1} without US, to 0.207 min^{-1} with US [41]. In a flow system, ozone was introduced into distilled water in a closed chamber to a steady-state, and then the O_3 concentration in the effluent was determined to be 3.51 ppm with the continuous US for 15 min, compared to 9.82 ppm without US [41].

Weavers and Hoffmann have also demonstrated the rapid decomposition of 245 μM O3 at pH = 2, leading to ca. 60 μM O_3 after 3 min US in a 500 kHz closed-system sonication reactor (96 W L−1) [60]. Hart and Henglein have reported that 628 μM O_3 was sonicated at 300 kHz in 37.5 mL of an 0.1 N $HClO_4$ aqueous solution, and that the O_3 concentration rapidly decreased to 40 μM after 3 min US [46]. Moreover, the rate of 1 mM O_3 decomposition in 10 s was detected to be about 3 mM min^{-1}, and the decomposition rate increased with O_3 concentration in aqueous solutions. The complete decomposition of the O_3 content of a pulsating gas bubble occurred with O_2 or Ar, while H_2O_2 formation takes place with greater efficiency in O_3-Ar bubbles where higher temperatures are produced in the acoustic compression phase [46].

5.2. Formation of hydroxyl radicals and hydrogen peroxide

The US/OZ combination is an effective oxidation system since one molecule of O_3 results in two %OH, based on reactions (1)‑(5) [54]. Hydrogen peroxide is the main product from the water sonolysis and O_3 decomposition [74].

DMPO (5,5-dimethyl-1-pyrroline N-oxide) is generally used as the spin trap to obtain the stable DMPO‑OH spin adduct and the technique of spin trapping EPR (electron paramagnetic resonance) has been applied for the qualitative identification and quantitative measurement of %OH. Zhao et al. have found the existence of %OH at pH 6.9 with 120 mM DMPO in OZ and US/OZ systems

[68]. The concentration of % OH that formed in water was detected to be 8 μM with OZ alone for 30 min bubbling, compared to 48 μM within an optimal US/OZ system.

Moreover, the relationship between the rate constant of NB degradation (*k*NB) and the rate constant of %OH formation (*k*%OH) was well established in the above system (reaction conditions: temperature 298 K; initial pH 6.85; initial NB concentration 50 μg L−1; total applied O_3 1.2 mg L^{-1}; US frequency 20 kHz and power density 38.5 W L^{-1}; initial DMPO concentration 120 mM; reaction time: 30 min) [68].

Guo et al. have reported that 2 mM terephthalic acid was used to trap %OH in US, OZ and US/OZ systems and the production from radical reactions was quantified by fluorescence measurement [78]. In 20 kHz US, OZ and US/OZ systems, 0.07, 13.5 and 15.2 μM %OH was achieved at pH 5, respectively, while the concentrations of %OH were 0.11, 17.0 and 18.1 μM at pH 7, relative to 0.15, 20.2 and 21.1 μM %OH at pH 9, respectively. Consequently, US promotes the formation of %OH in US/OZ systems regardless of pH conditions, and a higher %OH yield was achieved at pH 9.

Under acidic conditions, the formation of H_2O_2 by OZ alone is generally negligible, whereas molecular O_3 is regarded as the major oxidation species. An increase in H_2O_2 formation was observed when pure water was sonicated during continuous OZ, and the rate constant of H_2O_2 formation (kH_2O_2) reached 0.19 min^{-1} in the US/OZ system, compared to 0.016 min^{-1} with OZ alone. However, the kH_2O_2 in the US/OZ system is lower than that (0.31 min^{-1}) with US alone [48]. It can be speculated that the H_2O_2 produced *in situ* reacts with O3 in the US/OZ system (Reaction (11)‑(13)) [63,87]. By contrast, the *kH2O2* in the US/OZ system was found to be 0.27 min^{-1} in the presence of dye, since dye reacted with molecular O_3 to some degree to reduce the consumption of H_2O_2.

For pH < 5

$$H_2O_2 + O_3 \rightarrow {}^{\cdot}OH + HO_2^{\cdot} + O_2 \qquad (11)$$

For 5 < pH < 8,

$$H_2O_2 \rightarrow HO_2^{-} + H^{+} \qquad (12)$$

$$O_3 + HO_2^{-} \rightarrow {}^{\cdot}OH + {}^{\cdot}O_2^{-} + O_2 \qquad (13)$$

5.3. Indirect evidence for the formation of hydroxyl radicals

Evidence for the presence of %OH in the reaction pathway can be indirectly demonstrated when the degradation rate of organic pollutants significantly decreases upon the addition of an %OH scavenger.

NOM and certain inorganic species in natural waters are potential competitive reactants for %OH. To verify the impact of NOM on sonolytic degradation, Kang et al. have reported the degradation of 0.01 mM MTBE in 500 mL aqueous solutions by 358 kHz, 100 W L^{-1} US in the absence and presence of 2.1 and 4.2 mg L^{-1} NOM [55]. The results showed that the effect of NOM on the MTBE decomposition rate appears to be negligible, suggesting that the major reaction site for MTBE with %OH is in the vapor phase of the cavitation bubble and not in the bulk aqueous phase 4% calcium carbonate, used as an %OH scavenger, has been shown to significantly inhibit the decolorization rate of reactive blue 19 (RB19) by 20 kHz US/OZ in aqueous solutions [56]. The rate constant of 100 mg L^{-1} dye decreased from 0.234 min^{-1} without the %OH scavenger to 0.120 min^{-1} with %OH scavenger. At a dye concentration of 60 mg L^{-1}, the rate constant decreased from 0.204 min−1, without the %OH scavenger, to 0.162 min^{-1} with the %OH scavenger.

This indicates that %OH played a critical role in the degradation of dye RB19 by US/OZ. Alcohols, such as *tert*-butyl alcohol (TBA), are also common %OH scavengers. Wang et al. have found that the presence of 5‑15 mM TBA inhibited the degradation of 400 mg L^{-1} tetracycline at pH 7 under US/OZ (20 kHz, 142.8 W L^{-1}) [49]. The rate constant of tetracycline degradation decreased to 0.42 min^{-1} with 15 mM TBA, compared to 0.84 min−1 without the addition of TBA. This indicates that %OH plays an important role in the degradation of tetracycline under US/OZ.

