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Sonochemical processes for the degradation of antibiotics in aqueous solutions: a review

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Abstract

Antibiotic residues in water are general health and environmental risks due to the antibiotic-resistance phenomenon. Sonication has been included among the advanced oxidation processes (AOPs) used to remove recalcitrant contaminants in aquatic environments. Sonochemical processes have shown substantial advantages, including cleanliness, safety, energy savings and either negligible or no secondary pollution. This review provides a wide overview of the different protocols and degradation mechanisms for antibiotics that either use sonication alone or in hybrid processes, such as sonication with catalysts, Fenton and Fenton-like processes, photolysis, ozonation, etc.

Keywords: Antibiotic degradation, Sonication, Sonocatalysis, Sono/Fenton, Sonophotocatalysis, Sonozonation.

29 **Abbreviations of antibiotics:**

30 AMP, ampicillin; AMX, amoxicillin; AZI, azithromycin;

31 CAP, chloramphenicol; CDX, cefadroxil; CEF, ceftriaxone; CEFX, cefalexin; CFX,

32 Cefixime); CFZ, cefazolin; CIP, ciprofloxacin; CLA, clarithromycin; CLM, clindamycin;

33 CLX, cloxacillin; CPD, cephadroxyl; CPX, cephalixin; CTC, chlortetracycline; CTX,

34 cefotaxime;

35 DOXO, doxorubicin; DTC, deoxytetracycline; DXC, dicloxacillin;

36 EF, enrofloxacin;

37 FLU, flumequine;

38 GMF, gemifloxacin;

39 LEV, levofloxacin;

40 MNZ, metronidazole; MOX, moxifloxacin;

41 NAF, nafcillin; NOR, norfloxacin;

42 OFX, ofloxacin; OTC, oxytetracycline; OXA, oxacillin;

43 PG, penicillin G;

44 RIF, rifampin; RXM, Roxithromycin;

45 SA, sulfanilamide; SDZ, sulfadiazine; SMR, sulfamerazine; SMX, sulfamethoxazole; SMZ,

46 sulfamethazine; SSZ, sulfasalazine;

47 TC, tetracycline; TNZ, tinidazole; TYL, tylosin.

48

1 Introduction

Antibiotics were first discovered in 1928 by Alexander Fleming and the term was first used in 1942 by Waksman and his collaborators [1, 2]. Initially, the classical definition of antibiotics was: chemotherapeutic agents that can eradicate or restrain the growth of microorganisms, including bacteria, fungi or protozoa [3, 4, 5]. Antibiotics have been widely used for the treatment of infectious diseases in humans and animals to the present day [4]. Macrolides, β -lactams, quinolones, tetracyclines, and sulfonamides are the most consumed antibiotics [6]. Since the 1990s, however, antibiotic residues have been broadly observed in aqueous matrices and soil as well as in microorganism, animal and human bodies over the world thanks to the appearance of the advance analytical technologies [5, 6].

The presence of antibiotic residues in the environment can either be caused by their continuous discharge or inherent high persistence [7]. For example, CEFX and CTX have attained levels surpassing 1000 $\mu\text{g/L}$ in urban wastewater samples in Hong Kong and Shenzhen, South China [8]. 11 antibiotics in hospital wastewater and sewage treatment plants (STPs) have been identified in Beijing, China. Fluoroquinolones, in particular, were found to be the most abundant, with a highest concentration of 16.8 $\mu\text{g/L}$ in the hospital samples. The maximum concentrations of antibiotics in STPs and hospital wastewater were 1-3 orders of magnitude higher than those in the surface water from the Wenyu River and groundwater [9].

Antibiotic concentrations in wastewater and environmental water bodies are obviously correlated with variations in annual consumption data [10]. Some antibiotics, such as penicillins, are easily degraded, whereas others, such as fluoroquinolones (e.g. CIP), macrolides (e.g. TYL) and tetracyclines, are considerably more persistent, resulting in their residues being found in the environment, spreading and accumulating in organisms [10]. Antibiotic occurrence in water is generally in the range of a few to hundreds ng/L [3, 5, 6, 10]. For examples, 77 antibiotics have been reported in Danjiangkou Reservoir in China, but most were present at lower than 5.0 ng/L and

77 SMX was the most abundant one [11]. 22 antibiotics, including eight quinolones, nine
78 sulfonamides and five macrolides, have been detected in the Huangpu River in
79 Shanghai, China, where the concentration of sulfonamides was in the range of 34–859
80 ng/L [12]. Sulfonamides (0.86–1563 ng/L) were also found to be the dominant
81 antibiotics in Baiyangdian Lake, China [13]. 9 antibiotics, including sulfonamides,
82 tetracyclines, quinolones and macrolides, have been investigated in 6 urban rivers in
83 Guangzhou, South China. NOR was the most abundant followed by CIP, and the highest
84 concentration was 2702 ng/L [14]. The concentrations of 4 quinolone antibiotics, OFX,
85 NOR, CIP and EF, ranged from 3.49-660.13 ng/L in the Qingshitan reservoir, South
86 China [15]. In addition, according to Ghernaout, *et al.* [8], an elevated number of
87 antibiotics, made up of sulfonamides, trimethoprim and macrolides, was found in
88 Japanese urban rivers.

89 As a side effect of antibiotic use, antibiotic-resistance genes and antibiotic-
90 resistant bacteria may be formed in microorganisms, causing a significant threat to
91 human health and ecological safety [5, 10, 16]. For example, OXA-resistant bacteria
92 are currently a serious problem in Latin American hospitals [17]. Meanwhile, other
93 adverse effects, such as endocrine disruption and aquatic toxicity, can also destroy
94 ecosystems [16].

95 Biological degradation [5], adsorption [18], reverse osmosis [18], ion exchange
96 [18] and advanced oxidation processes (AOPs), including ozonation [5], photocatalysis
97 [19-24], electrochemical degradation [23, 24], non-thermal plasma [25], Fenton/photo-
98 Fenton reaction [5], sonochemical degradation, and combination [26, 27], have been
99 extensively studied as means to remove antibiotics from aqueous matrices. Biological
100 processes are widely used in industrial effluent treatments with large effluent flow rates,
101 but the high concentration of pollutants in effluents with high toxicity are recalcitrant
102 to the microorganisms, resulting in limited antibiotic removal efficiency (RE) [5]. High-
103 concentration antibiotics can be transported from water matrices onto solid adsorbents
104 via adsorption, but the loaded adsorbents must be subsequently treated, causing higher

105 treatment costs [28, 29]. Reverse osmosis has been used to remove antibiotics with
106 larger molecules, it can efficient to reduce levels of dissolved salts. However, with this
107 process, the contaminants are slowly concentrated rather than removed. Besides, the
108 deterioration/fouling of the membrane structure caused by high-concentration
109 compounds is another drawback. Therefore, frequent back-washing and regeneration is
110 required [30].

111 Due to the limitations of physical and biological processes, AOPs have gradually
112 emerged as means for the degradation/mineralization of organic pollutants over recent
113 decades [31]. As non-selective oxidation technologies, AOPs have attained the total
114 removal of antibiotics, efficient reductions in toxicity and antimicrobial activity, and
115 have also increased biodegradability [17, 31-38]. The generation of reactive oxygen
116 species (ROS), such as $\cdot\text{O}$, $\cdot\text{O}^{2-}$, $\cdot\text{OH}$, $\cdot\text{OOH}$, H_2O_2 , etc., via various methods was the
117 origin of AOPs [4, 10, 21, 22, 31, 33, 39-48].

118 Hydroxyl radicals ($\cdot\text{OH}$) and other ROS are released by ozone (O_3) decomposition
119 in water during the ozonation process. Meanwhile, O_3 often selectively reacts with
120 nucleophilic molecules. However, the high costs of equipment, maintenance and
121 operation, the high quantities of energy required, lower mass transfer, extreme pH-
122 dependence and potential effluent ecotoxicity limit the application of ozonation [49,
123 50]. Photocatalysis has often been applied under ambient conditions and may gain
124 energy from sunlight with the advantages of simple operation and scale-up applicability,
125 but it also suffers from mass-transfer limitations, and is affected by catalyst amount,
126 light wavelength, radiation intensity, pH and water quality. Additionally, the catalysts
127 consumed need to be specially treated or recycled, causing high overall costs [19-22,
128 26, 27, 30]. Electrochemical degradation is an effective, versatile, cost-effective, easy
129 and clean technology, and is suitable for the treatment of toxic wastewater that contains
130 high-concentration antibiotics and COD. However, the RE depends on the nature and
131 structure of the electrode material, electrolyte composition, the applied current and the
132 diffusion rates of substrates to the active sites of the anode. The low flow rates and high

133 operating costs limit the application of electrochemical methods [23, 24]. Non-thermal
134 plasma generated in electrical discharges in liquid or at the gas-liquid interface leads to
135 the formation of ROS and the power introduced into the plasma is very high, leading to
136 low energy yields [25]. The Fenton reaction is usually used in homogeneous and
137 heterogeneous systems and in conjugation with UV radiation to enhance the oxidation
138 process. However, the narrow acidic pH range of the operation and dissolved catalysts
139 limits this process [5].

140 Sonochemical degradation (sonolysis), namely, degradation that is driven or
141 enhanced by sonication, emerged in the 1990s. Ultrasound (US) is sound that exceeds
142 the human hearing range, and has a wide frequency range of 18 kHz to 500 MHz [37,
143 45, 51-54]. Ultrasonic propagation, with cycles of compression and rarefaction, causes
144 acoustic cavitation phenomena, which is defined as the sonochemical origin [52, 55-
145 61]. Such numerous cavitation bubbles are also referred to as microreactors, since they
146 act as the centre of chemical reactions [45, 62]. Gas-filled cavitation bubbles grow and
147 extensively implode under the positive pressure that occurs during the compression
148 cycle of US in water bulk [37, 45, 51, 52, 54]. Meanwhile, enormous local temperatures
149 (ca. 5000 K) and high pressures (ca. 500 atm), microjets and shockwaves are produced
150 [10, 27, 63, 64]. Subsequently, ROS are produced through the pyrolysis of water
151 molecules at the collapsing bubbles (hotspots), and oxidize the substrates in water [45,
152 51]. Among these formed ROS, $\cdot\text{OH}$ is a significantly important, very strong and
153 nonspecific oxidizing species [45, 51, 54]. Besides, hydrophobic volatile compounds
154 also suffer thermal decomposition at hotspots, and both the above actions contribute to
155 the degradation of organic contaminants [65-67].

156 In theory, a large variety of organic pollutants are capable of being degraded by
157 sonication without additional chemicals. Thus, sonication is usually seen as a green and
158 safe technique to perform wastewater treatment. However, the sonolysis of organic
159 contaminants has limited efficiency and consumes considerable amounts of energy [23,
160 45, 68]. To improve the RE and reduce energy consumption, sonication-based

161 combinations, such as sonocatalysis [69-73], Sono/Fenton [19, 21, 35, 43, 44, 74-77],
162 sonication-ozonation (Sonozonation) [78-81], sonication-persulfate (Sono/PS) [82],
163 sonophotocatalysis (Sono/Photo) [31, 39, 83-85], sonoelectrochemical degradation
164 [86-88], sonication-microwaves [89], sonication-hydrodynamic cavitation [90], and
165 ultrasound-assisted biological processes [91-93], have attracted great attention.

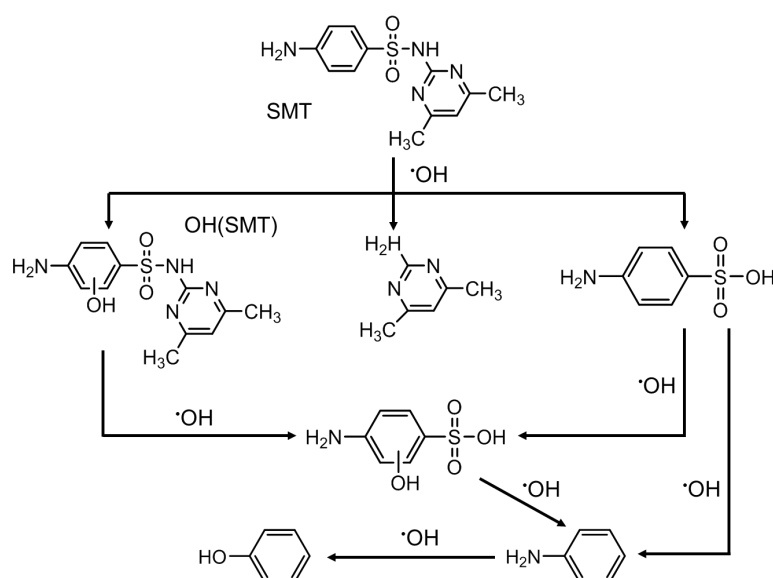
166 This review aims to provide an overview, and evaluate the REs, of the
167 degradation of antibiotics in aqueous matrices by various sonochemical processes,
168 including sonication alone [31, 36, 41, 46, 69, 71, 94-100], sonocatalysis [35, 40, 52,
169 72, 75, 101-110], Sono/Fenton [21, 22, 32, 33, 34, 35, 43, 44, 111, 112, 113], Sono/PS,
170 Sono/Photo [20, 31, 39, 83, 84, 85, 114-119], sonozonation [78, 79, 80, 120-123], etc.,
171 and will focus on the degradation mechanisms and influence of operating conditions
172 indicated in appropriate studies that have been published in the last few years.

173 **2 Antibiotic degradation by sonication alone**

174 **2.1 Mechanisms of sonolysis**

175 In general, sonochemical degradation occurs in three reaction zones relative to the
176 collapsing cavitation bubbles: inside the cavitation bubbles; in the interfacial region
177 between cavitation bubbles and the bulk solution; and in the bulk solution [5, 10, 45].
178 Inside and around the collapsing cavitation bubbles, the thermal dissociation of water
179 molecules and oxygen occurs to release ROS [45]. Moreover, hydrophobic volatile
180 compounds around the hotspots are also thermally decomposed [10, 45, 62, 63, 64].
181 Hydrophilic and non-volatile compounds, such as LEV [42], that remain in the bulk
182 solutions are oxidized by ROS. The sonochemical reaction with $\cdot\text{OH}$ has been
183 speculated to occur at the cavitation interface, where the maximum $\cdot\text{OH}$ concentration
184 is present [42]. Only ca. 10% of the radicals created in the interfacial region diffuse or
185 escape to the bulk liquid [10, 41]. Therefore, antibiotic degradation is strongly
186 dependent on the distance between non-volatile antibiotic molecules and the cavitation
187 bubbles, and this distance is determined by hydrophobicity [4, 41, 42, 45].

188 **Figure S1** clearly shows the HPLCs of SMT degradation and the appearance of
 189 intermediates with sonication time. In addition, LC/MS/MS analyses have indicated
 190 that the sonolytic degradation of SMT is mainly ascribed to OH oxidation. The
 191 sonolytic degradation pathway of SMT is shown in Scheme 1. As can be seen, SMT is
 192 first oxidized by $\cdot\text{OH}$ radicals, resulting in the formation of (OH)SMT and the cleavage
 193 of the N–S bond [41]. 4,6-dimethylpyrimidin-2-amine, sulfanilic acid and the mono-
 194 hydroxyl derivative of sulfanilic acid are probably produced by the cleavage of the N–
 195 S bond of SMT or (OH)SMT. The mono-hydroxyl derivative of sulfanilic acid may also
 196 be formed by the $\cdot\text{OH}$ radical that directly attacks the sulfanilic acid. Aniline is an
 197 intermediate product in SMT degradation via the breakage of the C–S bond in SMT or
 198 sulfanilic acid, and can be oxidized to phenol [41].



199

200

Scheme 1 Pathway of intermediate formation in the sonolytic degradation of SMT [41].

201

202

203

204

205

206

However, the sonochemical degradation products were rarely mineralized. About 100% of 180 μM SMT was decomposed, but only 8.31% TOC was reduced by sonication for 2 h at 800 kHz and 100 W. Fortunately, the effluent became much more biodegradable (BOD_5/COD was increased from 0.04 to 0.45), indicating that the toxicity of the effluent to microorganisms was obviously reduced [41].

Extensive investigation with the addition of a radical scavenger, such as isopropyl

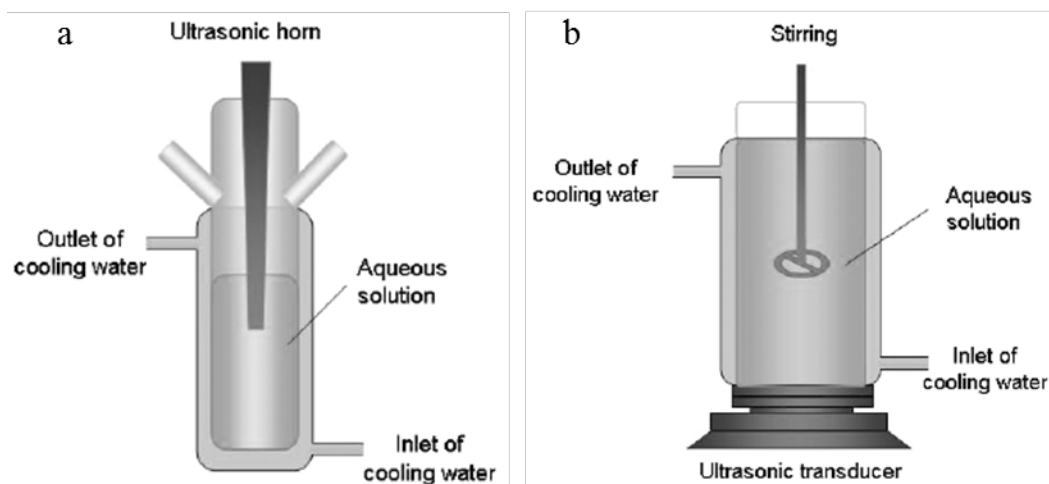
207 alcohol, ethanol, methanol [41], *n*-butanol [97], terephthalate (TA) and Suwannee River
208 Fulvic Acid (SRFA) [124], has revealed that reaction with $\cdot\text{OH}$ is the main degradation
209 route for antibiotics during sonication [41, 97, 124, 125]. For example, with a
210 hydrophobic character in the whole pH range, *n*-butanol diffuses to the gas/liquid
211 interface of the microbubbles where it is able to scavenge $\cdot\text{OH}$ and quench the antibiotic
212 degradation as a consequence [97]. In the presence of TA, CIP (a hydrophilic compound)
213 degradation was inhibited by a factor of 40–1500 depending on the frequency and initial
214 concentration, while degradation was slightly affected by SRFA [124]. TA reacts with
215 $\cdot\text{OH}$ in bulk solution and accumulates around cavitation bubbles, greatly quenching $\cdot\text{OH}$,
216 while SRFA stays in bulk solution and catches $\cdot\text{OH}$ and competes with CIP [124].

217 In addition, the inhibition of DXC degradation via the addition of a radical
218 scavenger (2-propanol or glucose) was observed [96]. DXC degradation was not
219 affected significantly when low- or high-concentration glucose (high hydrophilicity)
220 and low-concentration 2-propanol (miscible with water) were individually added. It
221 was speculated that both glucose and low-concentration 2-propanol are dissolved in the
222 bulk liquid far away from the bubbles, while DXC is relatively closer to the cavitation
223 bubbles. As a result, no competing reactions between glucose or 2-propanol with $\cdot\text{OH}$
224 occurred around the hotspots. However, a significant decrease in the DXC degradation
225 rate was observed in the presence of a high concentration of 2-propanol due to its
226 relatively high volatility [126]. Therefore, the addition of the radical scavengers
227 confirmed that $\cdot\text{OH}$ -mediated reactions either occur at the interface of the cavitation
228 bubbles, or in the bulk liquid depending on the properties of the antibiotics [65, 97].
229 Unreacted $\cdot\text{OH}$ will be recombined into H_2O_2 , for example, 77.6 and 57.3 μM of H_2O_2
230 have been observed as being generated after 30 min sonication in the presence of AMP
231 and NAF, respectively [69].

232 Overall, two reaction mechanisms are presumably responsible for the sonolysis of
233 antibiotics: pyrolysis and oxidation by the $\cdot\text{OH}$ generated in the system [27, 43, 52, 53].

234 2.2 Application of sonication for antibiotic degradation

235 Sonication systems used for the degradation of antibiotics mainly include
236 ultrasonic horn-type and bath-type apparatus, as shown in Figure 1.



237

238 **Figure 1** Schematic diagram of ultrasonic horn-type (a) and bath-type (b) setups for degradation. Reprinted from
239 ref. [68] Copyright (2006), with permission from Elsevier.

240 Hapeshi, *et al.* have investigated the degradation of OFX using a 20 kHz horn-
241 type ultrasonic reactor. The results showed that the RE of OFX increases with
242 increasing US power density and decreasing initial OFX concentration. Under the
243 optimal conditions, 27.7 μM OFX and 640 W/L of US power density, the RE of OFX
244 in a 350 mL solution reached 31% after 240 min sonication [36]. As a result, 12.5 nmol
245 of OFX was removed per minute by 20 kHz sonication, and the radical reactions are
246 responsible for OFX degradation.

247 Villegas-Guzman, *et al.* have studied the degradation of DXC using a 600 kHz
248 bath reactor [96]. 210 μM DXC was fully removed in 100 mL aqueous solution for 180
249 min under acid and neutral conditions. Thus, 117 nmol of DXC was removed per minute
250 by 600 kHz sonication with 0.6 W/L of power density. However, no significant change
251 in TOC concentration and a 30% reduction in COD were observed during 480 min of
252 sonication, indicating that either no or less mineralization occurred under sonication
253 alone.