When OZ is dominated by direct oxidation with molecular O_3, however, the degradation of organics is accelerated with carbonate. Zhang et al. have indicated that AO7 mainly undergoes a direct reaction with molecular O_3 rather than radical reaction by US/OZ at 20 kHz.

Therefore, the decolorization rate increased with the sodium-carbonateto- dye molar ratio [89]. Other %OH scavengers, such as alkalinity and humic acid, have also been demonstrated to decrease the degradation rate of amoxicillin in aqueous solution. The pseudo-first-order rate constants at pH 10 under 575 kHz, 14.6 W L^{-1} US in the absence and presence of 5 mg L^{-1} humic acid, 20.5 mg L^{-1} alkalinity, or both were determined to be 0.040, 0.027, 0.024 and 0.022 min^{-1}, respectively [65]. Due to a large amount of %OH formed under alkaline conditions, however, the addition of alkalinity, humic acid or both did not give any significant decrease in the removal rate of amoxicillin under OZ and US/OZ.

6. Effect of pH value on the degradation of organics by sonozonation

The pH value is a critical factor that affects O_3 decomposition and % OH formation in OZ and US/OZ systems. When degradation tends towards reaction with %OH, degradation is faster under alkaline conditions. By contrast, degradation is faster under acidic conditions when the pollutant favors the reaction with molecular O_3.

6.1. Preferential degradation under alkaline conditions

Phenol can be directly ozonated with molecular O_3 under acidic conditions, but can also be indirectly oxidized by %OH formed *in situ*. The *kUS/OZ* values of 2.5 mM phenol in 100 mL aqueous solutions with a 300 kHz US/OZ system reached 2.21×10^{-2}, 2.90×10^{-2} and 3.26×10^{-2} min^{-1} in 90 min at pH 2, 5.6 and 10, respectively, indicating that the alkaline condition favors the oxidative degradation of phenol with more %OH [47]. Moreover, *kUS/OZ* (3.26×10^{-2} min^{-1}) at pH 10 was much larger than the sum of the individual *kUS* and *kOZ* (2.85×10^{-2} min^{-1}), showing that the combination of US/OZ caused synergism under alkaline conditions. By contrast, *kUS/OZ* (2.21×10^{-2} min^{-1}) at pH 2 was less than the sum of the individual *kUS* and *kOZ* (3.21×10^{-2} min^{-1}), showing that the direct oxidation of phenol with molecular O_3 was reduced by the O_3 decomposition that occurs under 300 kHz US.

For the degradation of antibiotics in 250 mL aqueous solutions, the *kOZ* values of 25 mg L^{-1} amoxicillin reached 0.064, 0.321 and 1.97 min^{-1} at pH 3, 7 and 10, respectively, indicating that the alkaline condition also favors the oxidative degradation of amoxicillin [65].

Moreover, over 99% amoxicillin removal was achieved after 10 min ofOZ under neutral conditions, while 30 min OZ was not sufficient to removal amoxicillin molecules under acidic conditions. At pH 10, US/ OZ (575 kHz, 14.6 W L^{-1}) coupling gave the highest rate constant *kUS/OZ* of 2.5 min^{-1}, which is higher than the sum under the individual OZ or US protocols. Also, the effect of pH on the removal of 400 mg L^{-1} tetracycline in 120 mL solutions under 20 kHz, 142.8 W L^{-1} pulse US/OZ was investigated [49]. The *kUS/OZ* value reached 0.34, 0.52, 0.77 and 1.27 min^{-1} at pH 3, 5, 7 and 9, respectively. The alkaline condition favors the degradation of tetracycline within US/OZ system. Turning to the decolorization of dyes, Song et al. have reported the decolorization and degradation of C.I. direct red 23 (DR23) using US/OZ [52]. The *kUS/OZ* of 100 mg L^{-1} DR23 in 500 mL aqueous solutions was 2.2, 3.1, 3.7, 2.7 and 2.4 min^{-1} for 3 min at pH 4.0, 6.0, 8.0, 10.0, and 12.0 by US/OZ (20 kHz, 176 W L^{-1}), respectively. The optimum pH value for the reaction was 8.0, and both lower and higher pH conditions decreased the removal rate. Shen et al. have reported that the optimal SE value of US/OZ system for the degradation of reactive red X-3B (X3B) was 1.42, and 99.2% removal of 100 mg・L^{-1} X3B in 1 L aqueous solution was achieved in 6 min at pH 6.52 by US/OZ (40 kHz, 200 W・L^{-1}) [69]. Moreover, the decolorization efficiencies were 57.6%, 63.4% and 90.7% at pH 1, 5 and 10 after 2 min reaction, respectively, increasing the pseudo-first-order rate constant with increasing pH value. This indicates that the radical reaction is the dominant pathway for the degradation of X3B.

For the mineralization of organics, Yang et al. have illustrated the effect of pH value on COD removal during the degradation of phenol at the high concentration by US/OZ (50 kHz, 120 W) [50]. The removal efficiency of COD was 69.2%, 75.9%, 79.2%, and 78.0% at pH 4.0, 8.0, 11.0, and 12.0 for 240 min, respectively. The most effective removal of COD was obtained at pH 11.0. This suggests that the formation of %OH is accelerated via O_3 decomposition under alkaline conditions, which enhances phenol degradation and COD removal. For the TOC removal during the degradation of RY84 in aqueous solutions, the *kUS/OZ* of TOC was respectively 4.3×10^{-3}, 6.4×10^{-3}, 9.0×10^{-3}, 1.3×10^{-2}, 1.5×10^{-2}, and 1.1×10^{-2} at pH 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0 by US/OZ, all other things being equal. The highest *kUS/OZ* of TOC was obtained at pH 10.0 [51].

6.2. Preferential degradation under acidic conditions

Zeng and McKinley investigated the effect of audible frequency (0.43 kHz, 165 W L^{-1}) sonication on PCP degradation in 2 L of aqueous ozone solutions [72]. An inevitable consequence of higher initial pH 12 is the rapid decomposition of O3, leading to a lower PCP degradation efficiency than at pH 7.5. This implies that PCP degradation most likely follows a direct pathway involving reactions with molecular ozone, while reactions with the formed %OH is a minor pathway of OZ or US/OZ. Audible-frequency sonication caused strong turbulence, enhancing both O_3 dissolution and PCP degradation by OZ.

Ozone has a strong affinity for fumaric acid (FA), which can rapidly be ozonated due to the presence of a C=C bond. At pH 5, however, the ratio of *kOZ,FA/kOZ,SMX* was only 0.60, suggesting that molecular O_3 has a stronger affinity for sulfamethoxazole (SMX) than for FA [78].

To reveal the roles of US in SMX removal, 100 mg L^{-1} SMX solutions were processed under 20 kHz US, OZ and US/OZ [78]. At pH 5, an US/OZ SE value of 1.26 was achieved, suggesting that US can improve the mass transfer and dissolution of O_3 under acidic conditions and that the reaction of SMX with molecular O_3 is the predominant degradation pathway. At pH 7 and pH 9, however, SE values of only 1.07 and 1.06 were achieved, respectively, indicating that the degradation of SMX was diminished by O_3 decomposition under alkaline conditions, while the radical reaction played a partial role in the degradation.

Faryadi et al. have investigated the effect of pH on the removal efficiency of 65 mg L^{-1} RB in a 25-cm microchannel located in a 1.7 MHz US bath [67]. The flowrates of the O_3 and RB solutions were 25 and 6 mL min^{-1}, respectively. An increase in pH from 3 to 10 resulted in a decrease in the removal of RB in both modes. These reductions in the efficiency are from 67.4% to 59.4% for the microreactor with US and from 64.5% to 55.7% for the plain microreactor without US.

6.3. Slight effect of pH on the degradation

In earlier studies, Carriere et al. have used OZ to decolorize simulated wastewater containing a bisazo acid dye (acid red 158), and the decolorization rate of reaction was not sensitive to pH value [90]. Teramoto et al. have studied the effect of pH on the decolorization of naphthol yellow (NY) in the 3.17–9.12 range, but the decolorization rate was almost independent of the pH employed [88]. Moreover, pH had no effect on the rates of oxidation of CN^-, CNO^- and some dyes, such as methylene blue, indigo carmine blue and methanyl yellow. The presence of C]C, N]N or conjugated π -system in the dyes means that the rate of decomposition of these compounds by O_3 is much faster than that of the decomposition of O_3 by OH^-.

Lall et al. have observed the effect of pH values on the decolorizationof 100 mg L−1 RB19 by OZ at 5.5 and 11 [56]. The *kOZ* at both pH values of 5.5 and 11 was determined to be 0.18 min^{-1}. For US/OZ (20 kHz, 120 W L−1), both *kUS/OZ* for the pH values of 5.5 and 11 were determined to be 0.24 min^{-1}. At higher pH, the degradation rate of the dye was not increased by radical reaction due to enhanced trapping effects. Moreover, the carbonate ion is a prevalent species and the rate constant for the reaction of %OH with the carbonate ion is approximately 20 times greater than that for the reaction with the bicarbonate ion. Hence, the prevalence of the carbonate ion at the higher pH can significantly limit the reactive efficiency of the dye under OZ and US/OZ.

7. Effect of ultrasonic frequency

7.1. On the decomposition of ozone

When aqueous O_3 solutions are sonicated, ozone disappears rapidly and more H_2O_2 is produced. In US/OZ systems, ultrasonic frequency first influences the decomposition of O_3, and the formation of OH and H_2O_2. Barbier & Petrier have indicated that the rate of the initial decomposition of O_3 in a 300 mL solution with the same ultrasonic power was higher at 20 kHz than at 500 kHz at pH 2, but that more H_2O_2 was formed at the higher frequency [74]. The *kUS/OZ* values for 0.172‑0.158 μM O_3 decomposition were 0.29 and 0.17 min^{-1} and the initial rates of H_2O_2 formation were 3.0 and 5.2 μM min^{-1} at 20 and 500 kHz, respectively. It can be speculated that the contribution of %OH formed by the sonolysis of H_2O is higher at 500 kHz than at 20 kHz. These results are consistent with the investigation that used high initial O_3 concentrations (85‑245 μM) performed by Weavers & Hoffmann, in which the *kUS/OZ* value for 245 μM O3 decomposition was 0.84 and 0.66 min^{-1} at 20 and 500 kHz, respectively. This means that the mass transfer coefficient, *kLa*, was higher at 20 kHz than at 500 kHz [60]. In addition, *kUS/OZ* increased with increased ultrasonic power density at 20 and 500 kHz.

Kang et al. have observed the relative effects of frequency (205‑1078 kHz) on the O_3 decomposition rate during the sonication of aqueous solutions containing 0.14‑0.15 mM O_3 and 1.0 mM bicarbonate at pH 8.25 and 100 W L^{-1} of ultrasonic power density [55]. The highest and lowest first-order rate constants for O_3 sonolytic degradation were found to be at the lowest (205 kHz) and highest ultrasonic frequencies (1078 kHz), respectively, while the measured rates at the other frequencies were nearly the same.

7.2. On the formation of hydrogen peroxide

Hydrogen peroxide production was used as a direct indicator of the presence of free radicals, which can be produced by the sonolysis of water and O_3 decomposition in the US/OZ system. The %OH recombination reaction should be the major route for H_2O_2 formation.