254 To date, sonication has been extensively used to probe the RE of a large number
 255 of antibiotics, which are summarized in Table 1.

256 **Table 1** Summary of the degradation of antibiotics in water by sonication alone.

Antibiotics	F _{US} /P _E (kHz/W)	P _{US} (W)	t (min)	C ₀ /V (mg/L)/mL	pH	RE (%)	Other results	Refs.
OFX	20/224	-	240	10/350	-	31	Mainly radical reactions.	[36]
LEV	20/400	-	20	20/50	5.9	9.4	BOD ₅ /COD increased.	[42]
CIP	20/-	20	-	-/50	8.5	-	CIP is far away from cavitation bubbles.	[124]
CPX	24/200	17.3	60	20/50	6.5	~52	BOD ₅ /COD ratio was raised.	[127]
PG	35/860	-	70	200/50	3.0	66.7	RE is pH dependent.	[95]
PG	40/100	-	60	50/1000	-	-	24.8% COD was removed.	[114]
CIP	205/-	13.5	35/70	10 μM/300	3.5	~65	Molar volume is critical.	[70]
PG	205/-	13.5	35/70	10 μM/300	3.5	<10	Molar volume is critical.	[70]
OXA	275/60	20.7	120	20/250	5.6	100	Mineralization is difficult	[128]
CIP/NOR/ CPX/CDX/ OXA/CLX	354/-	26.4	75- 120	40 μM/300	6.5	-	Hydrophobicity was critical.	[129]
CIP	520/-	13.8	120	15/150	3.0- 10.0	57	RE is pH-dependent.	[38]
CIP	544/200	-	150	15/<1000	7.0	~60	544 kHz>801/1081 kHz	[125]
SDZ	580/-	22	120	25/250	5.5	90	H ₂ O ₂ affects negatively	[97]
DXC	600/60	34.8	300	0.21 mM/300	3.0	100	~ 0 mineralization was obtained.	[130]
DXC	600/60	34.8	480	98.8/100	5.5	100	30% of COD was eliminated.	[96]
SMZ	800/100	-	120	180 μM/-	-	100	8.31% TOC was reduced.	[41]

257 Note: F_{US}: ultrasonic frequency; P_E: electrical power input; P_{US}: the power dissipated by the reactor (calculated using
 258 the calorimetric method); t: sonication time; C₀: initial antibiotic concentration; V: volume of solution; RE: removal

259 efficiency; Refs.: references.

260 As listed in [Table 1](#), the sonolysis of CIP, CPX, LEV, PG and OFX, etc., have been
261 conducted at low US frequency (20-40 kHz) and high electrical power (200-860 W);
262 their REs are lower, lying in the range of 9.4%-66.7% after 20-240 min sonication. In
263 addition, COD was slightly removed, leading to an increasing BOD₅/COD ratio. By
264 contrast, the sonolysis of CDX, CIP, CLX, CPX, DXC, NOR, OXA, PG, SDZ and SMZ,
265 etc., was performed at medium US frequency (205-600 kHz) and lower electrical power
266 (60-200 W), and their REs are relatively higher, lying in the range of 10%-100% after
267 35-300 min sonication. However, the mineralization of antibiotics is difficult under
268 sonication alone.

269 2.3 Role of effective factors

270 Under sonication, the degradation of antibiotics mostly occurs via radical reactions in
271 the bulk liquid and generally follows pseudo-first order (PFO) kinetics [[38](#), [69](#), [96](#), [99](#)].
272 The degradation rate and RE of antibiotics are dependent on many factors, such as US
273 frequency [[36](#), [42](#), [97](#), [129](#)], power [[36](#), [96](#), [97](#)], and sonication mode (continuous or
274 pulse) [[70](#)], chemical structure and physicochemical properties [[129](#), [131](#)], initial
275 concentration [[36](#), [129](#), [131](#)], solution volume [[36](#), [69](#), [132](#)], pH value [[38](#), [97](#)],
276 temperature [[33](#), [40](#), [111](#), [125](#)], and sonication time [[36](#), [129](#), [131](#), [132](#)], etc. The
277 influence of the critical parameters on the sonochemical degradation of antibiotics is
278 discussed below.

279 2.3.1 Effect of US frequency and power

280 As summarized in [Table 1](#), the radical reactions that take place in the bulk liquid
281 dominate antibiotic degradation, while more reactive radicals are formed at higher
282 ultrasonic frequencies, e.g., 300-1000 kHz, than at lower frequencies, e.g. 20-45 kHz
283 [[54](#), [68](#)]. Therefore, higher REs for SDZ at 580 kHz and 22 W [[97](#)], and for AMP at 375
284 kHz and 24.4 W (actual ultrasonic powers, determined by calorimetric method) [[46](#)]
285 have been observed. Al-Hamadani, *et al.* have investigated the degradation of SMX by

286 sonication in the absence of catalysts [71]. The removal of 10 μM SMX was higher at
287 1000 kHz sonication for 60 min (72%, 160 nmol/min of removal rate) than at 28 kHz
288 sonication (33%, 55 nmol/min of removal rate), while all other experimental conditions
289 remained the same (0.18 W/mL of US power density at pH 7 and 15 °C in 1000 mL
290 solutions), because more $\cdot\text{OH}$ were generated at 1000 kHz than at 28 kHz [71]. In
291 addition, 187.29 nmol (90%) SDZ was removed per minute in 250 mL of 0.1 mM
292 aqueous SDZ solutions for 120 min under 580 kHz sonication at 30 °C and pH 5.5,
293 whereas 41.7 nmol (82%) AMP was removed per minute in 250 mL of 0.03 mM
294 aqueous AMP solutions after 180 min under 375 kHz sonication at 20 °C and pH 6.5.

295 Higher RE of antibiotics can be generally achieved at higher US energies and
296 higher dissipated powers [31, 36, 41, 69, 94-100]. At higher input powers (400-600 W),
297 however, a large number of gas bubbles exist in solution, which has been seen to scatter
298 the US to the walls of the vessel or back to the transducer. Thus, less energy is dissipated
299 into the liquid, as a result of cavitational activity, although the vessel was exposed to
300 higher power [42]. In addition, changing the solution volume inside the reactor also
301 changes the power density, which also significantly affects the degradation rate;
302 increasing the solution volume will decrease the degradation rate [132].

303 2.3.2 Effect of Physicochemical properties of antibiotics

304 The physicochemical properties of antibiotics greatly affect their sonochemical
305 degradation, with sonochemical eliminating showing significant selectivity for certain
306 antibiotics in aqueous matrices [129]. Serna-Galvis, *et al.*, have studied the degradation
307 of various antibiotics, including fluoroquinolones (CIP and NOR), penicillins (OXA
308 and CLX) and cephalosporins (CPX and CPD) using 354 kHz sonication [129].
309 Different degradation rates, $\text{CLX} > \text{OXA} > \text{CPX} > \text{NOR} > \text{CIP} > \text{CDX}$, were observed
310 under identical sonication conditions: 200 W; 375kHz; 300 mL of 40 μM of antibiotics,
311 pH 6.5 [129]. Similarly, NAF was degraded faster than AMP by 375 kHz and 24.4 W
312 sonication at pH 6.5 and 20 °C for 250 mL in 30 μM aqueous AMP solutions, and the
313 rate constants of PFO (k_I) of NAF and AMP were calculated to be 0.5 min^{-1} and 0.4

314 min^{-1} , respectively [69].

315 It has been demonstrated that the initial degradation rate of pollutants exhibited
316 good correlation with LogP (Octanol-water partition coefficient, i.e., the
317 hydrophobicity). Thus, the fast elimination of penicillins is attributed to their high
318 hydrophobicity, leading to the accumulation of penicillins near cavitation bubbles,
319 compared to fluoroquinolones or cephalosporins [129]. In addition, Lastre-Acosta, *et*
320 *al.* have indicated that the sonochemical degradation mechanism of SDZ is directly
321 related to the *pKa*-dependent speciation of SDZ molecules [97]. Moreover, small-sized
322 molecules (molar volumes less than 130 mL/mol) more quickly diffuse to bubble
323 interfaces and are impacted most by pulsing US, resulting in a higher portion of the
324 antibiotic in and around cavitation bubbles. Large-sized molecules slowly diffuse to the
325 bubble surface, resulting in a higher portion of these personal care products (PPCPs)
326 degrading in bulk solution [70].

327 2.3.3 Effect of pH value

328 The effect of pH value on antibiotic degradation is also related to the properties of
329 antibiotics (i.e., ionic species or molecule states). Some antibiotics are more
330 sophisticated, being zwitterions (a molecule containing both a basic and an acidic
331 group). For example, LEV has two different acid-dissociation constant values (*pKa* 5.7
332 and 7.9) [124]. De Bel, *et al.* have explored the effect of pH on CIP sonolysis at 520
333 kHz [38]. The k_l value (0.021 min^{-1}) at pH 3 is almost 4-fold higher than those at pH 7
334 (0.0058 min^{-1}) and pH 10 (0.0069 min^{-1}). The solution can even be considered readily
335 biodegradable after sonication at pH 3 ($\text{BOD}_5/\text{COD} > 0.4$) [38]. Degradation is clearly
336 faster when the main part of the CIP molecules carries an overall positive charge. These
337 positively charged molecules will accumulate at the negatively charged liquid–bubble
338 interface, where the concentration of ROS and the reaction temperature are higher.
339 Hence, degradation is faster [38]. Similarly, Villegas-Guzman, *et al.* have found that
340 the highest sonolysis of DXC was achieved under 600 kHz sonication at pH=3 [96].
341 Acidic media also favour the sonochemical degradation of DXC (pH=3.0) [30], LEV

342 (pH =5.9) [42], SDZ (pH=5.5) [97], and TNZ (pH=3.0) [100], etc.

343 By contrast, Wang, *et al.* have reported that the TC degradation rate is highly pH-
344 dependent, and that higher pH values favour TC degradation under sonication, due to
345 the transformation of TC molecules at different pH values [99].

346 2.3.4 Effect of temperature

347 Generally, the degradation rate of antibiotics increases with increasing temperature
348 [33, 40, 125]. The influence of temperature on the sonodegradation of antibiotics is
349 complicated. As far as we know, high temperature usually results in a high solvent
350 vapour pressure, followed by the formation of more water-vapour-containing cavitation
351 bubbles, causing the cavitation bubbles to collapse less violently, which leads to
352 reduced $\cdot\text{OH}$ production. However, the reduction of the viscosity and surface tension at
353 high temperatures leads to a low threshold intensity for cavitation, which can increase
354 the number of cavitation bubbles, and then promote the generation of $\cdot\text{OH}$ and $\text{HOO}\cdot$.
355 Moreover, the strengthened reactions of the hydroxyl radicals and mass transfer at high
356 temperatures are favourable to the removal of antibiotics [33, 40, 111, 125]. According
357 to De Bel *et al.*, increased temperature (15-45 °C) leads to faster CIP degradation (k_I
358 was increased from 0.0055 to 0.0105 min^{-1}). The low apparent activation energy (17.5
359 kJ/mol) suggests that the degradation of CIP is diffusion controlled (usually in the range
360 of 12-15 kJ/mol) [125]. Higher temperature (in the range of 30-60 °C) facilitates the
361 removal of FLU by the Sono/ H_2O_2 process [111]. 3% of FLU was removed from 200
362 mL of 1 mM aqueous FLU solutions for 120 min under 40 kHz and 120W sonication
363 at 60 °C and pH 4 in the presence of 20 mM H_2O_2 . The activation energy for the
364 degradation of FLU was 6.510 kJ/mol [111].

365 2.3.5 Effect of initial concentration of antibiotics

366 In general, low concentrations of antibiotics favour their sonochemical
367 degradation; RE decreases with increasing initial concentration [30, 31, 36, 41, 69, 94-
368 100]. The degradation of antibiotics is limited by the available surface at the bubble-

369 liquid interface. According to the Arrhenius law, for example, the apparent activation
370 energy for the sonochemical degradation of CIP has been determined to be 17.5 kJ/mol,
371 which suggests that the degradation of CIP is diffusion controlled. A Langmuir-type
372 heterogeneous-reaction-kinetics model could be used to explain why the k_l value
373 increases with decreasing initial CIP concentration from 0.0204 min⁻¹ (C_0 : 0.15 mg/L)
374 to 0.0009 min⁻¹ (C_0 : 150 mg/L). According to the model, the molecules at the interface
375 region of the cavitation bubbles can be readily oxidized by the formed $\cdot\text{OH}$ [125].

376 2.3.6 Effect of additives

377 Antibiotics can be degraded to a certain degree by sonication alone, but the REs
378 of non-volatile compounds are somewhat lower and degradation is really time
379 consuming. For example, it has been observed that only 30% DXC was degraded after
380 8 h [96], and most antibiotics were converted into hydrophilic organics rather than CO₂
381 [17]. Although the BOD₅/COD ratio (biodegradability) noticeably increased, e.g., from
382 0 to 0.36, after the sonochemical degradation of CPX [127], the mineralization of
383 antibiotics is challenging even after a long period of sonication [30, 98, 127, 128]. For
384 example, 180 μM SMZ was almost fully removed, but only 8.31% TOC was reduced
385 by sonication at 800 kHz and 100 W in 2 h [41]. Therefore, a great deal of effort has
386 been devoted to enhancing sonolysis to increase the RE, with an eye on practical
387 applications, using simple additives, such as noble gas Argon (Ar), anions, CCl₄, H₂O₂,
388 etc. in the sonication system.

389 Due to Ar's physical properties (e.g. solubility, thermal conductivity and specific
390 heat ratio), an Ar atmosphere favours sonolytic activity compared to diatomic gases [36,
391 109]. Gao, *et al.* have reported that the sonolytic degradation of SMZ is accelerated in
392 the presence of Ar or O₂, but inhibited by N₂ [41]. Meanwhile, the SMZ degradation
393 rate was slightly inhibited by NO₃⁻, Cl⁻ and SO₄²⁻, which is consistent with the
394 sonochemical degradation of TC [99], but significantly improved by HCO₃⁻ and Br⁻
395 [41]. The enhancement of TC degradation by adding HCO₃⁻ has also been
396 demonstrated [99], while a negligible influence was observed when adding mannitol or

397 calcium carbonate during the sonochemical degradation of OXA at a high frequency in
398 wastewater (from a municipal wastewater treatment plant) [128]. In another sonication
399 system, KI and H₂O₂ were used as an iodine source to enhance the RE of SMZ, and the
400 RE value increased from 3.4 to 85.1 under 60 min sonication with 0.04 mM SMZ, 2.4
401 mM KI and 120 mM H₂O₂ at 195 W US under acidic conditions. I[•] and I^{2-•} radicals
402 were the most predominant active species. The activation energy of SMZ degradation
403 was calculated to be 7.75 ± 0.61 kJ/mol (15–55 °C), which indicates that the reaction
404 is potentially a diffusion-controlled process [98]. Furthermore, the addition of CCl₄ can
405 also enhance sonochemical degradation, which is attributed mainly to the formation of
406 chlorine-containing oxidizing species, such as HClO, Cl₂, •Cl, •CCl₃ and •CCl₂, from
407 the sonolysis of CCl₄ [42, 133].

408 Zhang, *et al.* have investigated the degradation of sulfa antibiotics by potassium
409 ferrate in combination with sonication (Sono/Fe(VI)) [75]. SDZ, SMR and SMX were
410 all well degraded by sonication, and the reaction process was in accordance with
411 pseudo-second order reaction kinetics; the REs of SDZ, SMR and SMX were 77.5, 82.5
412 and 82.5% for 30 min sonication, respectively. H₂O₂ was often added to the sonication
413 system to enhance antibiotic degradation [36, 99, 100, 132]. Matouq, *et al.* have
414 investigated AMX degradation at 2.4 MHz sonication, with the addition of H₂O₂
415 providing a great increase to the RE of AMX [132]. The effect of adding H₂O₂ to the
416 sonochemical degradation of antibiotics has been summarized in Table 2.

417 As seen in Table 2, the sonolysis of TC, LEV, NOR, MTZ, OFX and FLU, etc.,
418 has been conducted in a US-frequency range of (20-2400 kHz) and a US-power range
419 of (100-750 W). Their REs are located in the range of 1.88%-81.00%, under sonication
420 alone, and 0-30%, under oxidation alone with 0.29-333.00 mM H₂O₂ for 30-240 min.
421 In some cases, significantly higher REs (5.9-93%) were given by sono/H₂O₂ processes
422 than in those performed with sonication alone, or oxidation with H₂O₂ alone. In addition,
423 COD was slightly removed, leading to increasing ratio of BOD₅/COD.

424 **Table 2** Summary of sonochemical degradation of antibiotics in the presence of H₂O₂.

Antibiotics	C _{H2O2} (mM)	F _{US} /P _E (kHz/W)	t (min)	C ₀ /V (mg/L)/mL	pH	RE _{H2O2} (%)	RE _{Sono} (%)	RE _{Sono/H2O2} (%)	Refs.
TC	0.29	20/400	60	10/100	5.5	~0	81.0	93.0	[99]
LEV	5.0	20/195	150	20/100	7.1	6.7	1.9	65.0	[43]
NOR	20.0	20/240	30	5/200	7.0	~0	<5.0	5.9	[20]
MTZ	60.0	20/-	180	500/200	3.0	-	42.0	68.0	[41]
OFX	100.0	20/224	240	10/350	-	-	31.0	50.0	[36]
TNZ	333.0	120/750	150	80/100	3.0	-	5.0	75.0	[100]
CLM	1.0	130/500	150	45/-	3.0	~25.0	~30.0	~45.0	[21]
CIP	1.0	580/-	60	100/250	3.0	5.9	35.8	36.5	[32]
AMX	5.0 mL	2400/9.5	90	50/50	3.5- 5.5	~30.0	-	70.0	[132]

425 Note: C_{H2O2}: H₂O₂ concentration; F_{US}: ultrasonic frequency; P_E: electrical power input; t: sonication time; C₀:
426 initial antibiotic concentration; V: volume of solution; RE: removal efficiency; Refs.: references.

427 However, the addition of H₂O₂, used as a radical promoter, does not always
428 promote sonication processes [20, 32]. When sonication was applied without H₂O₂,
429 degradation and mineralization (35.8 and 22.6%, respectively) were similar to the
430 results obtained in sono/H₂O₂ processes (36.5 and 24.4%, respectively) [32]. Therefore,
431 excess H₂O₂ can act as a ·OH scavenger and decrease the RE of antibiotics, resulting in
432 the presence of an optimal amount of H₂O₂ for the sonochemical degradation of the
433 target compounds.

434 In addition, Serna-Galvis, *et al.* have reported the role of mechanical agitation in
435 the removal of OXA (or AMP) via sonication [129], photo-Fenton, TiO₂ photo-electro
436 [17, 69, 128], and sono-Fenton processes [46]. These results suggest that mechanical
437 agitation is not required in the processes that involve sonication on the lab-scale [17,
438 46, 69, 128, 129]. The exception is the degradation of CIP in the US-assisted *Laccase*
439 catalytic process, in which degradation increased from 8% to 50%, due to improved
440 mass transfer, when the agitation speed was increased from 0 rpm to 200 rpm. However,
441 no further enhancement in degradation efficiency was observed when the agitation
442 speed was increased to 300 rpm [91].

443 Moreover, although the application of sonication has been shown to be feasible on
444 small scales, its use in large-scale treatment process is still a challenge because of high

445 energy requirements [105]. Therefore, sonication has been combined with other
446 additives (catalysts and persulfate) and other AOPs (Fenton reaction, photocatalysis,
447 ozonation, etc.) to increase the RE, reduce reaction times and enhance mineralization
448 [36, 38]. These hybrid methods are discussed below.

449 **3 Degradation of antibiotics by sonocatalysis**

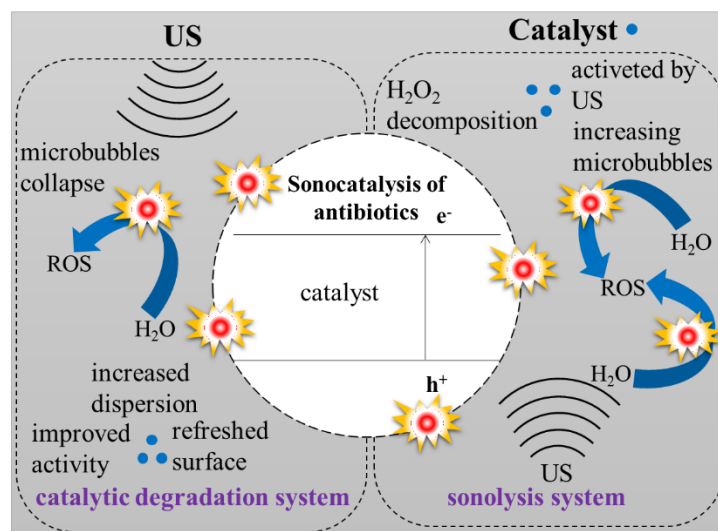
450 The ability of sonication to enhance the heterogeneous catalytic degradation of
451 antibiotics is discussed in this section, while the role of sonication in the homogeneous
452 catalytic degradation of antibiotics, mainly Fenton reactions, will be discussed in the
453 following section. In most cases, higher REs are obtained by sonocatalysis than the sum
454 of those obtained under catalysis and sonication alone [40, 44, 71, 102, 103, 106, 109,
455 134, 135]. More importantly, antibiotics, such as TC, OTC, CTC and DTC, can be
456 decomposed into a suite of non-toxic intermediates by sonocatalytic processes [136].
457 For example, GMF was first decomposed to aromatic and aliphatic intermediates in the
458 early stage of reactions, and then mineralized to CO₂, H₂O and inorganic ions, leading
459 to significant reductions in solution toxicity after the sonocatalytic degradation of GMF
460 [103]. Similarly, a substantial reduction in the toxicity of an AMP solution has been
461 observed after the sonocatalytic degradation of AMP with Zn(OH)F [101].