In an earlier study, Barbier and Petrier found that the degradation of 4-NP and TOC at low pH values using US/OZ was better at 500 kHz than at 20 kHz [74]. This effect is correlated to the higher yields of H_2O_2 formed under irradiation at the higher frequency, and hence to the higher rate of %OH escaping from the cavitation bubble. The H_2O_2 formation rate observed at high frequency is approximately 3.3 times greater than at low frequency [74]. It was demonstrated that the larger, 170 μm bubble formed at 20 kHz results in a longer collapse time of 10 μs, than that the smaller bubble of 4.6 μm that has very short collapse time of 0.4 μs at 500 kHz [91]. The transient species produced, therefore, have enough time to recombine inside the hot bubble. This recombination restores water, therefore decreasing the efficiency of the process [92,93]. Ultrasonic frequency thus plays a key role in the efficiency of O_3 utilization. The faster 4-NP mineralization rate at 500 kHz results from the enhanced O_3 utilization occurring at the high frequency. Identical sonolytic H_2O_2 production rates (i.e., 3.5×10^{-4} mM min^{-1}) have been achieved in O_2-saturated solutions and Ar-saturated solutions at 205 kHz at a power density of 240 W L^{-1} [55]. The H_2O_2 production rate is approximately twice as high at 240 W L^{-1} than at 100 W L−1 and is highest at 358 kHz and lowest at 1078 kHz. The iodine formation rate may be related to the %OH production rate by a stoichiometric factor of 2. The optimum frequency for I_2 (I_3^-) production from I− oxidation by H_2O_2 is between 358 and 618 kHz at 84 W L^{-1} [55].

Hua and Hoffmann have reported that the H2O2 production rate increased with increasing frequency for 20, 40, 80 and 500 kHz.

However, the H_2O_2 production rate is the lowest at the highest applied ultrasonic frequency of 1078 kHz [94]. Park et al. have evaluated the effect of frequency on O_3 concentration under OZ and US/OZ using 35 and 283 kHz at 20 W L^{-1} and pH 6.2. The effluent O3 concentration under OZ was constant during the reaction, while the O_3 concentration under US/OZ decreased to about 5–30% of the initial ozone concentration.

This means that additional O_3 decomposition under US/OZ can occur for the generation of %OH. In particular, the difference in the concentrations of H_2O_2 and the effluent ozone at 35 kHz was larger than that at 283 kHz. This is the reason why the synergistic effect at 35 kHz was larger than that at 283 kHz [57].

7.3. On the degradation of organics

Petrier and Francony have reported that the sonolysis of phenol has an optimal rate constant at 200 kHz, rather than at 20, 500, and 800 kHz at the same power density [55,95,96]. Furthermore, Weavers et al. have investigated the effect of frequency (20 and 500 kHz) on the degradation of 20 and 60 μM PCP by US, and high frequency (500 kHz) favors the degradation of PCP [79].

Kang et al. have studied the effect of ultrasonic frequency on the degradation of 0.5 mM MTBE using US/OZ over the frequency range of 205‑1078 kHz at 100 W L^{-1}. The highest overall reaction rates are observed at 358 and 618 kHz, and then at 205 and 1078 kHz [55].

Likewise, Park et al. have evaluated the effect of frequency on the degradation of DCAN under US and US/OZ over the range of 35, 170, 283, 450 and 935 kHz [57]. Of the five frequencies, 35 and 283 kHz were the best conditions for degradation. The DCAN degradation rate constant under US was higher at 283 kHz than at 35 kHz. By contrast, the degradation rate constants under US/OZ were higher at 35 kHz than at 283 kHz and 9.5‑20 W L^{-1}. The SE values of US/OZ were 2.56 and 2.15 at 35 and 283 kHz, respectively, and were the most significant of those related to the five frequencies.

Kidak and Doğan have recently reported the effect of frequency on the degradation of 25 mg L^{-1} amoxicillin solutions at constant power density (14.6 W L–1) [65]. The pseudo-first-order rate constants of degradation were 0.030, 0.010 and 0.009 min^{-1} at pH 7, and 0.040, 0.020 and 0.014 min^{-1} at pH 10 at 575, 861 and 1141 kHz, respectively.

It is clear that 575 kHz and pH 10 favor the degradation. Over 99% amoxicillin removal was achieved at pH 10 at 575 kHz frequency after 90 min. The removal rate of amoxicillin by OZ was 50 times faster than that of US. Moreover, the US/OZ coupling gave rise to a rate constant of 2.5 min^{-1}.

Mineralization during the degradation of 4-NP in 250 mL aqueous solutions under OZ and US/OZ occurs via non-selective %OH attack on the organic compounds. At low pH (pH = 2), the rate of TOC removal under OZ alone was much lower than under US/OZ (20 kHz).

Moreover, substrate mineralization at 500 kHz was 1.8 times faster than at 20 kHz and the same ultrasonic power (30 W) for the same O_3 consumption [74].

In conclusion, the synergism of US/OZ originates from the enhancement that US provides to the decomposition and dissolution of O_3, which further improves the mass transfer of O_3 between gas and liquid, increasing the production of %OH. This effect is favorable for the degradation of refractory pollutants and their mineralization. However, the direct OZ of olefins and unsaturated aromatics is suppressed to some extent. We suggest that ozone efficiency, energy efficiency, and material efficiency are studied and compared in the future so that the combined technology can be conveniently compared with other strategies and converted to industrial applications.

CRediT authorship contribution statement

Zhilin Wu: Conceptualization, Writing - original draft. **Anna Abramova:** Conceptualization, Writing - review & editing. **Roman Nikonov:** Conceptualization, Visualization. **Giancarlo Cravotto:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

We warmly acknowledge the Fondazione CRT (Bando 2019) for its financial support.

References

[1] H.M. Pinheiro, E. Touraud, O. Thomas, Aromatic amines from azo dye reduction: Status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters, Dyes Pigm. 61 (2004) 121‑139, https://doi.org/10.1016/j.dyepig.2003.10.009.

[2] I. Oller, S. Malato, Ja. Sanchez-Perez, Combination of advanced oxidation processes and biological treatments for wastewater decontamination─a review, Sci. Total Environ. 409 (2011) 4141‑4166, https://doi.org/10.1016/j.scitotenv.2010.08.061.