462 A bio-toxicity examination, using an inhibition test conducted on activated sludge,
463 revealed diminishing oxygen-consumption-inhibition percentage [IOUR (%)], from
464 33.6 to 22.1%, during the sono/ZnO/nano-cellulose process. The utilization of the
465 sono/ZnO/nano-cellulose process can convert TC molecules to less toxic compounds.
466 However, longer reaction times are required for complete conversion into non-toxic
467 substances [104].

468 **3.1 Mechanisms of sonocatalysis**

469 In sonocatalytic systems, [•]OH radicals are the dominant reactive species that
470 contribute to antibiotic degradation. The pronounced degradation effectiveness with the
471 catalysts under sonication can be assigned to their synergetic ability to produce ROS

472 and subsequent radical reactions [109]. Sonocatalysis includes two reaction pathways
473 (Figure 2): (1) catalytic degradation enhanced by sonication; (2) sonolysis enhanced by
474 the catalyst.



475

476

Figure 2 The mechanisms of antibiotic removal by sonocatalysis.

477 In an attempt to clarify the effects of sonication on heterogeneous catalysis,
478 increased dispersion has been considered as a reason for the increased reaction rate.
479 The removal of the passivating layer, the reduction of the catalyst particle size and
480 enhanced interparticle collisions, all induced by cavitation shock waves and local
481 turbulent microjets, may increase the number of active reaction sites on catalysts as
482 well as increasing the contact area, improving mass transfer and minimizing fouling,
483 which all result in increased catalytic activity [52].

484 In homogeneous systems, it is also critical to activate the catalyst and to keep it
485 active during antibiotic degradation. Sonication can improve mass transfer, catalyst
486 activation and the production of higher ROS concentrations, e.g., in Fenton reactions
487 [77, 137]. Organometallic compounds are often used for the homogeneous catalysis of
488 various reactions. The starting organometallic compound, however, is often
489 catalytically inactive until it loses the metal-bonded ligands (such as carbon monoxide)
490 from the metal. Sonication can induce ligand dissociation, making the initiation of
491 homogeneous catalysis by sonication practical. The transient, coordinatively

492 unsaturated species produced from the sonolysis of metal carbonyls are likely
493 candidates [37, 52].

494 On the other hand, solid catalyst particles may increase the density of
495 microbubbles, meaning that more ROS will be produced during bubbles collapse. H₂O₂
496 formation is significantly increased due to the dispersion of catalysts under sonication,
497 indicating that the dispersed catalyst particles can act as additional nuclei for the
498 pyrolysis of water molecules and the formation of [•]OH [40]. As a result, increased
499 radical transfer from cavitation bubbles to the interface and bulk solution is promoted,
500 and with it the RE of antibiotics [37, 52, 126]. In homogeneous systems, catalysts, such
501 as Fe²⁺, promote radical formation via the decomposition of H₂O₂, formed under
502 sonication, to enhance and accelerate the degradation of antibiotics [137, 138]. For
503 example, the sonolysis of SMZ was accelerated in the presence of ferrous ion. The
504 synergetic effect was mainly attributed to the production of additional [•]OH via Fenton
505 chemistry [41].

506 3.2 Application of sonocatalysis in antibiotic degradation

507 To date, a great many catalysts, including single walled carbon nanotubes (SWNTs)
508 [40, 71], novel Fe-Cu layered double hydroxide/biochar nanocomposites (Fe-Cu-
509 LDH/biochar) [102], biochar-supported ZnO nanorods (ZnO-biochar) [103], ZnO
510 nanostructures loaded on nano-cellulose (ZnO/NC) [104], cerium-substituted
511 magnetite (CeO₂/Fe₃O₄) [106], and novel Z-scheme composites (mMBIP-MWCNT-
512 In₂O₃) [107], etc., have been synthesized for the sonocatalytic degradation of antibiotics.
513 Moreover, semiconductors, such as Ni powder, Raney Ni, Pd or Pt and metal oxides
514 have recently been added to carbon to accelerate the degradation of antibiotics by
515 sonication [52, 103].

516 Al-Hamadani, *et al.* have investigated the degradation of SMX via sonication at
517 1000 kHz in the presence of SWNTs [40]. The REs of SMX reached 92% and 70% at
518 pH 7 for 60 min of treatment by sonocatalysis and sonication alone, respectively, with

519 the other conditions being constant (0.18 W/L of power density, 1 L of 2.5 mg/L SMX
 520 solution), and 48% of RE was achieved by the SWNT alone [40]. Hoseini, *et al.* have
 521 investigated the degradation of TC by sonocatalysis using TiO₂ nano-particles under 35
 522 kHz US [105]. The efficacy of sonication alone in the removal of TC was negligible,
 523 but the RE increased upon the addition of TiO₂.

524 The REs of various antibiotics under catalysis alone, sonication alone and
 525 sonocatalysis have been compared and summarized in Table 3.

526 **Table 3** Summary of sonocatalytic degradation of antibiotics in water.

Antibiotics	Catalyst	F _{US} /P _E (kHz/W)	t (min)	C ₀ /V (mg/L)/mL	pH	RE _{Catal.} (%)	RE _{Sono} (%)	RE _{Sono/Catal} (%)	SF	Refs.
AMX	0.8 g/L ZnO@Fe ₃ O ₄	20/60	120	10/100	3.0	47.0	9.6	90.0	1.6	[134]
CIP	0.2 g/L TiO ₂ /Montmorillonite	35/65	120	10/100	6.0	<25.0	8.1	65.0	~2.0	[135]
MOX	1 g/L NiFeLDH/rGO	36/150	60	20/100	8.0	33.8	8.2	72.4	1.7	[118]
TC	0.5 g/L ZnO/nano-cellulose	37/256	15	50/50	7.0	28.2	12.8	87.6	2.1	[104]
TC	0.5 g/L ZnO;	37/256	15	50/50	7.0	4.4	12.8	70.0	4.1	[104]
RIF	1.5 g/L ZrO ₂ -pumice	40/300	90	20/100	5.0	~10.0	7.2	~95.3	15.5	[109]
RIF	1.5 g/L ZrO ₂ -tuff	40/300	90	20/100	5.0	~10.0	7.2	83.1	9.1	[109]
CFZ	1 g/L Fe-Cu layered double hydroxide	40/300	80	47.6/100	6.5	32.6	6.8	97.6	2.5	[102]
NOR	0.3 g/L multilayer ZnO nanoflowers	40/200	80	2.0/50	7.5	19.2	6.4	47.5	1.9	[140]
OTC	0.75 g/L Fe _{2.8} Ce _{0.2} O ₄	40/300	120	50/150	4.7	37.0	17.0	64.0	1.2	[106]
GMF	1.5 g/L Nano-ZnO- biochar	40/300	45	20/100	5.5	15.1	10.4	96.1	3.8	[103]
SDZ	0.05 mM K ₂ FeO ₄	100/800	30	5.1/100	7.0	~68.0	~52.0	~80.0	~0.7	[75]
SMR	0.05 mM K ₂ FeO ₄	100/800	30	5.1/100	7.0	~70.0	~55.0	~82.0	~0.7	[75]
SMX	0.05 mM K ₂ FeO ₄	100/800	30	5.1/100	7.0	~70.0	~56.0	~75.0	~0.6	[75]
SMX	45 mg/L SWCNs	1000/180	60	2.5/1000	7.0	48.0	70.0	92.0	1.1	[40]

527 Note: F_{US}: ultrasonic frequency; P_E: electrical power input; t: sonication time; C₀: initial antibiotic concentration;
 528 V: volume of solution; RE: removal efficiency; SF: synergy factors = $RE_{Sono/Catal}/(RE_{Sono}+RE_{Catal})$ [71, 81, 109];
 529 Refs.: references.

530 As summarized in Table 3, the sonolysis of AMX, CIP, MOX, TC, TC and CIP,
 531 etc., has been conducted by sonocatalysis. At low US frequency ranges (20-40 kHz)

532 and US power ranges (60-350 W), REs are located in the range of 2.5%-17.0% under
533 sonication alone for 15-120 min. At high US frequency (100-1000 kHz) and power
534 (180-800 W), high REs (52-70%) were observed for the removal of SDZ, SMR and
535 SMX via sonication alone after 30-60 min. The adsorption by catalysts of these
536 antibiotics was also performed at a dosage of 0.2-1.5 g/L, and the REs were observed
537 to be in the range of 3.3-70%. The degradation of antibiotics by sonication was
538 enhanced greatly by the addition of catalysts, due to the synergistic effect, and the REs
539 reached a range of 47.5-95.3%.

540 In addition, most of the catalysts can be considered composite catalysts, in which
541 both the effective component and support play important role. Khataee, *et al.* have
542 investigated the sonocatalytic degradation of RIF using ZrO₂ nanoparticles on pumice
543 (ZrO₂-pumice) and tuff (ZrO₂-tuff), which were synthesized using a modified sol-gel
544 method [109]. About 95% and 83% of 20 mg/L RIF was removed by sonication at 40
545 kHz and 300 W using 1.5 g/L of ZrO₂-pumice or ZrO₂-tuff, respectively, under natural
546 pH conditions [109].

547 A ZnO-biochar nanocomposite has exhibited better sonocatalytic performance
548 than biochar and ZnO nanorods because of its huge surface area, narrow band gap and
549 enhanced cavitation phenomenon [103]. The enhancement in the adsorption capacity
550 of sonocatalyst is caused by reducing electron and hole recombination using fluorine
551 and enhancing the oxidation potential of the valence band of ZF1 (ZnO with F/Zn molar
552 ratio of 1:1) compared to ZnO. The prepared Z-scheme KTaO₃/FeVO₄/Bi₂O₃
553 sonocatalyst displayed much higher sonocatalytic activity in the sonocatalytic
554 degradation of CEF sodium than Z-scheme KTaO₃/Bi₂O₃ [110]. This excellent
555 sonocatalytic performance is attributed to the introduction of the FeVO₄ conductive
556 channel in which the valence state changes of Fe and V provides driving force for e⁻
557 transfer, which obviously enhances the sonocatalytic activity of KTaO₃/Bi₂O₃ [110].

558 3.3 Role of effective factors

559 Similar to degradation by sonication alone, sonocatalytic efficiency is also affected
560 by various factors, including initial substrate concentration [101, 105, 140], pH value
561 [40, 141], temperature [40, 142], catalyst amount [139], US power/frequency [40, 71]
562 and the presence of additives (IO_4^- [134], H_2O_2 [71, 102, 104, 134, 135, 139], and gases
563 [103, 106]).

564 3.3.1 Effect of US frequency

565 Al-Hamadani, *et al.* have investigated the effect of US frequency on the
566 degradation of SMX via sonocatalysis with glass beads (GBs) and SWCNs [71]. The
567 removal of SMX was enhanced significantly in the presence of GBs at 28 kHz, whereas
568 it was significantly reduced at 1000 kHz as the GB particle size was similar to or larger
569 than that of the cavitation bubbles at high frequency, leading to interference between
570 the US and GB particles that resulted in a reduction in H_2O_2 production [71].
571 Additionally, the presence of SWNTs was effective under low and high frequencies in
572 both the sonochemical degradation mechanism and adsorption mechanism because the
573 dispersed SWNT particles acted as additional nuclei for the pyrolysis of water
574 molecules and the formation of more $\cdot\text{OH}$. Moreover, the dispersion of SWNTs, due to
575 sonication, enhanced the adsorption process by providing more adsorption sites, leading
576 to increased adsorption capacity. However, maximum SMX removal was achieved at
577 both frequencies when GBs and SWNTs were combined, as a result of enhanced
578 sonochemical degradation via $\cdot\text{OH}$ formation and the adsorption process resulting from
579 SWNT dispersion [71].

580 3.3.2 Effect of pH value

581 Hoseini, *et al.* have investigated the effect of pH on TC degradation using
582 sonocatalysis with TiO_2 nanoparticles, and it was found that an increase in pH
583 attenuated TC degradation [105]. The relatively high *RE* values of sonocatalytic
584 degradation for PG using MgO and SMX, with SWCNs nanoparticles, were also

585 obtained under acidic conditions at pH 3.0 and pH 3.5, respectively [40, 141]. Seid-
586 Mohammadi, *et al.* have found that pH value clearly affects the removal of CPX in
587 sono/H₂O₂/NiO hybrid process, and that process efficiency was reduced at pH 9, with
588 pH 3 giving the highest RE (93.8%) [74].

589 3.3.3 Effect of temperature

590 The influence of increased temperature on the degradation of antibiotics is exerted
591 via: i) the cavitation intensity; ii) changes in the physicochemical properties of the
592 antibiotics; and iii) the type of cavities formed [40]. An increased k_1 was observed for
593 SMX with increased temperature (15-55 °C) in a sono/SWNT system. The low apparent
594 activation energy values (7.28 kJ/mol) for SMX indicate that the degradation of SMX
595 is influenced by diffusion. This is presumably because the degradation rate reflects the
596 fact that the SMX molecule in the bulk solution moves to the gas-liquid interface region,
597 where temperatures and $\cdot\text{OH}$ concentrations are high [40]. The removal rate for AZI
598 increased with increasing temperature (20-40°C) in the sono/ZnO system, especially
599 from 20 to 40 °C. However, a steady decrease in removal rate was observed at 40 to
600 60°C [142]. The removal of TYL was enhanced by increased temperature (10-40 °C).
601 The k_1 values of the degradation of TYL were 0.0107, 0.0126, 0.0148 and 0.0165 min⁻¹
602 at 10, 20, 30 and 40 °C, respectively [142].

603 3.3.4 Effect of initial concentration

604 Hoseini, *et al.* have investigated the effect of initial TC concentration on its
605 degradation by sonocatalysis using TiO₂ nanoparticles, and it was found that an increase
606 in initial TC concentration attenuated TC degradation [105]. Similarly, the *RE* values
607 of NOR and AMP also decreased with increased initial concentrations [101, 107].

608 3.3.5 Effect of catalyst amount

609 Gao, *et al.* have found that increases in both the MnSO₄ concentration of the wet
610 impregnation solution and the catalyst dosage enhanced the sonocatalytic degradation
611 of TC with Mn-modified diatomite [139]. NOR degradation rate also increased with an

612 increase in ZnO dosage [140].

613 3.3.6 Effect of additives

614 Adding noble gas Ar, CCl₄, or H₂O₂ to the sonocatalytic system can often enhance
615 RE, while the presence of inorganic and organic scavengers suppresses the performance
616 of the sonocatalytic removal of antibiotics [71, 102, 135]. Furthermore, the degradation
617 mechanisms, namely the interactions between $\cdot\text{OH}$ and the antibiotics, can be
618 demonstrated [71]. For example, the presence of ethanol suppressed SSZ degradation
619 due to the quenching of $\cdot\text{OH}$, while the addition of K₂S₂O₈ and H₂O₂ increased the RE
620 due to the formation of $\text{SO}_4^{\cdot-}$ and extra $\cdot\text{OH}$, respectively [52, 54, 73, 74, 97, 111, 126,
621 128].

622 Seid-Mohammadi, *et al.* have investigated the removal of CFX from aqueous
623 solutions using sono/H₂O₂/NiO process at 40 kHz. Under optimum conditions (pH 3,
624 reaction time 90 min, 40 mg/L CEX, 7.5 mg/L NiO and 30 mL/L (30%, w/w) H₂O₂),
625 the REs of CEX, COD and TOC were 93.9, 72.5 and 54.6%, respectively. The pH value
626 is the most critical factor [74]. Yazdani, *et al.* have investigated the sonocatalytic
627 degradation of AZI with ZnO, finding that H₂O₂ addition significantly increased the RE
628 of AZI from 90.6% to 98.4% [142]. H₂O₂ addition also improved the sonocatalytic REs
629 of RIF [109]. However, Hoseini, *et al.* have reported that the addition of H₂O₂
630 attenuated the sonocatalytic degradation of TC with TiO₂ nano-particles [105].

631 In addition, Dehghan, *et al.* have investigated the effect of adding IO₄⁻ on the
632 sonocatalytic degradation of AMX with a ZnO@Fe₃O₄ magnetic nanocomposite. It was
633 observed that the degradation rate was accelerated in the presence of IO₄⁻, showing the
634 greater oxidation potential compared to the other oxidant agents [134]. Moreover,
635 peroxydisulfate (S₂O₈²⁻) has been extensively investigated as a means to enhance the
636 sonocatalytic degradation of antibiotics [109, 140], which is discussed particularly in
637 chapter 5.

638 Besides, Khataee, *et al.* have investigated the sonocatalytic degradation of OTC

639 with CeO₂/Fe₃O₄, and it was found that the addition of O₂ and Ar improved the RE of
640 OTC by up to 78 % and 76 %, respectively [106]. The enhancement of adding gases on
641 RE is attributed to an increase in the number of nucleation sites in aqueous media, and
642 enhancements in the pressure and temperature of collapsing cavitation bubbles [103].

643 On the other hand, inorganic and organic scavenging additives reduced the REs of
644 antibiotics in sonocatalytic systems, indicating that [•]OH-mediation oxidation is
645 responsible for the degradation of antibiotics, including SMX [71], CFZ [102], AMX
646 [134], CIP [135], and TC [104, 139]. For example, the RE of TC decreased by over 25%
647 in the presence of tert-butanol [104]. The presence of isopropanol, KBr and NaN₃
648 sharply quenched a series of reactive oxygen species [139]. Of these water matrix
649 components, chloride and sulfate anions had the highest and lowest inhibiting effects
650 on the RE of AMX, respectively [134].

651 3.3.7 Reusability of catalysts

652 From the perspective of cost reduction and environmental protection, the
653 recyclability of catalysts is essential to promoting sonocatalytic processes. In many
654 cases, catalysts exhibited higher stability for the sonocatalytic degradation of antibiotics
655 due to the strong ultrasonic surface cleaning [108]. Under sonication, catalysts can
656 maintain their catalytic activity for antibiotic removal for 4-5 consecutive runs [73]. For
657 example, the RE of AMP was reduced by only 5% even after Zn(OH)F was reused for
658 four experiments [101]. Similarly, the REs of AMX with ZnO@Fe₃O₄ and CFZ with
659 Fe-Cu-LDH/biochar nanocomposite dropped by only 5-9 % after five successive runs
660 [102, 134]. Er³⁺: Y₃Al₅O₁₂@Ni (Fe_{0.05}Ga_{0.95})₂O₄-Au-BiVO₄ coated composite also
661 exhibited excellent recyclability and sustainability for the sonocatalytic degradation of
662 SA for five repetitive cycles without any apparent deactivation [72].

663 Overall, sonocatalysis can significantly increase the RE of antibiotics compared
664 with catalysis or sonication alone, but this process is still highly energy demanding and
665 limited to laboratory-scale investigation at present. Thus, additional chemicals are

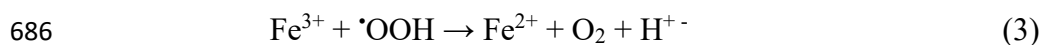
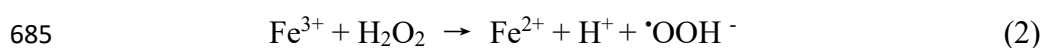
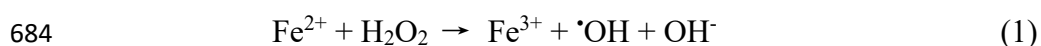
666 required in many cases to improve the RE. To overcome the drawbacks and reduce the
667 operating costs, a combination of sonication and other AOPs has been proposed to
668 exploit the benefits of the synergistic effects of the AOPs [37].

669 **4 Degradation of antibiotics by sono/Fenton and** 670 **sono/Fenton-like processes**

671 4.1 Mechanisms of sono/Fenton processes

672 Fenton oxidation is one of the AOP techniques that has been most widely applied
673 for antibiotic removal [17, 32-35]. So far, the Fenton processes that have been applied
674 to the degradation of antibiotics can be divided into: classic homogeneous Fenton
675 processes; and heterogeneous Fenton processes or Fenton-like processes. The classic
676 Fenton reaction usually occurs in acidic homogeneous systems where Fe^{2+} , or other
677 metal ions (Cu^{2+} , Zn^{2+} , etc.), and H_2O_2 exist simultaneously. By contrast, Fenton-like
678 reactions generally occur in acidic heterogeneous systems where solid catalysts (Fe^0 ,
679 Fe_3O_4 , etc.) and H_2O_2 exist simultaneously.

680 As a green oxidant, H_2O_2 is frequently used to form ROS for organic removal [43].
681 In classic Fenton processes, Fenton's reagent is a mixture of H_2O_2 and ferrous iron [48],
682 where the dissociation of the oxidant and the formation of highly reactive $\cdot\text{OH}$ are
683 included, as shown in Eq. (1) - (3) [47, 48].



687 In sono/Fenton processes, the radical reactions near the hotspots and/or in the bulk
688 liquid dominate the degradation of antibiotics [96]. On the one hand, sonication can
689 improve mass transfer, thus enhancing the generation of $\cdot\text{OH}$ and reducing the
690 consumption of chemicals [47, 48]. On the other, adding the right amount of Fe^{2+} (e.g.,

691 1.0 mM) can also enhance $\cdot\text{OH}$ production via the reactions between $\text{Fe}^{2+}/\text{Fe}^{3+}$ and H_2O_2 ,
692 including H_2O_2 that is formed *in situ* [17, 30, 34, 41, 43, 46, 69, 95, 96, 97, 139].

693 Unfortunately, excessive H_2O_2 and Fe^{2+} negatively influence the degradation of
694 antibiotics [30, 34, 96], since large doses of Fe^{2+} and H_2O_2 can act as scavengers for
695 $\cdot\text{OH}$ in aqueous matrices [34, 41, 95, 96]. In addition, the pH value of solutions
696 significantly affects the degradation of antibiotics [111]. For $\text{pH} > 4$, the total
697 concentration of Fe^{2+} and Fe^{3+} decreases considerably as their complexes and
698 hydroxides are formed in solution. At $\text{pH} < 2$, Fe^{2+} and Fe^{3+} exists as $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and
699 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ respectively, and the regeneration of Fe^{2+} in the form of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ from
700 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is slow. Meanwhile, H_2O_2 forms oxonium ions (H_3O_2^+). These are more
701 stable than H_2O_2 and their reactivity with ferrous ions decreases. In addition, the
702 scavenging effect of $\cdot\text{OH}$ by H^+ is enhanced at $\text{pH} < 2$ [111]. Therefore, the optimal pH
703 range for classic Fenton reactions is 2-4 [21, 22, 41, 111]. Also, the pH value affects the
704 chemical structures of the antibiotics, thus influencing REs in sono-Fenton process [96,
705 99].

706 4.2 Application of sono/Fenton processes on antibiotic degradation

707 Wang, *et al.* have reported the degradation of 50 mg/L TC via sonication at 20 kHz
708 and 100 W US in 1 L solution at pH 6, in the presence of 0.2 mM Fe^{2+} and 2.0 mM
709 H_2O_2 [34]. Consequently, an RE of 91.3% was achieved in 60 min using this
710 sono/Fenton process, which is higher than the sum of those obtained under Fenton
711 (70.2%) and sonication alone (6.7%). Meanwhile, mineralization reached 45.8% in the
712 sono/Fenton process, resulting in the toxicity of the TC solution being significantly
713 decreased [34].

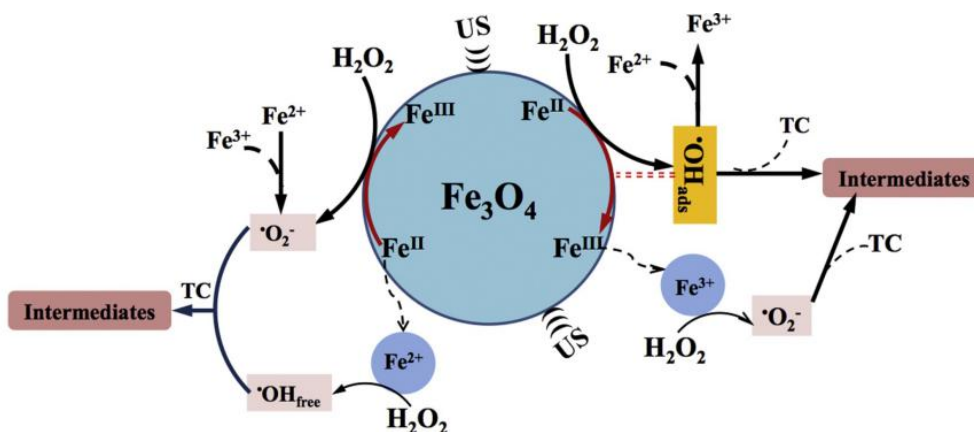
714 Labrada, *et al.* have studied CIP degradation in wastewater using a homogeneous
715 sono/Fenton process at high frequency [32]. 100 mg/L CIP was sonicated with 580 kHz
716 and 30.6 W US in a 250 mL solution at pH 3, in the presence of 2.4 mM Fe^{2+} and 14.2
717 mM H_2O_2 . An RE of about 98.4% was achieved using this sono/Fenton process in 15

718 min. However, the RE obtained by sono/Fenton is lower than the sum of those obtained
719 under Fenton and sonication alone (96.4% and 9.3%). However, the mineralization
720 reached 60% using the sono/Fenton process after 60 min [32]. Ammar *et al.* have
721 investigated the degradation of 500 mg/L MTZ by sonication at 20 kHz US in a 200
722 mL solution at pH 3.0 in the presence of 3 mM Fe²⁺ and 60 mM H₂O₂ [113]. The results
723 indicate that 98% of MTZ was removed using the sono/Fenton process in 180 min at
724 30 °C, which is higher than those obtained by sonication alone (42%) and Fenton
725 process alone (90.0%), but is lower than sum of REs of the two individual processes
726 [113]. At 40 kHz, 261.2 mg/L FLU was sonicated with 120 W US in a 200 mL solution
727 at pH 4.0 in the presence of 4 mM Fe²⁺ and 20 mM H₂O₂ [111] As a result, an RE of
728 93% was achieved using the sono/Fenton process in 120 min at 60 °C, which is
729 obviously higher than that (73%) obtained by the Fenton process alone [111]

730 Overall, this suggests that the synergistic effects of sonication and the Fenton
731 reaction for antibiotic degradation is dependent on the physicochemical properties of
732 the antibiotics and Fenton reagents rather than the character of the US used.

733 4.3 Mechanisms of sono/Fenton-like processes

734 The Fenton process requires a large amount of Fe²⁺ and acidic conditions, which
735 requires neutralization with alkaline, resulting in large-scale sedimentation and high
736 costs. With the development of Fenton-like technologies, the drawbacks of the
737 conventional Fenton process have been overcome to some extent [44]. Fe⁰, Fe₃O₄
738 particles and their nanoparticles are important catalysts to promote the decomposition
739 of H₂O₂ for the formation of •OH [21, 22, 33, 43, 44]. Unfortunately, the solid catalysts
740 may be poisoned during Fenton reactions, nano-catalysts particles can aggregate and
741 solid-catalyst passivation can occur, thus decreasing the degradation rate and limiting
742 potential applications [21, 22, 33, 119]. Therefore, sonication has been applied in the
743 Fenton-like process to maintain the activity of catalysts and improve antibiotic removal.
744 The mechanism of sono/Fenton-like processes is shown in Figure 3.

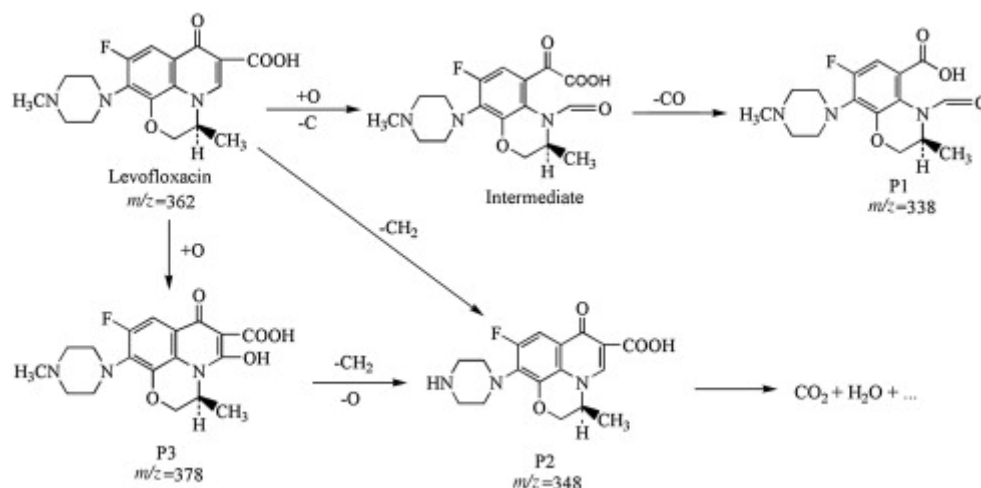


745

746 **Figure 3** Mechanism schematic of sono/Fenton-like processes. Reprinted from ref. [33] Copyright (2016), with
 747 permission from Elsevier.

748 As shown in **Figure 3**, solid-liquid interfacial iron corrosion, bulk homogenous
 749 oxygen activation and Fenton reactions are the main reaction pathways in sono/Fenton
 750 processes, during which sonication plays both mechanical and chemical roles [35]. The
 751 antibiotics and intermediates adsorbed onto the Fe_3O_4 surface are oxidized
 752 preferentially [33]. $\cdot\text{OH}$, $\cdot\text{O}_2^-$ and H_2O_2 , formed *in-situ* on the catalyst surface, have
 753 been identified as the dominant reactive species in Fenton-like processes [21, 22, 33,
 754 35, 44].

755 **Figure S2** exhibits the LC/MS analysis of the intermediate formation during the
 756 degradation of LEV in a sono/ $\text{H}_2\text{O}_2/\text{Fe}_3\text{O}_4$ (magnetic nanoparticles) process [43]. The
 757 degradation pathway of LEV is shown in **Scheme 2**. The formation of isatin and
 758 anthranilic acid analogues is attributed to the oxidation of LEV by $\cdot\text{OH}$. The
 759 demethylation of the piperazinyl ring and the degradation at the oxazinyl group result
 760 in the generation of the other two intermediates [43]. Unfortunately, this study does not
 761 provide the mineralization data of LEV and toxicity variation of LEV solutions by the
 762 treatment.



763

764 *Scheme 2* A tentative partial degradation pathway of LEV in a sono/H₂O₂/Fe₃O₄ (magnetic nanoparticles)
 765 system. Reprinted from ref. [43] Copyright (2015), with permission from Elsevier.

766 4.4 Application of sono/Fenton-like processes on antibiotic 767 degradation

768 So far, sono/Fenton-like processes have been used to remove some antibiotics,
 769 such as LEV, TC, NOR, CLA, RXM, TNZ, CLM, etc., and Fe₃O₄, nano-Fe⁰, ZnS
 770 quantum dots/SnO₂, nano-Cu⁰ and micro-Cu⁰, etc. have been used as catalysts. The
 771 concentrations of H₂O₂ addition cover a wide range, 5-1000 mM, and degradations have
 772 been performed in the pH range of 3.0-7.1. In sono/Fenton-like systems, the three
 773 factors, sonication, Fenton catalyst and H₂O₂, act together to cause a strong synergistic
 774 effect for the degradation of antibiotics (such as MNZ [44]). The application of
 775 sono/Fenton-like processes on the degradation of antibiotics has been summarized in
 776 [Table 4](#).

777 *Table 4* Summary of antibiotic degradation by sono/Fenton-like processes.

Antibiotics	Fenton reagents	F _{US} /P _E (kHz/W)	t (min)	C ₀ /V (mg/L)/mL	pH	RE	RE	RE	SF	Refs.
						Fenton-like (%)	Sono (%)	Sono/Fenton-like (%)		
LEV	1 g/L Fe ₃ O ₄ , 5 mM H ₂ O ₂	20/195	150	20/100	7.1	71.5	1.9	99.0	1.35	[43]
TC	1 g/L Fe ₃ O ₄ , 150 mM H ₂ O ₂	20/80	60	100/200	3.7	72.2	-	93.6	-	[33]

CLA	0.3 g/L ZnS quantum dots/SnO ₂ , 6 mM H ₂ O ₂	20/75	60	10/100	3.0	31.4	~8.0	61.2	~1.56	[119]
RXM	0.3 g/L ZnS quantum dots/SnO ₂ , 6 mM H ₂ O ₂	20/75	60	10/100	3.0	36.4	~12.0	65.5	~1.35	[119]
NOR	0.25 g/L nano-Cu ⁰ or micro-Cu ⁰ , 20 mM H ₂ O ₂	20/240	30	5/200	7.0	46.7	<5.0	91.5	>1.77	[20]
CEX	7.5 mg/L NiO, 30 mL/L H ₂ O ₂	40/-	90	40/<500	3.0	-	-	93.0	-	[74]
CLM	0.2 g/L Fe ⁰ , 1 M H ₂ O ₂	130/500	150	45/-	3.0	~40.0	~30.0	95.0	~1.36	[21]
TNZ	0.2 g/L Fe ⁰ , 1 M H ₂ O ₂	130/500	150	45/-	3.0	~20.0	-	93.0	-	[22]

778 Note: FUS: ultrasonic frequency; P_E: electrical power input; t: sonication time; C₀: initial antibiotic concentration; V:
779 volume of solution; RE: removal efficiency; SF: synergy factors = $RE_{sono}/Fenton-like/(RE_{sono}+RE_{Fenton-like})$ [71, 81,
780 109]; Refs.: references.

781 As shown in Table 4, the REs of most antibiotics are over 91.5% in 30-150 min,
782 except for the degradation of CLA and RXM in the system with 0.3 g/L ZnS/quantum
783 dots/SnO₂ and 6 mM H₂O₂, and the REs are obviously higher than the sum of those
784 obtained using Fenton-like processes and sonication alone in most cases. In addition,
785 the synergistic degradation of NOR in a heterogeneous sono/Fenton-like system with
786 Fe⁰/tetrphosphate has been reported [35]. 400 mL of a 10 mg/L NOR solution was
787 sonicated at pH 7 with 1 g/L Fe⁰ and 0.3 mM tetrphosphate. As a result, an RE of 90%
788 was achieved in 60 min using this sono/Fenton-like process, which is obviously higher
789 than the sum of those obtained using the Fenton-like process and sonication alone (50%
790 and <5%) [35].

791 Ma, *et al.* have investigated the degradation of NOR via the ultrasound-enhanced
792 nanosized zero-valent copper (Cu⁰) activation of hydrogen [20]. Compared with the
793 silent degradation system, significantly enhanced NOR removal was obtained in the
794 sono/Fenton-like process. The Cu⁺ released during Cu⁰ dissolution was the predominant

795 copper species that activated H₂O₂, yielding $\cdot\text{OH}$ in the sono/Cu⁰/H₂O₂ system.
796 According to radical quenching experiments and electron paramagnetic resonance
797 technique, free $\cdot\text{OH}$ in solution was verified as the primary reactive species, and
798 superoxide anion radicals ($\cdot\text{O}_2^-$) were regarded as the mediator for copper cycling, via
799 the reduction of Cu²⁺ to Cu⁺ [20].

800 Importantly, the toxicity of the solution increased during the first 60 min and then
801 decreased with treatment time for the degradation of TC in a sono/Fenton-like process
802 with a Fe₃O₄ catalyst [33]. In general, an increase in the biodegradability of wastewater
803 has been demonstrated after antibiotic degradation by sono/Fenton and sono/Fenton-
804 like processes [32], indicating that these processes are suitable for the treatment of
805 wastewater that contains highly toxic and bio-recalcitrant compounds [113].

806 4.5 Role of effective factors

807 The factors influencing the RE of antibiotics using sono/Fenton-like processes
808 includes the initial concentration of antibiotics, US power density, reaction temperature
809 [33], etc. In general, lower antibiotic concentrations, higher temperature (up to 60 °C),
810 higher US frequency and power are favourable for RE [21, 22]. The effects of the
811 critical factors, dose of catalysts, the concentration of H₂O₂, and the pH value of the
812 solution [21, 35, 43, 44, 74], are discussed below.

813 4.5.1 Effect of Fenton-Reagent dose

814 In general, a larger amount of catalyst increases the sites for H₂O₂ decomposition
815 and the production of more ROS, resulting in higher antibiotic RE [21]. Gholami, *et al.*
816 and Rahmani, *et al.* have investigated the effects of catalyst amount on the degradation
817 of CLM and TNZ using sono/Fenton-like processes with nanoscale Fe⁰, respectively
818 [21, 22]. The REs increased with increasing Fe⁰ nanoparticle dosage, and the highest
819 REs (93%-95%) were observed in a 130 kHz sonochemical system with 0.2 g/L Fe⁰
820 nanoparticles and 1 mM H₂O₂ [21, 22]. It was speculated that the increasing nano-Fe⁰
821 dosage results in an increase in total surface area and therefore increased adsorption

822 onto active sites. Over 0.2 g/L Fe⁰ nanoparticles, the RE values reached a plateau due
823 to the agglomeration of Fe⁰ nanoparticles and the scavenging of •OH in undesirable
824 reactions [21, 22].

825 Wei, *et al.* have reported the effect of Fe₃O₄ magnetic-nanoparticle amount on the
826 removal of LEV in a sono/Fenton-like process [43]. As the amount of Fe₃O₄ magnetic
827 nanoparticles increased from 0 to 1.0 g/L, the k_I value increased from 4.69×10^{-3} to
828 $21.3 \times 10^{-3} \text{ min}^{-1}$ in the 20 kHz sonication system. The higher catalyst dose favoured
829 LEV removal due to higher number of nucleation sites for the generation of •OH [43].

830 4.5.2 Effect of H₂O₂ concentration

831 Without H₂O₂ present initially, the RE of LEV was approximately 30%, which is
832 mostly attributed to the adsorption of LEV onto the catalyst. As H₂O₂ concentration
833 increased from 1.5 to 15.0 mM, the RE of LEV increased until it reached a peak. The
834 results are mainly related to the adsorption amount of H₂O₂ onto the catalyst [43].
835 During the degradation of CLM and TNZ in a sono/Fenton-like process with nanoscale
836 Fe⁰, the RE increased with increasing H₂O₂ concentration due to the increase of •OH
837 formed. The system had the highest efficiency with 1 mM H₂O₂ [21, 22].

838 However, excessive amounts of H₂O₂ adversely affected the REs [82], as the
839 excess H₂O₂ consumes the •OH formed *in situ* and inhibits iron corrosion. In the
840 chemical reaction of •OH with the nanoparticle, hydroxyl ions are produced, which are
841 less active than •OH and reduced system efficiency [21, 22].

842 4.5.3 Effect of pH value

843 In general, the pH value can affect the surface-charge properties, adsorption
844 behaviour and electron-transfer ability of the catalyst, which all affect catalytic
845 degradation. Thus, it is necessary to study the effect of the pH value on RE and
846 degradation kinetics in a wide range of pH conditions [44]. The acidic condition (pH 2-
847 4) has been demonstrated to be suitable for the Fenton reaction. Gholami, *et al.* and
848 Rahmani, *et al.* have investigated the effect of pH on the degradation of CLM and TNZ,

849 using a sono/Fenton-like process with nanoscale Fe⁰ [21, 22]. Over the pH range of 3-
850 9, the system had the highest efficiency under acidic conditions (pH 3), as Fe⁰ corrosion
851 and the reactivity of [•]OH were greatly influenced by H⁺ concentration [21, 22].

852 Guo, *et al.* have reported the effect of pH value on the degradation of LEV in a
853 sono/Fenton-like process with Fe₃O₄ magnetic nanoparticles [43]. Over the pH range
854 of 4-9, the *k₁* values of LEV degradation were calculated to be 2.13 × 10⁻², 2.85 × 10⁻²
855 and 1.26 × 10⁻² min⁻¹ at pH 4, pH 8 and pH 9, respectively. It seems that pH 8 is the
856 optimal condition. LEV exists as different species depending on pH value. At 5.7 ≤ pH ≤
857 7.9, LEV mainly exists in its zwitterion form in solution, while at pH > 7.9 and <5.7,
858 LEV exists in its cationic or anionic form in solution, respectively. Therefore, the
859 hydrophilicity and solubility of LEV at different pH values play the critical role in its
860 oxidative degradation by [•]OH. In addition, pH value affects not only LEV adsorption
861 onto the catalyst, but also the heterogeneous Fenton-like reaction on the catalyst surface.
862 The enhanced degradation of LEV over the wide range 4.0 ≤ pH ≤ 8.0 occurred due to
863 nucleation sites on the catalyst for the formation of cavities. At pH 9.0, the decrease of
864 RE was partly due to the decrease in H₂O₂ adsorption onto the catalyst, which was
865 covered with Fe(OH)₆³⁻, and the self-decomposition of H₂O₂, resulting in the low
866 availability of H₂O₂ and a low yield of [•]OH [43].

867 20 mg/L MNZ has been degraded with 157.4 mM H₂O₂ and 500 mg/L nano-Fe₃O₄
868 at 30 °C within a wide pH range, from 3 to 9, and the REs were considerably enhanced
869 by sonication [44]. The RE reached its highest value (98%) after 5 h at pH 3, and the *k₁*
870 was 1.4 × 10⁻² min⁻¹. *k₁* decreased to 1.25 × 10⁻², 7 × 10⁻³, 6 × 10⁻³ and 3.1 × 10⁻³ min⁻¹ at
871 pH 5.00, 5.79, 7.00 and 9.00, respectively. This dependence on pH is similar to that of
872 the traditional Fenton reaction, and was attribute to a sharp decrease in the
873 concentration of Fe in the oxidation state Fe²⁺ with increasing pH value, thus hindering
874 the activity of the catalyst [44].

875 4.5.4 Effect of temperature

876 The k_1 of TC removal (0.04-0.12 min⁻¹) was enhanced by increased temperature
877 (22-50 °C) in the sono/Fe₃O₄/H₂O₂ system. The chemical reaction was the dominant
878 step during the degradation of TC, and the activation energy was 33.8 kJ/mol. The RE
879 of TC was almost the same (> 90%) for all temperatures in 60 min, which indicates that
880 a sufficient amount of [•]OH was generated by the sono/Fe₃O₄/H₂O₂ process [33].

881 4.5.5 Stability of catalysts

882 The stability and recyclability of catalysts are important to the promotion of the
883 sono/Fenton-like process [44]. Fortunately, the stability of the catalyst is significantly
884 improved with sonication [33]. The reusability of Fe₃O₄ was evaluated 3 times under
885 identical oxidation conditions, and the RE decreased slightly after 3 cycles. Moreover,
886 these values were still much higher than those obtained in the simple catalytic process
887 [33].