[3] J. Siemiatycki, L. Richardson, K. Straif, B. Latreille, R. Lakhani, S. Campbell, M.-C. Rousseau, P. Boffetta, Listing occupational carcinogens, Environ. Health Perspect. 112 (2004) 1447‑1459, https://doi.org/10.1289/ehp.7047.

[4] R. Van der Oost, J. Beyer, N.P.E. Vermeulen, Fish bioaccumulation and biomarkers in environmental risk assessment: a review, Environ. Toxicol. Pharmacol. 13 (2003) 57‑149, https://doi.org/10.1016/S1382-6689(02)00126-6.

[5] F. Wania, D. Mackay, Tracking the distribution of persistent organic pollutants, Environ. Sci. Technol. 30 (1996) 390A‑397A, https://doi.org/10.1021/es962399q.

[6] Y. Lee, U. von Gunten, Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate VI, and ozone) and non-selective oxidants (hydroxyl radical), Water Res. 44 (2010) 555‑566, https://doi.org/10.1016/j.watres.2009.11.045.

[7] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today. 53 (1999) 51–59, https://doi.org/10.1016/S0920-5861(99)00102-9.

[8] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: a review, Water Res. 44 (2010) 2997–3027, https://doi.org/10.1016/j.watres.2010.02.039.

[9] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84, https://doi.org/10.1080/10643380500326564.

[10] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98 (2003) 33–50, https://doi.org/10.1016/S0304-3894(02)00282-0.

[11] C.A. Martinez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, Appl. Catal., B. 87 (2009) 105–145, https://doi.org/10.1016/j.apcatb.2008.09.017.

[12] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Wet air oxidation, Ind. Eng. Chem. Res. 34 (1995) 2–48, https://doi.org/10.1021/ie00040a001.

[13] M. Magureanu, N.B. Mandache, V.I. Parvulescu, Degradation of pharmaceutical compounds in water by non-thermal plasma treatment, Water Res. 81 (2015) 124–136, https://doi.org/10.1016/j.watres.2015.05.037.

[14] P. Manoj Kumar Reddy, B. Rama Raju, J. Karuppiah, E. Linga Reddy, C. Subrahmanyam, Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor, Chem. Eng. J. 217 (2013) 41–47, https://doi.org/10.1016/j.cej.2012.11.116.

[15] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551, https://doi.org/10.1016/S1093-0191(03)00032-7.

[16] J. Hoigne, H. Bader, The role of hydroxyl radical reactions in ozonation processes in aqueous solutions, Water Res. 10 (1976) 377–386, https://doi.org/10.1016/0043-1354(76)90055-5.

[17] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: A general review, Appl. Catal., B. 47 (2004) 219–256, https://doi.org/10.1016/j.apcatb.2003.09.010.

[18] J.L. Wang, L.J. Xu, Advanced oxidation processes for wastewater treatment: Formation of hydroxyl radical and application, Crit. Rev. Environ. Sci. Technol. 42 (2012) 251–325, https://doi.org/10.1080/10643389.2010.507698.

[19] K. Ikehata, N. Jodeiri Naghashkar, M. Gamal El-Din, Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes, A review, Ozone Sci. Eng. 28 (2006) 353–414, https://doi.org/10.1080/01919510600985937.

[20] W.H. Glaze, J.-W. Kang, D.H. Chapin, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, Ozone Sci. Eng. 9 (1987) 335–352, https://doi.org/10.1080/01919518708552148.

[21] S. Okouchi, O. Nojima, T. Arai, Cavitation-induced degradation of phenol by ultrasound, Water Sci. Technol. 26 (1992) 2053–2056, https://doi.org/10.2166/wst.1992.0659.

[22] M. Gutierrez, A. Henglein, Sonolytic decomposition of poly(vinylpyrrolidone), ethanol, and tetranitromethane in aqueous solution, J. Phys. Chem. 92 (1988) 2978–2981, https://doi.org/10.1021/j100321a052.

[23] S. Parsons, M. Williams, Advanced oxidation processes for water and wastewatertreatment, in: S. Parsons (Ed.), IWA Publishing, 2004: p. 4. https://books.google.de/books?id=7NeNgJWaavgC.

[24] V.K. Sharma, Oxidative transformations of environmental pharmaceuticals by Cl_2, ClO_2, O_3, and Fe(VI): Kinetics assessment, Chemosphere. 73 (2008) 1379–1386, https://doi.org/10.1016/j.chemosphere.2008.08.033.

[25] U. Von Gunten, Ozonation of drinking water: Part I Oxidation kinetics and product formation, Water Res. 37 (2003) 1443–1467, https://doi.org/10.1016/S0043-1354(02)00457-8.

[26] J. Hoigne, H. Bader, Ozone initiated oxidations of solutes in wastewater: a reaction kinetic approach, Prog. Water Technol. 10 (1978) 657–671, https://doi.org/10.1016/B978-0-08-022939-3.50055-6.

[27] W.C. Bray, The interaction of ozone and hydrogen peroxide in aqueous solution, J. Am. Chem. Soc. 60 (1938) 82–87, https://doi.org/10.1021/ja01268a027.

[28] K.S. Suslick, Sonochemistry, Science. 247 (1990) 1439–1445, https://doi.org/10.1126/science.247.4949.1439.

[29] T.J. Mason, Sonochemistry and the environment – Providing a “green” link between chemistry, physics and engineering, Ultrason. Sonochem. 14 (2007) 476–483, https://doi.org/10.1016/j.ultsonch.2006.10.008.

[30] K. Vilkhu, R. Mawson, L. Simons, D. Bates, Applications and opportunities for ultrasound assisted extraction in the food industry – A review, Innov. FoodSci. Emerg. Technol. 9 (2008) 161–169, https://doi.org/10.1016/j.ifset.2007.04.014.

[31] P.R. Gogate, I.Z. Shirgaonkar, M. Sivakumar, P. Senthilkumar, N.P. Vichare, A.B. Pandit, Cavitation reactors: efficiency assessment using a model reaction, AIChEJ. 47 (2001) 2526–2538, https://doi.org/10.1002/aic.690471115.