888 Fe⁰ particles can be reused in the relative long-term and not lead to high
889 concentration levels of dissolved iron in the treated effluents (<0.6 mg/L) [35]. A
890 consecutive triplicate-repeated sono/Fe⁰/tetrapolyphosphate experiment was conducted
891 to examine the reusability of Fe⁰ particles for NOR degradation. The k_1 for the three
892 repeated runs were 0.039, 0.032 and 0.029 min⁻¹, respectively. This indicates that
893 sonication is able to effectively clean and refresh the surface of used Fe⁰ particles over
894 a long-term treatment schedule. The Sono/Fe⁰/tetrapolyphosphate system only led to
895 acceptable levels of dissolved iron in the effluents even after repeated runs.

896 **5 Degradation of antibiotics by sonication with** 897 **peroxydisulfate (PS) and peroxymonosulfate (PMS)**

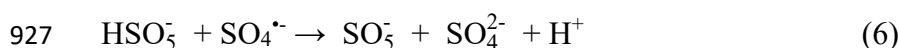
898 5.1 Mechanisms of sono/PS and sono/PMS processes

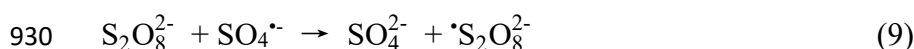
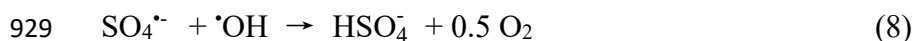
899 Sulfate radical-based advanced oxidation processes (SR-AOP) are considered to
900 be a promising technology for wastewater treatment [143]. In this technique, sulfate

901 radicals ($\text{SO}_4^{\cdot-}$, SR) can be formed by the activation of persulfate salts (PS, SO_5^{2-} or
 902 $\text{S}_2\text{O}_8^{2-}$) or peroxymonosulfate (PMS, HSO_5^-) via multiple approaches, including heat,
 903 UV, sonication, alkaline pH and transition metal ions [21, 119, 144-146]. The triple salt
 904 $\text{KHSO}_5 \cdot 0.5 \text{KHSO}_4 \cdot 0.5 \text{K}_2\text{SO}_4$ (Oxone) is a form with higher stability [147]. SR-AOP
 905 appears to be more advantageous, efficient and powerful than $\cdot\text{OH}$ -based AOPs [143,
 906 145], as SR appears to be more stable than $\cdot\text{OH}$ in reacting with target antibiotics and
 907 is able to oxidize antibiotics efficiently over a wide pH range of 2-8 [148, 149].

908 In general, $\cdot\text{OH}$ is a powerful oxidant with a redox potential of 1.89-2.8 V [150,
 909 151]. In comparison, SR has an equal or even higher redox potential (1.81–3.1 V),
 910 depending on activation method [113, 146, 150, 152]. SR is generated from PS, which
 911 has a higher standard redox potential (2.01 V) than PMS (1.81 V) [145, 150]. Therefore,
 912 the RE order of acid orange 7 by heat activation is $\text{PS} \gg \text{PMS} > \text{H}_2\text{O}_2$, but by UV
 913 activation, the RE order of acid orange 7 becomes $\text{PS} > \text{H}_2\text{O}_2 > \text{PMS}$ [153, 154]. Under
 914 sonication activation, the REs of 25 mg/L furfural with PS or PMS reached 95.3% or
 915 58.4%, respectively [155]. However, the REs of SMX by UV activation were observed
 916 to follow a different order: $\text{PMS} > \text{PS} > \text{H}_2\text{O}_2$ [156]. Even with a TiO_2 catalyst, k_I by
 917 UV activation still shows the same order: $\text{PMS} > \text{PS} > \text{H}_2\text{O}_2$ [157]. A similar order was
 918 observed during the degradation of rhodamine B by $\text{Fe}^{2+}/\text{PMS}$ or PS/MoS_2 [158].
 919 Therefore, the oxidation potential of PS and PMS was affected by the whole oxidation
 920 system rather than by one factor.

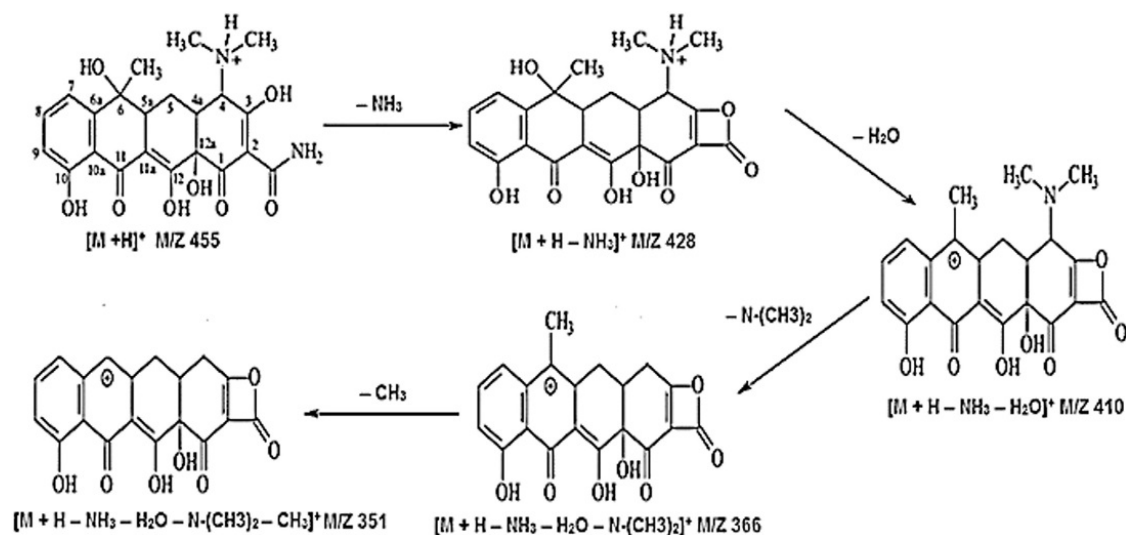
921 Sonication not only offers a new option for the removal of recalcitrant organic
 922 pollutants, but also promotes SR production from the reactions of PS and PMS with
 923 $\cdot\text{OH}$ that is formed *in situ* during sonication, as shown in Eqs (4)-(9) [31, 34, 104, 131,
 924 150, 159, 160]:





931 Therefore, the SR and $\bullet OH$ that are formed from the activation of PS or PMS under
 932 sonication have been considered the origins of antibiotic degradation [82, 131].
 933 Subsequently, the cleavage of chemical bonds of antibiotic molecules, such as the S–N,
 934 S–C and N–C of SMZ [82], or the removal of the N-methyl, hydroxyl and amino groups
 935 of TC occurs via oxidation with SR and $\bullet OH$ [131].

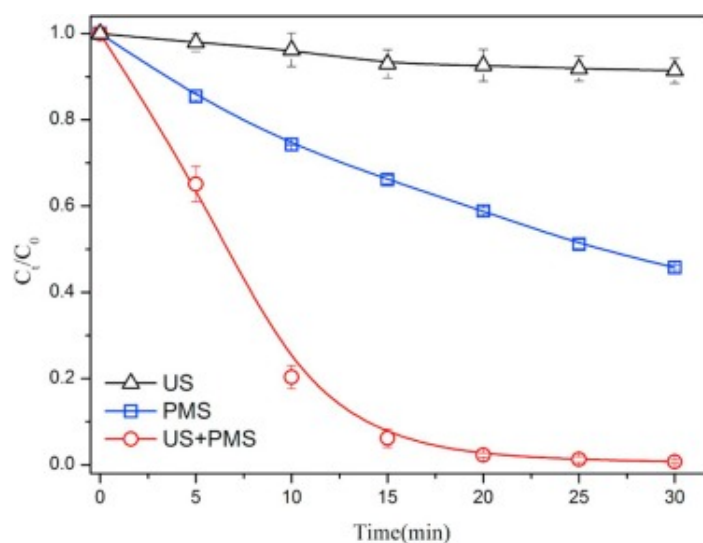
936 Figure S3 shows the LC-MS of the intermediates during the degradation of TC
 937 using the sono/ $S_2O_8^{2-}$ process [160]. Three new peaks, observed after 120 min of
 938 reaction, were related to the formation of polar by-products. The protonated TC
 939 molecular ion $[M+H]^+$ and the 4 main by-products generated are shown in the
 940 degradation pathway of TC via the sono/ $S_2O_8^{2-}$ process (Scheme 3) [160]. After 120
 941 min sonication of 100 mL of 0.052 mM TC with 4 mM PS at pH 10, 35 kHz and 500
 942 W, nearly 96.5% of TC, 74% of COD and 61.2% of TOC were removed, indicating that
 943 the mineralization of TC was achieved to a certain degree, but incompletely.



945 **Scheme 3.** Proposed degradation pathway for the TC antibiotic in a sono/ $S_2O_8^{2-}$ process. Reprinted from ref.
 946 [160] Copyright (2017), with permission from Elsevier.

947 **5.2 Application of Sono/PS or PMS on antibiotic degradation**

948 Safari, *et al.* have reported that 95.0% of 30 mg/L TC was removed by sonication
 949 in the presence of PS in 100 mL of a TC solution under 35 kHz and 500 W at pH 10.0
 950 after 120 min. Meanwhile, the REs of COD and TOC reached 72.8% and 59.7%,
 951 respectively [131]. Yin, *et al.* have reported that the REs of 50 mg/L SMZ reached 8.6%,
 952 54.3% and 99.6% using sonication alone, PMS alone and Sono/PMS, respectively,
 953 under 20 kHz and 600 W at pH 7.5 for 30 min (Figure 4) [82].



954

955 **Figure 4** SMT degradation by different processes: US, PMS and US/PMS systems. Reprinted from ref. [82]

956

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957 So far, the sonochemical degradation of antibiotics, such as CAP, CIP, TC, SMZ,
 958 SDZ, etc., with PS in aqueous solution have been studied. 5-100 mg/L of antibiotics
 959 has been sonicated for 30-240 min with 1-200 mM PS or Oxone in 50-1000 mL of
 960 aqueous solution. The application of sonication for the degradation of antibiotics with
 961 PS or Oxone has been summarized in Table 5.

962

Table 5 Summary of the degradation of antibiotics by sonication with PS or Oxone.

Antibiotics	C _{PS} (mM)	F _{US} /P _E (kHz/W)	t (min)	C ₀ /V (mg/L)/mL	pH	RE _{PS} (%)	RE _{Sono} (%)	RE _{Sono/PS} (%)	SF	Refs.
TC	2	20/100	60	50/1000	3.0	-	6.7	91.3	-	[34]
TC	200	20/80	90	100/200	3.7	~20.0	~0	51.5	~2.60	[149]
TC	5	35/500	120	23/100	10.0	57.3	26.9	88.5	1.05	[160]

CAP	4	22/200	240	20/50	1.0	<5.0	37.3	62.4	>1.47	[145]
CIP	4.4	40/350	60	50/<1000	4.5	7.5	2.5	18.5	1.85	[19]
SDZ	1.84	20/-	60	-/400	3.0– 7.0	-	9.7	13.7	-	[76]
SMZ	1	40/60	60	5/500	7.0	-	1.6	7.2	-	[161]
SMZ	Oxone 2	20/600	30	50/<100	7.5	54.3	8.6	99.6	1.58	[82]

963 Note: C_{PS}: PS concentration; F_{US}: ultrasonic frequency; P_E: electrical power input; C₀: initial concentration of
964 antibiotic solution; V: the volume of antibiotic solution; RE: removal efficiency; SF: synergy factors =
965 $RE_{sono/PS}/(RE_{sono}+RE_{PS})$ [71, 81, 109]; Refs.: references.

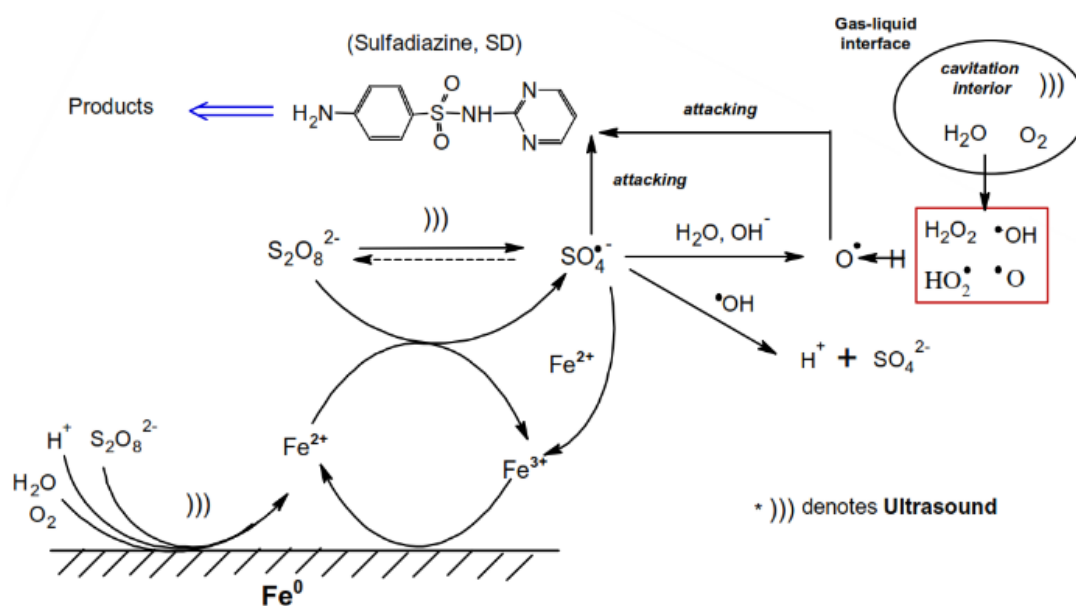
966 As summarized in Table 5, the dosage of PS or Oxone was in the range of 2-5 mM.
967 Combined sonication with PS or Oxone exhibits higher degradation of antibiotics than
968 sonication alone or oxidation alone under the given conditions. Meanwhile,
969 mineralization can be achieved to a certain degree [34, 162]. For example, the RE of
970 TC reached 96.5% using sono/PS, and 74% of COD removal and 61.2% of TOC
971 removal were achieved [160]. However, some antibiotics, such as CAP, are difficult to
972 degraded using such combined process, even after long treatment times (240 min).

973 5.3 Mechanism of sono/PS and sono/PMS in the presence of 974 catalysts

975 To effectively remove antibiotics from aqueous solutions using sono/PS, PMS or
976 Oxone, catalysts have been added to enhance RE [149, 163]. For example, Fe⁰ or PS
977 alone cannot cause significant SDZ degradation, and sonication alone only led to
978 marginal degradation of SDZ after 1 h treatment (9.7% RE). Moreover, the RE of SDZ
979 reached only 9.8% and 13.7% in 1 h using a combination of two factors, such as
980 sono/Fe⁰ and sono/PS, respectively. By contrast, 45.5% of SDZ was removed in 1 h
981 using the Fe⁰/PS combination due to the catalytic decomposition of PS by Fe⁰ and
982 higher SR formation. However, surface passivation prevented the dissolution of Fe⁰ and
983 the release of Fe²⁺, hampering the continuous degradation of SDZ. Therefore,
984 sonication was used to remove the passivation film and improve mass transfer, inducing
985 an SDZ RE of 95.7% in 1 h in the sono/Fe⁰/PS reaction system [76]. Similarly, it is also

986 difficult to remove TC by sonication alone, or PS alone. Furthermore, little TC was
 987 removed with only the Fe₃O₄ catalyst and even the catalyst with sonication due to the
 988 insignificant adsorption of TC onto Fe₃O₄ and the inadequate formation of active
 989 radicals. However, the RE of TC increased greatly and reached 50.5% and 51.5% in 90
 990 min using the Fe₃O₄/PS and sono/PS combinations, respectively, due to the activation
 991 of PS by the catalyst or sonication; the formation of more SR and •OH on the surface
 992 of catalyst. More significantly, the RE of TC reached 89% with sono/Fe₃O₄/PS since
 993 the activity of Fe₃O₄ was maintained by sonication and PS was activated by Fe₃O₄ and
 994 sonication simultaneously to produce more SR [149].

995 Fe⁰ [76, 161], ZnO [104], Fe²⁺ [111, 113], Co²⁺ [145, 162], Ag [150], Fe₃O₄ [163],
 996 etc. can enhance the activation of PS, PMS or Oxone in sonication systems. Obviously,
 997 transition metals or their ions and oxides were the important catalysts for the activation
 998 of PS, PMS or Oxone to generate SR [19, 76, 140, 145, 149, 150, 159, 161, 162]. The
 999 cavitation effects mean that sonication not only induces the release of SR from PS or
 1000 PMS, but also enhances mass transfer in the solid-liquid interphases, and removes the
 1001 passivated films, while continuously keeping the catalyst surface active. The
 1002 degradation mechanisms of SDZ by sono/Fe⁰/PS are shown in Scheme 4 [76].



1003

1004 *Scheme 4* The degradation mechanism of SDZ by sono/Fe⁰/PS. Reprinted from ref. [76] Copyright (2014), with

1005

1006 As shown in [Scheme 4](#), sonication played important roles in the Fe⁰/PS system,
 1007 including producing radicals, enhancing iron-corrosion reactions and accelerating the
 1008 radical reactions in the bulk liquid [[76](#), [149](#)]. The microstreaming or microjets,
 1009 shockwaves, and turbulence generated by sonication promoted mixing at the solid-
 1010 liquid interfaces and the continuous cleaning of the solid catalyst surface, which favour
 1011 the above reactions [[149](#)].

1012 Based on an HPLC-ESI-MS examination, oxidation by SR was the main SDZ
 1013 degradation pathway, as shown in [Scheme 5](#) [[76](#)]. The main degradation step was the
 1014 oxidation of the amine group (α -position in the benzene ring) by SR to generate the
 1015 nitro-SD derivatives. SR then further attacks the nitro-SD derivatives (the C–N bonds
 1016 on the γ -position in the heterocyclic ring), leading to ring opening. Another degradation
 1017 pathway was the direct oxidative cleavage of the S–N bond, and then the intermediate
 1018 (4-[2-iminopyr-imidine-1(2H)-yl]aniline), which was formed via reaction between the
 1019 products, 2-aminopyrimidine and sulfanilic acid. Furthermore, the low molecular
 1020 weight organic acids (formate and acetate), inorganic ions (nitrate, nitrite and sulfate)
 1021 were examined using an ion chromatograph, which demonstrated the mineralization of
 1022 SDZ [[76](#)]. Unfortunately, this study does not provide the variation of TOC and toxicity
 1023 of the SDZ solutions by the treatment.

1024 Pan, *et al.* have investigated SMZ degradation in a pre-magnetized Fe⁰/PS process
 1025 enhanced by sonication [[161](#)]. The stronger signals of the DMPO–SO₄ and DMPO–OH
 1026 adducts illustrated that more SR and \cdot OH radicals were produced in the system and that
 1027 this occurred more quickly. Similarly, \cdot OH played important roles in the degradation of
 1028 TC by sonication with Fe₃O₄ and PS. The oxidation of TC mainly took place on the
 1029 surface of Fe₃O₄ and the concentration of leaching iron during the reaction could be
 1030 neglected [[149](#)].

1031 Moreover, Hu, *et al.* have demonstrated that the sonocatalytic degradation of NOR
 1032 is principally induced by \cdot OH and SR in the system with PS and multilayer flower-like

1043 5.4 Application of sono/PS and PMS/catalyst in antibiotic 1044 degradation

1045 So far, the sono/PS and PMS/catalyst processes have been extensively applied in
1046 antibiotic degradation. For example, the elimination of FLU was significantly
1047 accelerated and the RE increased when 1.0 mM PS was added to a sono/Fenton system.
1048 As a result, 98% of FLU elimination was achieved in 80 min [111]. Roy, *et al.* have
1049 investigated SDZ degradation in a sono/Fenton-like process with PS and yolk-shell
1050 $\text{Fe}_3\text{O}_4@\text{hollow}@m\text{SiO}_2$ nanoparticles [164]. The faster leaching of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions from
1051 the metal core of the $\text{Fe}_3\text{O}_4@\text{hollow}@m\text{SiO}_2$ particles, due to micro-convection
1052 generated by sonication, enhanced SDZ degradation [164].

1053 Rahmani, *et al.* have reported the sonocatalytic degradation of CIP associated with
1054 PS and Zn^0 under 40 kHz and 350 W sonication [19]. With 4.4 mM PS and 1.84 mM
1055 Zn^0 at pH 4.5 for 60 min, the RE of CIP reached 55% under sono/ Zn^0 /PS in 1 L of a 50
1056 mg/L CIP solution, which was much higher than those (39.7, 18.5, 9.9, 7.5, 3.3 and
1057 2.5%) obtained by PS/ Zn^0 , sono/PS, sono/ Zn^0 , PS, Zn^0 and sonication alone,
1058 respectively [19]. This indicates that the production of $\cdot\text{OH}$, activation of PS and Zn^0
1059 dispersion in solution were enhanced by sonication [19]. In the presence of 10 mM
1060 PMS, periodate, PS and percarbonate, the sonocatalytic RE of TC reached 99.6, 94.2,
1061 90.4 and 98.2% in 50 mL of 50 mg/L TC solutions with 0.5 g/L ZnO/nano-cellulose at
1062 pH 4.0 for 30 min, respectively, under 37 kHz and 256 W sonication, which are higher
1063 than that of the sono/ZnO/nano-cellulose process (87.6%) [104].