[32] P. Cintas, J.-L. Luche, Green chemistry: the sonochemical approach, Green Chem. 1 (1999) 115–125, https://doi.org/10.1039/a900593e.

[33] Z. Wu, J. Lifka, B. Ondruschka, Comparison of energy efficiency of various ultrasonic devices in aquasonochemical reactions, Chem. Eng. Technol. 29 (2006) 610–615, https://doi.org/10.1002/ceat.200500362.

[34] Z. Wu, B. Ondruschka, Roles of hydrophobicity and volatility of organic substrates on sonolytic kinetics in aqueous solutions, J. Phys. Chem. A. 109 (2005) 6521–6526, https://doi.org/10.1021/jp051768e.

[35] Z. Wu, B. Ondruschka, G. Cravotto, Degradation of phenol under combined irradiation of microwaves and ultrasound, Environ. Sci. Technol. 42 (2008) 8083–8087, https://doi.org/10.1021/es8013375.

[36] Z. Wu, G. Cravotto, M. Adrians, B. Ondruschka, W. Li, Critical factors in sonochemical degradation of fumaric acid, Ultrason. Sonochem. 27 (2015) 148–152, https://doi.org/10.1016/j.ultsonch.2015.05.009.

[37] Z. Wu, B. Ondruschka, G. Cravotto, D. Garella, J. Asgari, Oxidation of primary aromatic amines under irradiation with ultrasound and/or microwaves, Synth. Commun. 38 (2008) 2619–2624, https://doi.org/10.1080/00397910802219387.

[38] Z. Wu, G. Cravotto, E.C. Gaudino, A. Giacomino, J. Medlock, W. Bonrath, Ultrasonically improved semi-hydrogenation of alkynes to (Z-)alkenes over novel lead-free Pd/Boehmite catalysts, Ultrason. Sonochem. 35 (2017) 664–672, https://doi.org/10.1016/j.ultsonch.2016.05.019.

[39] G. Cravotto, A. Binello, S. Di Carlo, L. Orio, Z.-L. Wu, B. Ondruschka, Oxidative degradation of chlorophenol derivatives promoted by microwaves or power ultrasound: a mechanism investigation, Environ. Sci. Pollut. R 17 (2010) 674‑687, https://doi.org/10.1007/s11356-009-0253-y.

[40] G.R. Burleson, T.M. Murray, M. Pollard, Inactivation of viruses and bacteria by ozone, with and without sonication, J. Appl. Microbiol. 29 (1975) 340‑344.

[41] E. Dahl, Physicochemical aspects of disinfection of water by means of ultrasound and ozone, Water Res. 10 (1976) 677‑684, https://doi.org/10.1016/0043-1354(76)90005-1.

[42] Z. Wu, M. Franke, B. Ondruschka, Y. Zhang, Y. Ren, P. Braeutigam, W. Wang, Enhanced effect of suction-cavitation on the ozonation of phenol, J. Hazard. Mater. 190 (2011) 375‑380, https://doi.org/10.1016/j.jhazmat.2011.03.054.

[43] Z. Wu, B. Ondruschka, Y. Zhang, D.H. Bremner, H. Shen, M. Franke, Chemistry driven by suction, Green Chem. 11 (2009) 1026, https://doi.org/10.1039/b902224d.

[44] Z. Wu, G. Cravotto, B. Ondruschka, A. Stolle, W. Li, Decomposition of chloroform and succinic acid by ozonation in a suction-cavitation system: effects of gas flow, Sep. Purif. Technol. 161 (2016) 25‑31, https://doi.org/10.1016/j.seppur.2016.01.031.

[45] Z. Wu, H. Shen, B. Ondruschka, Y. Zhang, W. Wang, D.H. Bremner, Removal of blue-green algae using the hybrid method of hydrodynamic cavitation and ozonation, J. Hazard. Mater. 235‑236 (2012) 152‑158, https://doi.org/10.1016/j.jhazmat.2012.07.034.

[46] E.J. Hart, A. Henglein, Sonolysis of ozone in aqueous solution, J. Phys. Chem. 90 (1986) 3061‑3062, https://doi.org/10.1021/j100405a007.

[47] R. Kidak, N.H. Ince, Catalysis of advanced oxidation reactions by ultrasound: A case study with phenol, J. Hazard. Mater. 146 (2007) 630 ‑ 635, https://doi.org/10.1016/j.jhazmat.2007.04.106.

[48] I. Gultekin, N. Ince, Degradation of aryl-azo-naphthol dyes by ultrasound, ozone and their combination: effect of alpha-substituents, Ultrason. Sonochem. 13 (2006) 208 ‑ 214, https://doi.org/10.1016/j.ultsonch.2005.03.002.

[49] Y. Wang, H. Zhang, L. Chen, S. Wang, D. Zhang, Ozonation combined with ultrasound for the degradation of tetracycline in a rectangular air-lift reactor, Sep. Purif. Technol. 84 (2012) 138‑146, https://doi.org/10.1016/j.seppur.2011.06.035.

[50] L.P. Yang, W.Y. Hu, H.M. Huang, B. Yan, Degradation of high concentration phenol by ozonation in combination with ultrasonic irradiation, Desalin. Water Treat. 21 (2010) 87–95, https://doi.org/10.5004/dwt.2010.1233.

[51] Z. He, S. Song, M. Xia, J. Qiu, H. Ying, B. Lu, Y. Jiang, J. Chen, Mineralization of C.I. Reactive Yellow 84 in aqueous solution by sonolytic ozonation, Chemosphere. 69 (2007) 191–199. doi:10.1016/j.chemosphere.2007.04.045.

[52] S. Song, H. Ying, Z. He, J. Chen, Mechanism of decolorization and degradation of CI Direct Red 23 by ozonation combined with sonolysis, Chemosphere 66 (2007) 1782–1788, https://doi.org/10.1016/j.chemosphere.2006.07.090.

[53] J.W. Kang, M.R. Hoffmann, Kinetics and mechanism of the sonolytic destruction of methyl tert- butyl ether by ultrasonic irradiation in the presence of ozone, Environ. Sci. Technol. 32 (1998) 3194–3199, https://doi.org/10.1021/es970874u.

[54] J. Lifka, B. Ondruschka, The effective increase of aquasonolysis of methyl tertiary butyl ether, Eng. Life Sci. 2 (2002) 340–344, https://doi.org/10.1002/1618-2863(20021105)2:11<340::AID-ELSC340>3.0.CO;2-6.

[55] J.-W. Kang, H.-M. Hung, A. Lin, M.R. Hoffmann, Sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation: the role of O_3, H_2O_2, frequency, and power density, Environ. Sci. Technol. 33 (1999) 3199–3205, https://doi.org/10.1021/es9810383.

[56] R. Lall, R. Mutharasan, Y.T. Shah, P. Dhurjati, Decolorization of the dye, reactive blue 19, using ozonation, ultrasound, and ultrasound-enhanced ozonation, Water Environ. Res. 75 (2003) 171–179, https://doi.org/10.2175/106143003X140953.

[57] B. Park, D. Shin, E. Cho, J. Khim, Effect of ultrasonic frequency and power density for degradation of dichloroacetonitrile by sonolytic ozonation, Jpn. J. Appl. Phys. 51 (2012) 07GD07, https://doi.org/10.1143/JJAP.51.07GD07.

[58] S. Song, Z. He, J. Chen, US/O3 combination degradation of aniline in aqueous solution, Ultrason. Sonochem. 14 (2007) 84–88, https://doi.org/10.1016/j.ultsonch.2005.11.010.

[59] I. Hua, M.R. Hoffmann, Kinetics and mechanism of the sonolytic degradation of CCl4: intermediates and byproducts, Environ. Sci. Technol. 30 (1996) 864–871, https://doi.org/10.1021/es9502942.

[60] L.K. Weavers, M.R. Hoffmann, Sonolytic decomposition of ozone in aqueous solution: mass transfer effects, Environ. Sci. Technol. 32 (1998) 3941–3947, https://doi.org/10.1021/es980620o.

[61] H. Zhang, L. Duan, D. Zhang, Decolorization of methyl orange by ozonation in combination with ultrasonic irradiation, J. Hazard. Mater. 138 (2006) 53 – 59, https://doi.org/10.1016/j.jhazmat.2006.05.034.

[62] D.L. Flamm, Analysis of ozone at low concentrations with boric acid buffered KI, Environ. Sci. Technol. 11 (1977) 978–983, https://doi.org/10.1021/es60133a006.

[63] K. Yasui, T. Tuziuti, W. Kanematsu, Mechanism of OH radical production from ozone bubbles in water after stopping cavitation, Ultrason. Sonochem. 58 (2019), https://doi.org/10.1016/j.ultsonch.2019.104707.

[64] N.H. Ince, G. Tezcanlí, Reactive dyestuff degradation by combined sonolysis and ozonation, Dyes Pigm. 49 (2001) 145–153, https://doi.org/10.1016/S0143-7208(01)00019-5.

[65] R. Kıdak, Ş. Doğan, Medium-high frequency ultrasound and ozone based advanced oxidation for amoxicillin removal in water, Ultrason. Sonochem. 40 (2018) 131 – 139, https://doi.org/10.1016/j.ultsonch.2017.01.033.

[66] T.J. Mason, J.P. Lorimer, D.M. Bates, Quantifying sonochemistry: Casting some light on a black art, Ultrasonics. 30 (1992) 40–42, https://doi.org/10.1016/0041-624X(92)90030-P.

[67] M. Faryadi, M. Rahimi, M. Akbari, Process modeling and optimization of Rhodamine B dye ozonation in a novel microreactor equipped with high frequency ultrasound wave, Korean J. Chem. Eng. 33 (2016) 922–933, https://doi.org/10.1007/s11814-015-0188-6.

[68] L. Zhao, W. Ma, J. Ma, G. Wen, Q. Liu, Relationship between acceleration of hydroxyl radical initiation and increase of multiple-ultrasonic field amount in the process of ultrasound catalytic ozonation for degradation of nitrobenzene in aqueous solution, Ultrason. Sonochem. 22 (2015) 198–204, https://doi.org/10.1016/j.ultsonch.2014.07.014.

[69] Y. Shen, Q. Xu, R. Wei, J. Ma, Y. Wang, Mechanism and dynamic study of reactive red X-3B dye degradation by ultrasonic-assisted ozone oxidation process, Ultrason. Sonochem. 38 (2017) 681–692, https://doi.org/10.1016/j.ultsonch.2016.08.006.

[70] C.E. Schiaffo, P.H. Dussault, Ozonolysis in solvent/water mixtures: direct conversion of alkenes to aldehydes and ketones, J. Org. Chem. 73 (2008) 4688 – 4690,https://doi.org/10.1021/jo800323x.

[71] Y. Pi, J. Wang, The mechanism and pathway of the ozonation of 4-chlorophenol in aqueous solution, Sci. China Ser. B Chem. 49 (2006) 379‑384, https://doi.org/10.1007/s11426-006-0379-4.

[72] L. Zeng, J.W. McKinley, Degradation of pentachlorophenol in aqueous solution by audible-frequency sonolytic ozonation, J. Hazard. Mater. 135 (2006) 218 ‑ 225, https://doi.org/10.1016/j.jhazmat.2005.11.051.

[73] J. Staehelin, R.E. Buhler, J. Hoigne, Ozone decomposition in water studied by pulse radiolysis. 2. OH and HO_4 as chain intermediates, J. Phys. Chem. 88 (1984) 5999‑6004, https://doi.org/10.1021/j150668a051.

[74] P.F. Barbier, C. Petrier, Study at 20 kHz and 500 kHz of the ultrasound-ozone advanced oxidation system: 4-nitrophenol degradation, J. Adv. Oxid. Technol. 1 (1996) 154‑159, https://doi.org/10.1515/jaots-1996-0208.