1064 Besides the removal of antibiotics, the mineralization of antibiotic solutions can
1065 be significantly enhanced by sonication with PS, PMS and catalysts. Su, *et al.* have
1066 investigated the sonocatalytic degradation of AMX and the removal of COD with Co^{2+}
1067 and Oxone [162]. The REs of COD were in the order of: Oxone < Oxone/ Co^{2+} <
1068 Sono/Oxone < Sono/Oxone/ Co^{2+} . More than 98% of COD removal was achieved by
1069 sonication with 20 kHz and 200 W at 24 °C for 60 min in the presence of 0.095 mM

1070 AMX and 0.025 mM Co²⁺ [162]. Consequently, sonication reduced the energy barrier
 1071 of the reaction and enhanced the COD removal of antibiotics [162]. The degradation of
 1072 antibiotics by sonication with PS or PMS and catalysts has been summarized in Table
 1073 6. As shown in Table 6, 20-40 kHz US has usually been used to enhance the degradation
 1074 of antibiotics via oxidation with a PS/Catalyst. CIP, NOR and CAP are difficult to
 1075 oxidize, and their REs only reached 55.0%-68.5% under sono/PS/Catal after 60-240
 1076 min of treatment. By contrast, the REs of SDZ, TC and SMZ reached higher values
 1077 (95.7%-98.3%) after 15-60 min of treatment. Importantly, all synergy factors fall over
 1078 the range from 1.3-1.9. Meanwhile, mineralization can be achieved to a certain degree
 1079 by sono/PS/Catal. For example, 50 mL of 0.1 mM AMX was sonicated with 20 kHz
 1080 and 300 W US in the presence of 5 mM Oxone and 0.25 mM Co²⁺ at pH 7 for 60 min,
 1081 giving a RE of COD of 85%, which is higher than that (51%) of oxidation with 5 mM
 1082 Oxone and 0.25 mM Co²⁺ without sonication [162]. In addition, 89% of COD was
 1083 removed as the RE of TC reached 93% under sono/PS/Fe₃O₄ nanoparticles [163].

1084 **Table 6** The degradation of antibiotics by sonication with PS and catalysts.

Antibiotics	PS/Catal. (mM/mM)	F _{US} /P _E (kHz/W)	t (min)	C ₀ /V (mg/L)/mL	pH	RE _{PS/Catal.} (%)	RE _{Sono} (%)	RE _{Sono/PS/Catal.} (%)	SF	Refs.
CIP	PS/Zn ⁰ 4.4/1.84	40/350	60	100/<1 000	4.5	39.7	2.5	55.0	1.3	[19]
NOR	PS/Zn ⁰ 0.42/6.14	40/200	80	2.0/50	7.5	-	6.4	66.8	-	[140]
CAP	PS/Co ²⁺ 5.0/0.1	22/200	240	20/50	1.0	<5.0	37.3	68.5	1.6	[145]
SDZ	PS/Fe ⁰ 1.84/0.92	20/40	60	20/400	3.0- 7.0	45.5	9.7	95.7	1.7	[76]
TC	PMS/ZnO/NC 10.0/0.5 g/L	37/256	15	50/50	7.0	-	12.8	96.4	-	[104]
SMZ	PS/Fe ⁰ 1.0/0.1	40/60	60	5/500	7.0	49.3	1.6	98.3	1.9	[161]

1085 Note: F_{US}: ultrasonic frequency; P_E: electrical power input; C₀: initial antibiotic concentration; V: the volume of
 1086 antibiotic solution; RE: removal efficiency; SF: synergy factors = $RE_{Sono/PS/Catal} / (RE_{Sono} + RE_{PS/Catal})$ [71, 81, 109];
 1087 Refs.: references.

1088 5.5 Role of effective factors

1089 As shown in Table 5 and Table 6, the removal of antibiotics is highly pH dependent
1090 and acidic conditions favour the degradation of antibiotics by sono/PS and
1091 sono/PS/Catal [76, 149, 145]. Other factors, including US frequency, initial
1092 concentration of antibiotics, concentration of PS or PMS, contact time and temperature
1093 [76, 131, 159, 160, 162], are also important. Additives are also critical for antibiotic
1094 degradation under sonication with PS, PMS, Oxone, or/and catalyst [19, 34, 76, 82, 104,
1095 111, 112, 113, 131, 140, 145, 148, 149, 150, 160, 161, 162, 163].

1096 The sonocatalytic degradation of antibiotics, such as TC [31], AMX [159, 162],
1097 etc., with PS or PMS generally follows PFO kinetics [131]. For example, a k_l value for
1098 20 mg/L SDZ in a 400 mL solution was measured to be about 0.057 min^{-1} at pH 7 and
1099 room temperature under 20 kHz and 40 W sonication with 0.92 mM Fe^0 and 1.84 mM
1100 PS [76]. In general, initial antibiotic concentration, catalyst dosage, PS and PMS
1101 concentration, and the initial pH value of the solution, temperature and US frequency
1102 and power affect the degradation kinetics [112, 131, 149, 160]. At lower US power
1103 ranges, the RE increased with increased US power [76, 112, 148, 149, 161], but the
1104 benefits of increasing US power over an optimal power value were not observed [149].
1105 In addition, RE increased with an increase in temperature [131, 160, 162], while RE
1106 decreased with an increase of the initial antibiotic concentration [76, 131, 140, 149, 162,
1107 163]. However, the amount of antibiotics removed increased with increasing initial
1108 concentration. For example, 45.9, 88.9 and 121.9 mg/L TC were oxidized by sonication
1109 with $\text{Fe}_3\text{O}_4/\text{PS}$ when its initial concentrations were 50, 100 and 200 mg/L, respectively
1110 [149]. The effects of catalyst dosage, PS or PMS concentration, pH value, and other
1111 additives, on the degradation of antibiotics using sono/PS or PMS/ and catalyst are
1112 discussed below.

1113 5.5.1 Effect of catalyst dosage

1114 Ammar, *et al.* have investigated the effect of Fe^{2+} concentration on the degradation

1115 of MTZ in a sono/Fenton/PS process [113]. The results revealed that the Fe^{2+}
1116 concentration was low enough to make the treated solution directly compatible with a
1117 safe environment, and the combination is an efficient method for the high elimination
1118 of MTZ [113].

1119 Based on the sonocatalytic degradation of SMZ with pre-magnetized Fe^0/PS , Pan,
1120 *et al.* have demonstrated that the degradation rate of SMZ is mainly determined by the
1121 amount of Fe^{2+} produced from Fe^0 [161]. The SMZ removal at 60 min was 84.8%,
1122 96.1%, 97.8%, 100% and 99.3% at 0.05, 0.1, 0.2, 0.4 and 0.8 mM Fe^0 , respectively.
1123 Thus, the removal of SMZ increased with increasing Fe^0 doses over the above range.
1124 Meanwhile, k_l value increased from 0.028 min^{-1} , at 0.05 mM Fe^0 , to 0.176 min^{-1} at
1125 0.40 mM Fe^0 , but slightly decreased at 0.80 mM Fe^0 (0.143 min^{-1}) due to the
1126 consumption of SR by excess Fe^{2+} . Thus, 0.40 mM Fe^0 was noted to be the optimum
1127 dosage and the optimum ratio of Fe^0/PS was denoted as 2/5 [161].

1128 Hou, *et al.* have concluded that initial degradation rates increase with various doses
1129 of Fe_3O_4 , in the range from 0 to 2.0 g/L, in the sonocatalytic degradation of TC with
1130 $\text{Fe}_3\text{O}_4/\text{PS}$ [149]. As an initiator, Fe_3O_4 activates PS to generate SR, and then accelerates
1131 the decomposition of TC. However, the final RE was similar, as a result of the same
1132 concentration of PS, since the SR yield is dependent on PS concentration [149]. In
1133 addition, the degradation rate of TC increases with increasing martite nanoparticle
1134 dosage, and the sonocatalytic RE of 100 mg/L TC reached 87% with 0.5 g/L martite
1135 (Fe_2O_3)/3 mM Oxone at pH 4 for 60 min [112].

1136 5.5.2 Effect of PS or PMS concentration

1137 In general, the degradation rate of antibiotics increases with increased initial PS
1138 concentration [149, 160]. During the sonocatalytic degradation of TC with $\text{Fe}_3\text{O}_4/\text{PS}$,
1139 the RE of TC increased with increasing PS concentration from 20 to 200 mM [149].
1140 However, when the PS concentration was over 200 mM, the RE decreased as excessive
1141 amounts of PS produced sulfate anions rather than active SR. It is also speculated that

1142 the SR formed could be scavenged by excess PS, thus inhibiting the generation of $\cdot\text{OH}$,
1143 meaning that it is sufficient to provide SR with 200 mM PS [149].

1144 Soltani, *et al.* have demonstrated the similar effect of lower Oxone concentration
1145 on the sonocatalytic degradation of TC with martite nanoparticles and Oxone [112].
1146 The results revealed that increasing the Oxone dosage from 1 to 7 mM increases the
1147 decomposition rate from 0.0282 to 0.0588 min^{-1} . Similarly, excessive amounts of
1148 Oxone (5 and 7 mM) led to insignificant improvements in the decomposition rate of
1149 TC. It was assumed that the excessive amounts of HSO_5^- react with SR to form $\text{SO}_5^{\cdot-}$,
1150 which has lower oxidation potential than $\text{SO}_4^{\cdot-}$, leading to poorer decomposition of TC.
1151 In addition, the reaction between sulfate radicals intensified when the Oxone
1152 concentration was excessive, leading to the generation of PS ions. Subsequently, the
1153 addition of extra amounts of Oxone not only causes the scavenging of SR, but also
1154 generates the less reactive species [112].

1155 5.5.3 Effect of pH value

1156 The pH value of a solution not only affects the leaching of metal and their oxides,
1157 but also influences the dissociation of antibiotics, and the adsorption of antibiotics onto
1158 the catalysts, thus manipulating the sonocatalytic degradation of antibiotics with PS or
1159 PMS.

1160 5.5.3.1 RE decreased under alkaline conditions.

1161 In homogeneous systems, antibiotics such as TC exist in the molecular form under
1162 acidic conditions, resulting in higher affinity to the cavitation bubbles where oxidation
1163 with higher concentration $\cdot\text{OH}$ and the pyrolysis of molecules can occur [34]. Thus,
1164 higher RE has been achieved under acidic conditions. For example, 90.5%-91.3% of 50
1165 mg/L TC degradation and 25.7%-28.3% of TOC removal were achieved in 1 L solutions
1166 at pH 3 to pH 6 in 60 min under 20 kHz and 100 W sonication with 2 mM Fe^{2+} and 2
1167 mM PS. However, the differences in the REs at the various pH values under acidic
1168 conditions are not significant. Therefore, it is not necessary to adjust the initial pH to a
1169 very low level, and an initial pH of 6 is an optimal pH condition [34]. Similarly, the

1170 sonocatalytic degradation of 20 mg/L CAP has been carried out in 50 mL solutions by
1171 22 kHz and 200 W sonication for 240 min with 5 mM PS and 0.1 mM Co^{2+} [145]. The
1172 results revealed that the RE of CAP decreases with increasing pH value, while k_t values
1173 are higher under acidic solutions (pH 1.0-3.3) than those obtained in neutral or basic
1174 solutions (pH 5.0-10.0) [145].

1175 In heterogeneous systems, such as sono/ Fe^0 /PS, the efficient degradation of SDZ
1176 (95.7%–98.4%) has been achieved at a pH range of 3.0–7.0 [76], but the performance
1177 was greatly slowed (35.7%) at pH 10.0. Acidic conditions favour the corrosion of Fe^0
1178 and produce more soluble Fe^{2+} , while alkaline conditions cause the precipitation of
1179 soluble iron ions and the passivation of the Fe^0 surface, resulting in a low production
1180 of oxidative radicals, both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$. Moreover, the $\text{SO}_4^{\cdot-}$ formed reacts with H_2O
1181 and OH^- under neutral or alkaline conditions, and also inhibits the reactivity of $\cdot\text{OH}$.
1182 [76].

1183 Furthermore, a gradual decrease in solution pH was observed during the
1184 degradation of antibiotics at an initial pH 3.0–7.0; the formation of carboxyl acid
1185 products and the decomposition of PS led to this pH decrease. At an initial pH of 10.0,
1186 the pH value decreased to 6.5 by the end of degradation [76]. Pan *et al.* have found that
1187 pH value decreases faster with reaction time during the degradation of SMZ in a
1188 sono/premagnetized- Fe^0 /PS system than in other systems [161]. As pH dropped quickly,
1189 Fe^{2+} was produced faster, leading to the formation of more $\text{SO}_4^{\cdot-}$, a higher RE of SMZ,
1190 and better synergistic effects in the sono/premagnetized- Fe^0 /PS system [161].

1191 5.5.3.2 Insignificant effect of pH value

1192 Hou, *et al.* have found that the TC degradation rate increases with decreasing pH
1193 value in a system of Sono/ Fe_3O_4 /PS, but the REs were all similar after 1.5 h sonication
1194 [149]; the final REs were 89%, 86% and 85% at pH 3.7, 7.0 and 9.0, respectively. This
1195 indicates that pH value had an insignificant effect on the RE of TC.

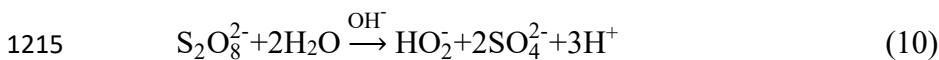
1196 Carboxyl acids, such as acetic acid and sulfate acid, are produced during the
1197 reaction. Therefore, the final pH value decreased from initial pH values of 3.70, 7.00

1198 and 9.00 to 2.66, 2.63 and 2.68 after 1.5 h reaction, respectively. This is probably the
1199 reason why similar REs were achieved by the end of the reactions at various initial pH
1200 values [149]. Similarly, the pH value decreased from 4.0 to 3.4, from 7.0 to 5.8 and
1201 from 10.0 to 7.3 during TC degradation via sono/PS in the absence of a buffer solution
1202 [160].

1203 5.5.3.3 RE increased under alkaline conditions.

1204 The TC degradation rate under sono/PS is highly dependent on the initial pH value.
1205 After 120 min of reaction, the TC degradation rates were 77.4%, 62.5% and 88.5% at
1206 pH 4, 7 and 10, without adding any buffer solution, respectively [160].

1207 TC is an amphoteric molecule with pK_a values of 3.3, 7.7 and 9.7. TC molecules
1208 are predominantly neutral and positively charged at pH = 4 and negatively charged at
1209 pH = 9. The negatively charged TC molecules tend to attract reactive species such as
1210 $\cdot\text{OH}$ because of the high electrical density on ring system, which resulted in an
1211 acceleration in the degradation of TC [160, 165]. Moreover, alkaline-activated PS is
1212 primarily responsible for the production of $\text{SO}_4^{\cdot-}$, $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ at pH \geq 10. Furthermore,
1213 SR can react with OH^- to generate $\cdot\text{OH}$ under alkaline conditions [160, 165]. Therefore,
1214 increasing pH enhances the decomposition of PS to form $\cdot\text{OH}$ and SR.



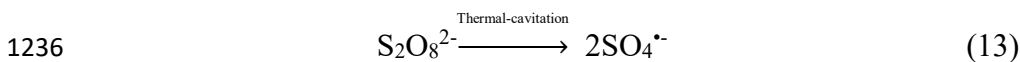
1218 SR is the predominant species responsible for TC degradation at pH 4, whereas
1219 TC degradation was caused by both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ at pH 7. Thus, the competing
1220 reactions between SR and $\cdot\text{OH}$, and TC reduce the TC degradation rate at pH 7 [160].

1221 Similarly, TC degradation under a sono/martite/oxone process has been studied at
1222 initial pH values of 4, 7 and 9, and the k_I values were 0.0481, 0.0545 and 0.0641 min^{-1}
1223 1 , respectively [112]. On the one hand, the scavenging of SR and disintegration of the

1224 active species by H^+ was thought to cause slight decreases in the TC degradation rate
1225 under acidic conditions. The increased degradation rate with increased initial pH can
1226 be explained by the conversion of $SO_4^{\bullet-}$ and $\cdot OH$ in the presence of OH^- under alkaline
1227 conditions. On the other hand, the reaction between $\cdot OH$ and SR leads to the production
1228 of HSO_4^- in the bulk solution, and then the dissociation of HSO_4^- into sulfate ions
1229 releases H^+ ions, decreasing the pH of the solution [166]. Therefore, an insignificant
1230 increase in the degradation rate was observed with increasing initial pH value [112].

1231 5.5.4 Effect of temperature

1232 Increasing temperature dramatically improved the cavitation activity and
1233 chemical effects, resulting in higher degradation rates of antibiotics under sono/ $S_2O_8^{2-}$
1234 [131, 160] or Sono/Oxone [162] processes. PS activation can be performed by heat to
1235 produce SR, as shown in Eq. (13) [131, 160].



1237 The k_{obs} of SDZ increased (3.56-27.39 h^{-1}) with increased bulk temperature (10-
1238 50 $^{\circ}C$) in the sono/ Fe^0 /PS system. The pseudo activation energy was 38.2 kJ/mol,
1239 demonstrating that higher temperature was beneficial to the removal of SDZ and
1240 verifying that thermal treatment can also be a persulfate activator. The activation energy
1241 obtained in sono/ Fe^0 /PS was approximately one order of magnitude lower than that
1242 obtained in the heat/PS system and Fe^0 /PS system, which indicates that the effective
1243 removal of SDZ can also be achieved by sono/ Fe^0 /PS processes even at a low bulk
1244 temperature (10 $^{\circ}C$) [76]. Upon increasing the temperature from 25 to 65 $^{\circ}C$, the
1245 degradation rate constant increased from 0.0229 to 0.1042 min^{-1} under the sono/ $S_2O_8^{2-}$
1246 process [131]. Complete TC degradation occurs after 40, 60 and 75 min of reaction at
1247 65, 55 and 45 $^{\circ}C$ respectively. The low activation energy (32.01 kJ/mol) indicates that
1248 the degradation of TC by sono/ $S_2O_8^{2-}$ is thermodynamically feasible [131]. Increasing
1249 temperature (25-65 $^{\circ}C$) enhanced the TC degradation rate constant (0.0175 to 0.1573
1250 min^{-1}) during the sono/ $S_2O_8^{2-}$ process. TC was completely removed after 60, 90 and

1251 120 min of reaction at 65, 55 and 45 °C respectively. An activation energy value of
1252 42.66 kJ/mol was obtained [160]. Su *et al.* have observed an insignificant enhancement
1253 in COD removal in AMX solution by temperature (24 to 40 °C) during a
1254 sono/Co²⁺/Oxone process (the RE of COD reached more than 85% in 60 min at ambient
1255 temperature) [162].

1256 5.5.5 Effect of other additives

1257 5.5.5.1 Addition of H₂O₂.

1258 H₂O₂ is a common oxidant and also the precursor to producing [•]OH, which is
1259 frequently used to accelerate the degradation of organic pollutants [113]. Under
1260 sonication, the formation of extra [•]OH, from H₂O₂ decomposition, enhanced MTZ
1261 removal [113]. In a homogenous Fe²⁺/PS (3 mM/1 mM) system, the RE of 500 mg/L
1262 MTZ in 200 mL solution reached 97% at pH 3 in 90 min of sonication with 20 kHz and
1263 the addition of 60 mM H₂O₂, as compared to an RE of 72% in the absence of PS [113].
1264 In another homogenous Fe²⁺/PS (4 mM/1 mM) system, the RE of 261 mg/L FLU in
1265 200 mL solution reached 98% at pH 4 after 80 min of sonication with 40 kHz and the
1266 addition of 20 mM H₂O₂, compared to an RE of 73% in sono/H₂O₂ [111].

1267 In a heterogeneous martite/Oxone /(0.5 g/L/3 mM) system, the RE of 100 mg/L
1268 TC in 100 mL solution reached 87% at pH 4 in 60 min under 37 kHz and 320 W
1269 sonication with martite-nanoparticle-activated Oxone, compared to an RE of 78% in
1270 unmilled martite (sono/unmilled martite/Oxone) [112]. Only 6.5% of TC was removed
1271 by the adsorption process, while the decomposition of TC by Oxone alone was lower
1272 than 44%. As a result, when the H₂O₂ concentration rose from 10 to 40 mM, the *k₁* value
1273 increased from 0.0533 to 0.0907 min⁻¹. However, increasing H₂O₂ concentration up to
1274 50 mM caused a substantial drop in the decomposition rate of TC [112].

1275 5.5.5.2 Addition of scavengers.

1276 The quenching effect of t-BuOH, EtOH and 1,4-benzoquinone is a signal for
1277 verifying the roles of [•]OH, O₂^{•-} and SO₄^{•-} in TC degradation by sono/Fe₃O₄/PS processes
1278 [149]. The results revealed that TC degradation is suppressed with the addition of 1.05

1279 M EtOH. This indicates that $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ are the major radicals for the degradation
1280 of TC. In theory, EtOH is a scavenger of $\text{SO}_4^{\bullet-}$ and can also react with $\cdot\text{OH}$, and the
1281 reaction constants of EtOH with $\text{SO}_4^{\bullet-}$ and OH are $1.6\text{--}7.7\times 10^7$ and $1.2\text{--}2.8\times 10^9 \text{ M}^{-1}\text{S}^{-1}$,
1282 respectively [149].

1283 In order to investigate the role of $\text{O}_2^{\bullet-}$, 1,4-benzoquinone was used as an $\text{O}_2^{\bullet-}$
1284 quencher in a TC degradation via a sono/ Fe_3O_4 /PS process [149]. The addition of 0.021
1285 M 1,4-benzoquinone did not significantly affect the TC degradation in the initial stages.
1286 However, the suppression became significant after 30 min, indicating the delayed
1287 formation of $\text{O}_2^{\bullet-}$ during the reaction [149].

1288 t-BuOH is generally used as an OH scavenger and the reaction constant is 3.8--
1289 $7.6\times 10^8 \text{ M}^{-1}\text{S}^{-1}$. Excess t-BuOH (1.05 M) was added to the solution to check the
1290 contribution percentage of $\cdot\text{OH}$ [149].

1291 Zhou, *et al.* have demonstrated that SDZ degradation is inhibited by SO_4^{2-} , NO_3^- ,
1292 $\text{HCO}_3^-/\text{CO}_3^{2-}$ and H_2PO_4^- to different extents in a sono/ Fe^0 /PS system [148]. Such
1293 inorganic anions would mainly react with $\text{SO}_4^{\bullet-}$ and/or $\cdot\text{OH}$ to form sub-radicals of
1294 less oxidative potential, which was also proven by the sonocatalytic degradation of SDZ
1295 in a sono/yolk-shell $\text{Fe}_3\text{O}_4@$ hollow@ mSiO_2 nanoparticle/PS system [164]. The
1296 inhibition effect was revealed to be probably due to the stronger metal ion complexation
1297 and radical scavenging in the hollow core of the yolk-shell nanoparticles [164].
1298 Moreover, the presence of carbonate and even persulfate ions suppressed the
1299 sonocatalytic degradation of TC with martite nanoparticles and Oxone [112]. However,
1300 Cl^- enhanced the SDZ degradation with a low dose (5 mM), but inhibited it at a high
1301 dosage (100 mM) [148]. Moreover, the enhanced effects of chloride and carbon
1302 tetrachloride have also been demonstrated in the sonocatalytic degradation of TC [112].

1303 At pH 3 and 5 with a buffer solution, the REs of SDZ reached 54.6% and 58.4%,
1304 respectively, which were lower than in the un-buffered systems. It was also speculated
1305 that the additional phosphate species (mainly HPO_4^{2-} and H_2PO_4^- at pH 3.0–5.0) play

1306 the scavenging role for SR via complexation of the phosphate species. It also indicates
1307 that the soluble iron ions inhibit SDZ degradation. As the predominant oxidant under
1308 stable neutral or alkaline conditions, $\cdot\text{OH}$ was strongly scavenged by phosphate species,
1309 and significant inhibition of SDZ degradation was therefore found at pH 7 and 10 with
1310 a buffer solution [76].

1311 Finally, the addition of humic acid in concentrations above 10 mg/L also reduced
1312 the degradation rate of TC in a sono/PS process, although the effect could be
1313 compensated using higher concentrations of PS [160]. The low RE of TOC is due to the
1314 generation of recalcitrant products during TC degradation [160]. Therefore, a longer
1315 exposure time is required for the efficient mineralization of antibiotics [112].

1316 5.5.6 Stability of catalysts

1317 In the heterogenous sonocatalytic system with martite nanoparticles and Oxone,
1318 the decomposition rate of TC dropped by only 10.8% after four consecutive
1319 experimental runs, indicating the appropriate reusability potential of martite
1320 nanoparticles [112]. In a sonocatalytic system with Fe_3O_4 and PS, the RE of TC reached
1321 89% in 1.5 h in the primary experiment, and then the RE decreased to 73.5% after three
1322 repetitive experiments. A low dissolved iron concentration (<0.2 mM) was detected in
1323 the solution. It was speculated that Fe(III)-bearing iron oxides formed on the surface of
1324 the catalyst, which may be more soluble, less active and stable, and thus cause the RE
1325 decline. As for effect of sonication on the catalyst particle size distribution, the particle
1326 size distribution of the used catalysts is similar to that of the fresh catalysts, indicating
1327 that Fe_3O_4 is stable under sonication [149].

1328 **6 Degradation of antibiotics by sonophotocatalysis**

1329 **(sonication/photocatalysis)**

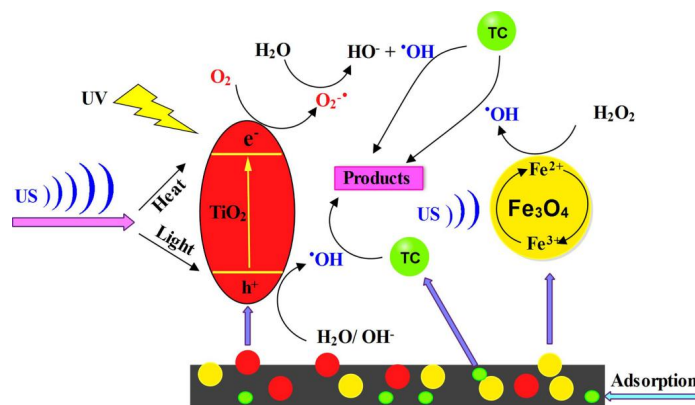
1330 6.1 Mechanism of sonophotocatalysis

1331 Photocatalysis that are based on semiconductors provide favourable results,

1332 compared to other AOPs, in the destruction of persistent organics. In recent years,
 1333 conventional photocatalytic processes have exhibited some problems, such as difficulty
 1334 in the separation and recovery of catalysts, the production of secondary pollution, and
 1335 the high consumption of catalysts and energy, etc. [31]. Furthermore, the lack of
 1336 efficient photoactivity under solar-light, the high recombination rate of photo-induced
 1337 electron-hole ($e_{CB}^- - h_{VB}^+$) pairs, and low resistance to photo-corrosion has limited their
 1338 practicality in environmental applications [84]. To overcome these obstacles,
 1339 photocatalysis is usually combined with sonication, chemical oxidants or microwave
 1340 techniques [31].

1341 Sonophotocatalysis has attracted much attention because it is generally considered
 1342 to be an applicable and environmentally friendly process [114]. The synergistic effect
 1343 of sonocatalysis and photocatalysis generates a large number of ROS, and thus
 1344 enhances the oxidation process to remove organic contaminants [84]. The cavitation
 1345 effects induced by sonication eliminate the defects of photocatalysis, including the
 1346 decrease in UV-available sites, mass transfer limitations and the blocking of the catalyst
 1347 surface by contaminants [84]. The degradation mechanisms of TC by
 1348 sonophotocatalysis are shown in Figure 5.

1349



1350

1351 **Figure 5** Degradation mechanisms of TC by sonophotocatalysis. Reprinted from ref. [31] Copyright (2019), with
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1353 6.2 Application of sonophotocatalysis in antibiotic degradation

1354 Vinesh, *et al.* have investigated the degradation of TC by sonophotocatalysis under
 1355 simulated visible light with a reduced graphene-oxide (rGO) supported electron-
 1356 deficient B-doped TiO₂ (Au/B-TiO₂/rGO) nanocomposite synthesized via the
 1357 hydrothermal method [117]. The RE of TC under sonolysis, photocatalysis and
 1358 sonophotocatalysis was found to be 25, 65 and 100%, respectively, when the reaction
 1359 was performed in the presence of sonolysis and photocatalysis under 40 kHz, 600 W
 1360 US, 300 W of visible light power with 0.25 g/L Au/B-TiO₂/rGO in 60 min (40 mL, 15
 1361 mg/L). The enhanced sonophotocatalytic activity (SF: ~1.3) observed was attributed to
 1362 the generation of more ROS by the combination of sonication and photocatalysis [117].
 1363 According to trapping tests, holes, [•]OH and [•]O₂ contributed to the degradation process
 1364 [31].

1365 The application of sonophotocatalysis for the degradation of antibiotics has been
 1366 summarized in Table 7.

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1371 **Table 7** Degradation of antibiotics by sonophotocatalysis.

AB	Catalysts	$\lambda_{UV/vis}/P_U$ ν_{vis} (nm/W)	F_{US}/P_E (kHz/W)	t (min)	C_0/V (mg/L)/ mL	pH	RE _{Ph} _{oto} (%)	RE _{Sono} (%)	RE _{Sono/} _{Photo} (%)	SF	Refs.
OF	1 g/L TiO ₂	350–400 /3.2 W/m ²	20/192*	120	10/300	6.0	85.0	15.0	~100.0	~1.0	[85]
TC	0.3 g/L TiO ₂ /MAC @T	254/6	20/40	60	30/<500	5.5	47.4	2.1	59.2	1.2	[31]
TC	0.25 g/L Au/B-TiO ₂	-300	40/600	60	15/40	-	65.0	25.0	100.0	1.3	[117]

	/rGO										
CL A	0.3 g/L ZnS QDs/SnO ₂	254/4	20/75	60	10/100	3.0	68.2	~8.0	86.7	1.7	[119]
RX M	0.3 g/L ZnS QDs/SnO ₂	254/4	20/75	60	10/100	3.0	72.6	~12.0	90.3	~1.1	[119]
AM X	1.0 g/L gC ₃ N ₄ - 20@Ni-Ti LDH	420- 470/400	20/200	150	-/100	-	87.0	53.0	99.0	0.7	[39]
MO X	1 g/L NiFe- LDH/rGO	-/10	36/150	60	20/100	8.0	62.7	8.2	90.4	1.3	[118]

1372 Note: ABX: Antibiotics; $\lambda_{UV/vis}$: wavelength of light; P_{UV} : light power; W/m^2 : light power intensity; Fus: ultrasonic
1373 frequency; PE: electrical power input; C_0 : initial antibiotic concentration ; V: the volume of antibiotic solution; RE:
1374 removal efficiency; synergy factors = $RE_{Sono/Photo}/(RE_{Sono}+RE_{Photo})$ [71, 81, 109]; Refs.: references.

1375 As listed in Table 7, TiO₂ and its composites, as well as transition metal oxides,
1376 have usually been used as the catalysts for the degradation of antibiotics by
1377 sonophotocatalysis. The applications of sonophotocatalysts in the degradation of
1378 antibiotics are discussed below.

1379 6.2.1 TiO₂ and its composites

1380 TiO₂ is a common catalyst for promoting the photocatalytic degradation of organic
1381 contaminants. Hapeshi, *et al.* have investigated the degradation of OFX by
1382 sonophotocatalysis with TiO₂ (Conditions: 300 mL of 10 mg/L OFX, pH 6.0, 1.0 g/L
1383 catalysts, 20 kHz, 640 W/L US power, 350-400 nm UV, 3.2 W/m² UV power, 120 min
1384 treatment at 27 ± 2 °C) [85]. The working solution, containing 10 mg/L OFX, was
1385 prepared by spiking the appropriate mass of the compound in the secondary treated
1386 wastewater (collected from the urban wastewater treatment plant (UWTP) of Limassol,
1387 Cyprus) and then performing the necessary dilutions. The results revealed that the
1388 sonophotocatalytic degradation of OFX follows PFO kinetics. The k_I values were
1389 0.1054, 0.0713, 0.0203 and 0.0131 min⁻¹ for sono/Photo/TiO₂, photo/TiO₂, sono/TiO₂
1390 and sonication alone, respectively. The REs of OFX for 120 min reached 15, 62, 85 and

1391 ~100% for sonication, sono/TiO₂, photo/TiO₂ and sono/photo/TiO₂, respectively.
 1392 Therefore, degradation by sonophotocatalysis was generally faster than all the
 1393 individual processes, presumably due to the enhanced formation of reactive radicals.
 1394 Additionally, the presence of the TiO₂ catalyst significantly increased the RE of OFX
 1395 by sonication. It was assumed that the increase is attributed to the additional cavitation
 1396 activity, which is used as an alternative energy source for TiO₂ to generate positive
 1397 holes [85].

1398 Kakavandi *et al.* have investigated the degradation of TC by sonophotocatalysis
 1399 using TiO₂ that was decorated on magnetic activated carbon (MAC@T), where MAC
 1400 was fabricated via the magnetization of AC using Fe₃O₄ nanoparticles [31]. The REs of
 1401 TC for 60 min under various sonocatalytic and photocatalytic processes are listed in
 1402 Table 8.

1403 **Table 8** REs of TC for 60 min under various sonication and photocatalytic processes (Conditions: <500 mL of 30
 1404 mg/L TC, pH 5.5, 0.3 g/L catalysts, 20 kHz, 40 W US power, 6 W UV power, 60 min treatment at 25 ± 2 °C,).

Process	Photo*	Sono*	Sono/Photo*	MAC@T	Sono/MAC@T	Photo/MAC@T	Photo/TiO ₂	Sono/Photo/MAC@T
RE(%)	2.1	4.0	7.4	36.8	38.5	47.4	44.9	59.2

1405 * Without catalysts [31].

1406 As listed in Table 8, it was assumed that the negligible REs of TC are caused by
 1407 very low generation efficiencies of free radicals in photolysis or sonication alone. The
 1408 increased RE value using the sono/photo process indicates the synergistic effect
 1409 between sonication and photolysis [31]. 36.8% of RE obtained by MAC@T composite
 1410 indicated the RE by adsorption onto the catalyst, while an RE of 47.4% by
 1411 photo/MAC@T is comparable with that (44.9%) obtained by traditional photo/TiO₂ due
 1412 to the synergistic effect of adsorption and photocatalytic degradation. The highest RE
 1413 (59.2%) was obtained using the sonophotocatalysis process with MAC@T. This is
 1414 because the catalyst played roles for adsorption, photocatalysis and sonocatalysis
 1415 simultaneously. Furthermore, the synergistic effect is associated with a contribution by

1416 sonication and the subsequent production of ROS in the system, while the surface of
1417 the catalyst was cleaned by sonication continuously to maintain the activity of catalyst
1418 [31].

1419 6.2.2 Fenton and Fenton-like reactions

1420 Zhou, *et al.* have compared the degradation kinetics and REs of SMZ using 5
1421 different sonocatalytic and photocatalytic systems with Fe₃O₄ [116]. The SMZ
1422 degradation in the sono/photo/Fe₃O₄/OA system follows PFO kinetics under the
1423 conditions used - 25 mg/L SMZ, 0.4 g/L Fe₃O₄, 0.8 mM oxalic acid (OA), UV (365 nm,
1424 9 W), US (20 kHz, 330 W), initial pH 3, 20 °C, and the k_1 value reached 3.5×10^{-2}
1425 min⁻¹, which is about 10-times higher than that obtained in the sono/Fe₃O₄/OA system
1426 ($k_1 = 0.36 \times 10^{-2}$ min⁻¹). However, the degradation of SMZ in the photo/Fe₃O₄/OA
1427 system does not follow PFO kinetics, because there was an initial degradation lag
1428 period. Thus, sonication was used to reduce the initial lag period of SMZ degradation
1429 [116].

1430 The high stability of the SMZ molecule meant that lower REs (ca. 10–20%) were
1431 observed after 60 min in the sono/Fe₃O₄, sono/photo/Fe₃O₄ and sono/Fe₃O₄/OA
1432 systems, but higher SMZ REs were achieved in the photo/Fe₃O₄/OA system and
1433 sono/photo/Fe₃O₄/OA system [116]. It was speculated that the rapid release of dissolved
1434 iron species in the initial reaction phases, induced by Fenton-like reactions, resulted in
1435 the efficient production of ROS. Moreover, in the sono/photo/OA and sono/Fe₃O₄/OA
1436 systems, oxalate mostly acts as a competitive reactant. By contrast, in the
1437 Photo/Fe₃O₄/OA and Sono/Photo/Fe₃O₄/OA systems OA acts as both a reactant and an
1438 ROS initiator [116]. The synergistic degradation of SMZ has also been demonstrated in
1439 a Sono/Photo/Goethite- Fe³⁺/OA system by integrating *in-situ* H₂O₂ generation under
1440 UV illumination and efficient Fe²⁺ species regeneration (Initial parameters: 25 mg/L
1441 SMZ , 0.5 g/L goethite, 0.8 mM OA, 330W US and pH 3, initial Fe³⁺ concentration of
1442 250 μM) [115]. The cleavage of the S–N bond in the SMZ molecule was dominant
1443 under •OH attack. Meanwhile, organic mineralization and wastewater detoxification

1444 were achieved.

1445 Transition metal oxide (ZnO) or sulfide (ZnS and SnO₂) have been used to
1446 accelerate the degradation of antibiotics in sono/photo/Fenton-like processes [83, 119].
1447 After pretreatment, the degradation of antibiotics becomes possible using biological
1448 treatment processes. The degradation of 10 mg/L RXM and CLA was studied in a
1449 sono/photo/Fenton-like system with ZnS quantum dots decorated onto SnO₂ nanosheets
1450 prepared using the hydrothermal method [119]. Without catalysts, REs were low using
1451 the Photo method alone, sonication alone, photo/H₂O₂, sono/H₂O₂ and
1452 sono/photo/H₂O₂, due to the insufficient formation of [•]OH. With 0.3 g/L catalyst and 6
1453 mM H₂O₂, only 31.4% of 10 mg/L CLA and 36.4% of 10 mg/L RXM were removed
1454 from 100 mL aqueous solutions at pH 3 after 60 min. When sonication (20 kHz, 75 W)
1455 was used to enhance the degradation in the above system, the REs of CLA and RXM
1456 increased to 61.2% and 65.5%, while higher REs (68.2% and 72.6%) were obtained in
1457 the same system, but in the presence of UV (254 nm, 4 W). Surprisingly, The REs of
1458 CLA and RXM reached 86.7% and 90.3% in the sono/photo/Fenton process [119].
1459 Consequently, the superior performance and synergistic effects of the
1460 sono/photo/catalyst process were attributed to the promotion of [•]OH generation [119].

1461 6.2.3 Other nano-composites

1462 Khataee, *et al.* have investigated the degradation of MOX by the
1463 sonophotocatalytic method using a NiFe-layered double hydroxide/reduced graphene
1464 oxide (NiFe-LDH/rGO) nanocomposite [118]. The RE of MOX (90.4%) by
1465 sonophotocatalysis under the used conditions - 100 mL of 20 mg/L MOX, pH 8.0, 1.0
1466 g/L catalysts, 36 kHz, 150 W US power, 10 W UV power, 60 min treatment - was higher
1467 than the REs of sonocatalysis (72.4%) and photocatalysis (62.7%), but lower than their
1468 sum. The results revealed that [•]OH and [•]O₂ radicals play the dominant role in MOX
1469 degradation.

1470 Abazari, *et al.* have investigated the degradation of AMX by sonophotocatalysis

1471 with nanocomposites of g-C₃N₄@Ni-Ti layered double hydroxides (g-C₃N₄@Ni-Ti
1472 LDH) synthesized using the hydrothermal method with NH₄F [39]. The conditions -
1473 100 mL AMX, pH 8.0, 1.0 g/L catalysts, 20 kHz, 200 W US power, 420-470 nm, 400
1474 W UV power and 150 min treatment – allowed the following RE order to be determined:
1475 sonocatalysis < photocatalysis < sonophotocatalysis. The formation of •OH on the
1476 surface of the g-C₃N₄-20@Ni-Ti LDH particles was approved using the terephthalic
1477 acid probe in photoluminescence spectroscopy [39]. Thus, the observed enhancement
1478 in the sonophotocatalytic activity of the nanocomposites can be related to their higher
1479 specific surface areas, the intimacy of the contact interfaces of their individual
1480 components, i.e., pristine g-C₃N₄ and Ni-Ti LDH, the synergistic effect between these
1481 components and restriction of electron-hole recombination.

1482 Ghoreishian, *et al.* have investigated the degradation of TC by sonophotocatalysis
1483 with flower-like rGO/CdWO₄ hierarchical structures that were synthesized using a
1484 facile wet-chemistry method without any calcination [84]. rGO/CdWO₄ exhibited
1485 significant photoelectrochemical performance under the conditions used - 500 mL of
1486 13.54 mg/L AMX, 0.432 g catalysts, 60 min treatment - and demonstrated superior
1487 sonophotocatalytic activity and mineralization efficiency compared with CdWO₄ [84].
1488 Thus, the higher catalytic activity of rGO/CdWO₄ is attributable to rGO, which catches
1489 TC residuals from aqueous solution and acts as a charge acceptor to promote the
1490 separation of photo-generated carriers via its π - π conjugated structure.

1491 6.3 Other concerning issues

1492 6.3.1 Effective factors

1493 Due to the emerging nature of sonophotocatalysis, little has been reported on the
1494 effects of critical factors. The performance of sonophotocatalytic systems is influenced
1495 by various parameters, such as US and UV conditions, catalyst dosage, pH value, initial
1496 antibiotic concentration, additives, etc. [31, 83-85]. In general, the RE of antibiotics
1497 increases with increasing US intensity, UV intensity [39] and catalyst dosage [20, 31,

1498 85, 118, 119, 167], and acidic conditions favour degradation [20, 116]. For example,
1499 Tavasol, *et al.* have designed a photocatalyst of sea sediment/titanate to remove CPX
1500 from aqueous media in the presence of sono/photo/H₂O₂ [26]. Under the conditions -
1501 150 mL of 100 mg/L CPX, pH 6.8, 40 kHz US, 15 W UV power, 100 min treatment -
1502 the removal of antibiotics was achieved with increasing titanium content loaded onto
1503 the sediments (1.5 g/L catalysts), due to higher surface area and higher photocatalytic
1504 activity that it provides [26].

1505 In some cases, the ratio of catalyst and acid (e.g., Fe₃O₄/OA) is also an important
1506 factor for the degradation of antibiotics [116]. As discussed above, sonocatalysis or
1507 photocatalysis alone are not adequate to effectively remove antibiotics from aqueous
1508 solutions, but the addition of either H₂O₂ or PS significantly enhances the RE, while
1509 RE increases with increasing concentration of additives [20, 163]. For example, OFX
1510 degradation increases slightly upon increasing the H₂O₂ concentration, but with an
1511 optimum level of H₂O₂ concentration at 0.14 mM. [85]. Zeng, *et al.* have investigated
1512 the degradation of LEV by visible-light-driven sonophotocatalysis and PS activation
1513 over 3D urchin-like MoS₂/C nanoparticles [100]. The radical species [•]OH and SO₄^{•-}
1514 were accelerated, while [•]O₂ was limited in this coupled system, which largely
1515 facilitates its excellent degradation performance with a synergistic effect [167].