[75] L.K. Weavers, F.H. Ling, M.R. Hoffmann, Aromatic compound degradation in water using a combination of sonolysis and ozonolysis, Environ. Sci. Technol. 32 (1998) 2727‑2733, https://doi.org/10.1021/es970675a.

[76] A. D. O. Martins, V.M. Canalli, C.M.N. Azevedo, M. Pires, Degradation of pararosaniline (C.I. Basic Red 9 monohydrochloride) dye by ozonation and sonolysis, Dyes Pigm. 68 (2006) 227‑234. doi:10.1016/j.dyepig.2005.02.002.

[77] X. Zhou, W. Guo, S. Yang, H. Zheng, N. Ren, Ultrasonic-assisted ozone oxidation process of triphenylmethane dye degradation: Evidence for the promotion effects of ultrasonic on malachite green decolorization and degradation mechanism, Bioresour. Technol. 128 (2013) 827‑830, https://doi.org/10.1016/j.biortech.2012.10.086.

[78] W. Guo, R. Yin, X. Zhou, J. Du, H. Cao, S. Yang, N. Ren, Sulfamethoxazole degradation by ultrasound/ozone oxidation process in water: kinetics, mechanisms, and pathways, Ultrason. Sonochem. 22 (2015) 182‑187, https://doi.org/10.1016/j.ultsonch.2014.07.008.

[79] L.K. Weavers, N. Malmstadt, M.R. Hoffmann, Kinetics and mechanism of pentachlorophenol degradation by sonication, ozonation, and sonolytic ozonation, Environ. Sci. Technol. 34 (2000) 1280‑1285, https://doi.org/10.1021/es980795y.

[80] K. Vinodgopal, J. Peller, O. Makogon, P.V. Kamat, Ultrasonic mineralization of a reactive textile azo dye Remazol black B, Water Res. 32 (1998) 3646–3650, https://doi.org/10.1016/S0043-1354(98)00154-7.

[81] T.M. Olson, P.F. Barbier, Oxidation kinetics of natural organic matter by sonolysis and ozone, Water Res. 28 (1994) 1383–1391, https://doi.org/10.1016/0043-1354(94)90305-0.

[82] J.L. Sotelo, F.J. Beltran, F.J. Benitez, J. Beltran-Heredia, Henry’s law constant for the ozone-water system, Water Res. 23 (1989) 1239–1246, https://doi.org/10.1016/0043-1354(89)90186-3.

[83] E.F. Karamah, S. Bismo, W.W. Purwanto, Significance of acoustic and hydrodynamic cavitations in enhancing ozone mass transfer, Ozone Sci. Eng. 35 (2013) 482–488, https://doi.org/10.1080/01919512.2013.820640.

[84] P. Sobieszuk, J. Aubin, R. Pohorecki, Hydrodynamics and mass transfer in gas-liquid flows in microreactors, Chem. Eng. Technol. 35 (2012) 1346–1358, https://doi.org/10.1002/ceat.201100643.

[85] H. Zhang, G. Chen, J. Yue, Q. Yuan, Hydrodynamics and mass transfer of gas-liquid flow in a falling film microreactor, AIChEJ 55 (2009) 1110–1120, https://doi.org/10.1002/aic.11743.

[86] V. Hessel, P. Angeli, A. Gavriilidis, H. Lowe, Gas-liquid and gas-liquid-solid microstructured reactors: contacting principles and applications, Ind. Eng. Chem. Res. 44 (2005) 9750–9769, https://doi.org/10.1021/ie0503139.

[87] J. Staehelin, J. Hoigne, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, Environ. Sci. Technol. 16 (1982) 676–681, https://doi.org/10.1021/es00104a009.

[88] M. Teramoto, S. Imamura, N. Yatagai, Y. Nishikawa, H. Teranishi, N. Yatagai, Y. Nishikawa, Kinetics of the self-decomposition of ozone and the ozonation of yanide ion and dyes in aqueous solutions, J. Chem. Eng. Jpn. 14 (1981) 383–388, https://doi.org/10.1252/jcej.14.383.

[89] H. Zhang, Y. Lv, F. Liu, D. Zhang, Degradation of C.I. Acid Orange 7 by ultrasound enhanced ozonation in a rectangular air-lift reactor, Chem. Eng. J. 138 (2008) 231–238, https://doi.org/10.1016/j.cej.2007.06.031.

[90] J. Carriere, J.P. Jones, A.D. Broadbent, Decolorization of textile dye solutions, Ozone Sci. Eng. 15 (1993) 189–200, https://doi.org/10.1080/ 01919519308552483.

[91] A. Henglein, Sonochemistry: Historical developments and modern aspects, Ultrasonics 25 (1987) 6‑16, https://doi.org/10.1016/0041-624X(87)90003-5.

[92] C.-H. Fischer, E.J. Hart, A. Henglein, Ultrasonic irradiation of water in the presence of 18,18O2: isotope exchange and isotopic distribution of H_2O_2, J. Phys. Chem. 90 (1986) 1954‑1956, https://doi.org/10.1021/j100400a043.

[93] E.J. Hart, A. Henglein, Sonochemistry of aqueous solutions: H_2‑O_2 combustion in cavitation bubbles, J. Phys. Chem. 91 (1987) 3654‑3656, https://doi.org/10.1021/j100297a038.

[94] I. Hua, M.R. Hoffmann, Optimization of ultrasonic irradiation as an advanced oxidation technology, Environ. Sci. Technol. 31 (1997) 2237‑2243, https://doi.org/10.1021/es960717f.

[95] C. Petrier, A. Francony, Incidence of wave-frequency on the reaction rates during ultrasonic wastewater treatment, Water Sci. Technol. 35 (1997) 175‑180, https://doi.org/10.1016/S0273-1223(97)00023-1.

[96] C. Petrier, A. Francony, Ultrasonic waste-water treatment: Incidence of ultrasonic frequency on the rate of phenol and carbon tetrachloride degradation, Ultrason. Sonochem. 4 (1997) 295‑300, https://doi.org/10.1016/S1350-4177(97)00036-9.