1516 By contrast, the addition of inhibitors decreases the degradation of antibiotics as a
1517 means to probe the role of [•]OH that is formed *in situ*. For example, the inhibitory effect
1518 of different inorganic salts on NOR degradation in a sono/nano-Cu⁰/H₂O₂ system
1519 followed the sequence: Na₂SO₄ > NaNO₃ > ≈ no salt > NaCl > NaHCO₃ [20]. However,
1520 a contradictory result has been observed, in which a decreasing sequence of the
1521 inhibitory effect of anions towards TC degradation in a sono/photo/MAC@T process
1522 was observed to be: Cl⁻ > HCO₃⁻ > PO₄³⁻ > NO₃⁻ > SO₄²⁻ [31].

1523 6.3.2 Mineralization and detoxification

1524 Because of the significant synergy in the sonophotocatalysis of antibiotics, the

1525 mineralization and detoxification of aqueous antibiotics solution have been improved
1526 [115, 116]. For example, under the conditions used - 40 mL of 15 mg/L TC, 0.25 g/L
1527 catalysts, 40 kHz, 600 W US power, 300 W UV power, 60 min treatment - 12.1, 45.7
1528 and 73.6 % TOC removal have been achieved by sonolysis, photocatalysis and
1529 sonophotocatalysis, respectively [117].

1530 The significant synergistic degradation of SMZ can be further evidenced by the
1531 results of mineralization and detoxification of treated water samples. 78% of TOC was
1532 removed in a sono/photo/Fe₃O₄/OA system after 1 h of reaction time, with an increase
1533 of the corresponding EC 50 from 17% (the raw sample) to 89%. The efficiencies of
1534 mineralization and detoxification were much higher than those achieved in the other six
1535 systems [116]. Montoya-Rodríguez *et al.* have observed 100% removal of AMP after
1536 75 min of treatment with the sonochemical process. Moreover, the antimicrobial
1537 activity of AMP significantly decreased, which was related to attacks of [•]OH on the
1538 active nucleus [46]. In addition, the highest mineralization of the pollutant (40% of
1539 TOC removal) was achieved after 180 min of treatment with a sono/photo/Fenton
1540 process [46].

1541 Toxicity depends on the chemical properties and concentration of not only the
1542 OFX that was initially present, but also of its transformation products (TPs).
1543 Interestingly, the by-products formed during the dissolved organic matter (DOM)
1544 oxidation seem to play a similar role with regards to the toxicity changes as that of the
1545 by-products formed during OFX degradation [85]. Antimicrobial activity (AA) has
1546 been assessed by the Kirby-Bauer method using *Staphylococcus aureus* as the indicator
1547 microorganism. As a result, 100% of AA was removed after 60 and 20 min for AMP
1548 and NAF by the sono/photo/Fenton process, respectively [69].

1549 6.3.3 Stability and reusability of catalysts

1550 The stability and reusability of catalysts used in sonophotocatalysis are critical to
1551 the promotion of the degradation of antibiotics. Evaluations have revealed that some

1552 catalysts are robust. For example, insignificant loss was observed in the
1553 sonophotocatalytic activity of the nanocomposites of g-C₃N₄-20@Ni-Ti LDH even
1554 after five consecutive runs [39]. Both Fe leaching and loss of decontamination were
1555 slight after reuse, indicating that MAC@T has high stability and reusability [31]. The
1556 rapid degradation of SMZ and the decomposition of oxalate could still be achieved in
1557 the heterogeneous sonophotolytic Fenton-like system using goethite over five
1558 consecutive reaction cycles [115]. Besides, wastewater treatment is plausible using a
1559 reusable synthesized NiFe-LDH/rGO nanocomposite [118].

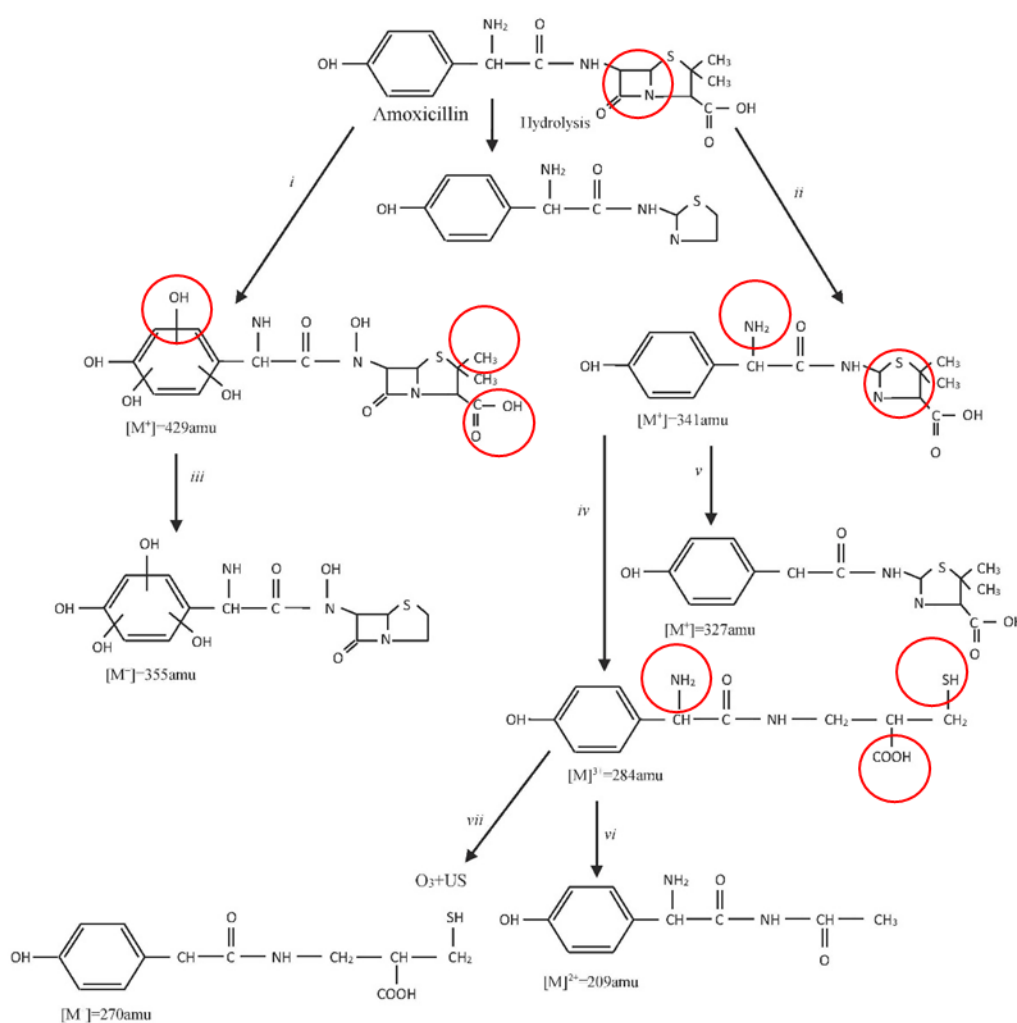
1560 **7 Degradation of antibiotics by sonozonation** 1561 **(Sonication/Ozonation)**

1562 7.1 Mechanisms of sonozonation

1563 Ozone is a powerful oxidant that can directly react with contaminants or
1564 decompose into more powerful oxidants - free radicals. Ozonation has usually been
1565 used to remove refractory organics, including antibiotics, and improve biodegradability.
1566 However, high costs, poor gas-liquid mass transfer and selective oxidation have limited
1567 its use. Due to the cavitation effects, such as hotspots, microjets, shockwaves,
1568 turbulence, etc., sonication enables the mass transfer and [•]OH production to be
1569 improved, leading to significantly high degradation rates for antibiotics [78, 79, 80, 120,
1570 121]. It was speculated that cavitation effects reduce the liquid-film thickness of gas
1571 bubbles containing O₃, and increase the gas/liquid specific surface area. Meanwhile,
1572 the diffusion of free radicals, generated in the vapour phase of cavitation bubbles and
1573 O₃/O₂ bubbles, into the bulk solution is enhanced under sonication to oxidize
1574 hydrophilic antibiotics [79].

1575 For example, AMX cannot be efficiently oxidized through sonication alone, but
1576 can be removed efficiently using ozonation or sonozonation [78]. Moreover, the
1577 oxidative degradation efficiency of AMX using the above methods has been identified
1578 by intermediate analysis with GC-MS, mineralization analysis and the Microtox

1579 toxicity test [78]. In ozonation processes, six products, formed via the hydroxylation of
 1580 AMX, demethylation, decarboxylation and the opening of beta-lactam and thiazole
 1581 rings with ROS, have been observed under alkaline conditions. The degradation
 1582 pathway of AMX by sonozonation is similar to that of ozonation. Scheme 6 shows the
 1583 pathway of intermediate formation during the degradation of AMX by the sonication,
 1584 ozonation and sonozonation processes. Meanwhile, the mineralization degrees reached
 1585 10% by sonication alone, 32% by ozonation alone and 45% by sonozonation under
 1586 optimized conditions.

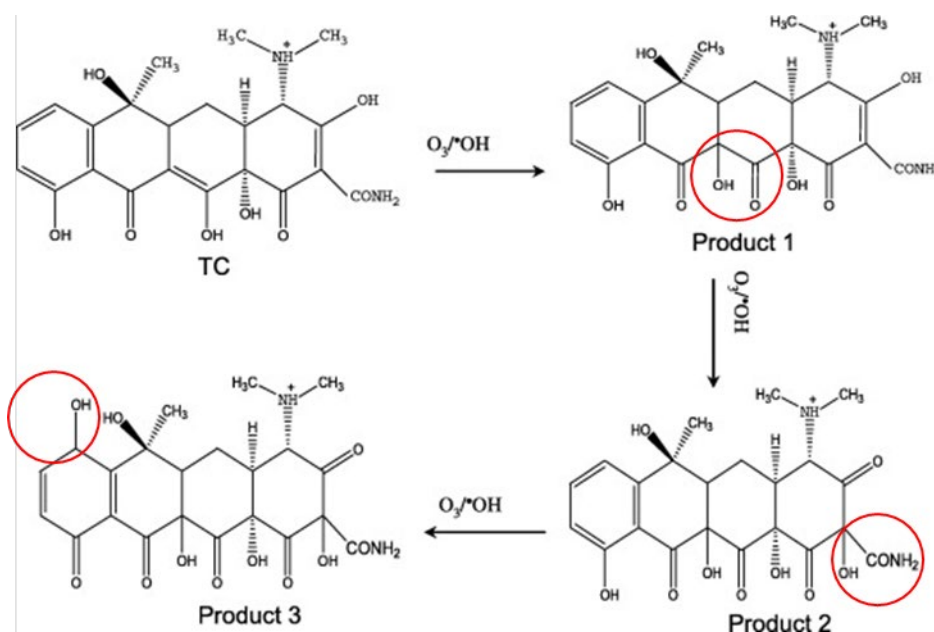


1587

1588 **Scheme 6.** Pathway of intermediate formation during the degradation of AMX by sonication alone, ozonation
 1589 alone and sonozonation at pH 10, 575 kHz, 75 W, 15 mg/L O₃(aq). Reprinted from ref. [78] Copyright (2012), with
 1590 permission from Elsevier.

1591 **Figure S4** shows the LC-APCI-MS of five major intermediates formed during the

1592 degradation of TC by sonozonation, indicating the degradation pathway of TC (Scheme
 1593 6) [80]. As shown in Scheme 7, Product 1 was generated by an initial 1,3-dipolar
 1594 cycloaddition towards the C_{11a}-C₁₂ double-bond and a rearrangement with the hydroxyl
 1595 at position C₁₂. Subsequently, Product 2 was formed via the further oxidization of the
 1596 double-bond C₂-C₃ in Product 1. Product 3 was finally synthesized by O₃ or [•]OH by
 1597 successively attacking ring D (bearing hydroxyl group) of Product 2. Therefore, [•]OH
 1598 dominates the degradation of TC in the sonozonation system [80].



1599

1600 **Scheme 7.** The degradation pathway of TC in the sonozonation system. Reprinted from ref. [80] Copyright (2012),
 1601 with permission from Elsevier.

1602 Recently, we have reported the mechanisms, reactors and effective factors of
 1603 sonozonation for organic degradation [81]. In this review, the applications of
 1604 sonozonation and the roles of effective factors on antibiotic degradation are discussed.

1605 7.2 Application of sonozonation on antibiotic degradation

1606 Kıdak *et al.* have investigated the degradation of AMX by sonozonation at 575
 1607 kHz US [78]. Under the optimized sonozonation conditions - 250 mL of 25 mg/L AMX
 1608 solution, 0.13 mg/L O₃, 575 kHz, 75 W, pH 10, 90 min treatment - the highest
 1609 degradation rate constant ($k_1 = 2.5 \text{ min}^{-1}$), highest mineralization (45% of TOC removal)
 1610 and reduced toxicity ($EC_{50}\% = 67.5$) were achieved, compared with those obtained by

1611 sonication alone ($k_1 = 0.04 \text{ min}^{-1}$ and 10% of TOC removal) and ozonation alone
1612 ($k_1=1.97 \text{ min}^{-1}$ and 32% of TOC removal and $EC_{50}\%= 13.6$) [78]. Based on the k_1 values
1613 obtained by the various processes, the synergistic factor of sonozonation for AMX
1614 degradation was calculated to be 1.24.

1615 Naddeo *et al.* have investigated the degradation of SMX using sonozonation with
1616 20 kHz and 370W/L US [120]. 61% of SMX was removed from 200 mL of a 10 mg/L
1617 SMX solution, with 3.3 g/h of O_3 dose, after 40 min in the sonozonation system, while
1618 51% SMX was removed by ozonation alone [120]. The enhancement of SMX
1619 degradation by sonozonation can reduce the consumption of chemicals, which is
1620 particularly interesting for performing the scale-up of sonozonation process [120].

1621 Guo *et al.* have also investigated the degradation of SMX by sonozonation with 20
1622 kHz and 600W/L US [121]. A 100 mg/L (0.5 mM) SMX solution was treated in a 1.5
1623 L-reactor with 3.0 g/h of O_3 dose, and about 95% of SMX was removed after 5 min
1624 treatment in the sonozonation system, while only 3% and about 85% SMX was
1625 removed by sonication alone and ozonation alone [121].

1626 7.3 Role of effective factors

1627 The RE of antibiotics by sonozonation is influenced by various parameters,
1628 including O_3 concentration/flow rate [79, 80, 120], pH value [78, 79, 80, 120, 121],
1629 initial antibiotic concentration [79, 80], US power/frequency [79, 80], and additives [78,
1630 79, 80], as discussed below.

1631 7.3.1 Effect of gaseous O_3 concentration, flowrate and dosage

1632 In general, O_3 concentration in a gas increases with the yield or dosage of O_3
1633 production under an identical gas flowrate. Naddeo *et al.* have noted that the
1634 degradation of SMX was enhanced by increasing ozone flows in the sonozonation
1635 system, which was attributed to improved O_3 mass transfer [120]. Guo *et al.* have found
1636 that the RE of SMX doubled as O_3 dosage increased from 2 to 5 g/h, because the
1637 increasing ozone concentration was able to improve the mass transfer of O_3 from the

1638 gas to liquid phase [79]. In addition, the increasing O₃ concentration increase the
1639 amount of O₃ molecules and ·OH that were available to react with antibiotics in solution
1640 [79].

1641 Wang *et al.* have also demonstrated that the RE of TC increases with increasing
1642 gaseous O₃ concentration and gas flowrate in a sonozonation system [80]. On the one
1643 hand, k_l values were 0.42, 0.66, 0.85 and 1.34 min⁻¹ at 30, 35, 40 and 50 L/h of gas
1644 flowrate, respectively. The increasing gas flowrate increases the net surface area and
1645 improved O₃ mass transfer from the gas phase to aqueous phase, thus increasing the
1646 volumetric mass transfer coefficient of O₃ [80]. On the other hand, k_l values reached
1647 0.66, 0.77, 0.84 and 1.04 min⁻¹ at 35.8, 44.5, 45.6 and 47 mg/L of gaseous O₃
1648 concentration, respectively. This suggests that the increasing gaseous O₃ concentration
1649 increased the equilibrium O₃ concentration in the aqueous phase, according to Henry's
1650 law. The increasing equilibrium O₃ concentration also improved O₃ mass transfer from
1651 the gas phase to the liquid phase [80].

1652 7.3.2 Effect of pH value

1653 The pathways of ozonation generally include direct oxidation by O₃ molecules,
1654 which is more selective and predominant under acidic conditions, and the indirect
1655 oxidation by ·OH that is formed *in situ*, which is non-selective and predominant under
1656 alkaline conditions [79, 80]. Therefore, the predominant reaction and reaction rate
1657 during ozonation can be controlled by adjusting pH value, which is also considered a
1658 critical factor for the efficiency of sonozonation [79]. The increase of reaction rate
1659 means that a shorter reaction time is required to complete the degradation of antibiotics,
1660 while O₃ consumption and operation costs are reduced [121].

1661 Guo *et al.* have found that the degradation rate of SMX increases with increasing
1662 pH value. SMX has two *pKa* values, of 1.6 and 5.7, resulting in protonated, non-
1663 protonated and deprotonated forms at different pH values. The amino groups are
1664 possible reaction centres that are most susceptible to O₃ electrophilic attack. The non-

1665 protonated form is the predominant form at $\text{pH} < 7$, and is less susceptible to O_3 attack
1666 than the deprotonated form, leading to lower k_l values under acidic conditions (0.29
1667 min^{-1} at $\text{pH} 3$; 0.30 min^{-1} at $\text{pH} 5$). At $\text{pH} 7$, SMX molecules were converted into the
1668 completely deprotonated form, which had a higher reactivity towards O_3 molecules.
1669 Under basic conditions, the oxidation of SMX was enhanced due to the generation of
1670 numerous $\cdot\text{OH}$ species (0.42 min^{-1} at $\text{pH} 7$; 0.50 min^{-1} at $\text{pH} 9$). Consequently, the
1671 degradation rate of SMX under basic conditions was higher than under acidic
1672 conditions [79].

1673 Furthermore, the enhancement of sonication on SMX degradation by ozonation
1674 varied by 6–26% under different pH values, and the highest enhanced effect was
1675 observed at $\text{pH} 5$ [121]. This suggests that sonication promoted the diffusion of O_3
1676 molecules in water under acidic conditions and increased the contact area between O_3
1677 and SMX, resulting in increased RE of SMX by direct-oxidation with O_3 molecules.
1678 Under neutral and alkali conditions, sonication increased the degradation rates of SMX
1679 by only 6-7%. This indicates that sonication slightly enhanced O_3 decomposition and
1680 the yield of $\cdot\text{OH}$, which is responsible for the indirect-oxidation [121].

1681 TC degradation rate has also increased as the pH value increased from 3 to 9 in a
1682 sonozonation process [80]. Similarly, there are four different species of TC molecule,
1683 TCH_3^+ , TCH_2 , TCH^- and TC^{2-} , in which the protonation-deprotonation reactions
1684 depend on pH value. The deprotonated TC with a positively charged group at higher
1685 pH values is more easily attacked by O_3 molecules and/or $\cdot\text{OH}$ than TC itself. Thus, the
1686 TC degradation rate increases with increasing pH [80]. Likewise, AMX is a hydrophilic
1687 and weak polyprotic acid with three pK_a values of 2.67, 7.11 and 9.55 at 37°C . At pH
1688 10, dissolution is favoured for the more degradable forms of AMX when the amine is
1689 deprotonated and a pair of electrons is available for electrophilic attack, while the
1690 increased solubility of AMX at $\text{pH} 10$ leads to higher reaction rates in the presence of
1691 the readily abundant radicals formed in the 575 kHz US field [78].

1692 7.3.3 Effect of initial antibiotic concentration

1693 Since the concentrations of O₃ and •OH available are almost identical under the
1694 same operation conditions in a sonozonation system, and are independent of the initial
1695 antibiotic concentrations, the degradation rate decreases mostly with increasing
1696 antibiotic concentration. For example, the k_l value of SMX degradation decreased
1697 three-fold (from 0.37 to 0.09 min⁻¹) as SMX concentration increased from 50 to 400
1698 mg/L in a sonozonation system. The additional reason for this is the fact that the
1699 competing reactions between SMX and its degradation products gradually turned
1700 predominant with the increasing initial SMX concentration. Such competing reactions
1701 reduced the reaction rates of SMX with O₃ and •OH [79]. Similarly, the TC degradation
1702 rate also decreased with increasing initial TC concentration in a sonozonation system,
1703 and the k_l value decreased from 0.92 to 0.59 min⁻¹ when TC concentration increased
1704 from 200 to 800 mg/L [80].

1705 7.3.4 Effect of power density of US

1706 Increasing US power density can generally enhance the turbulence effect, resulting
1707 in increased antibiotic degradation rates, as the enhanced turbulence favours O₃ mass
1708 transfer from the gas to liquid phase [79]. It has been speculated that powerful
1709 sonication enhances mechanical mixing, making O₃-containing bubbles smaller and
1710 reducing the thickness of liquid films [80]. In addition, more O₃ molecules can be
1711 decomposed to generate more ROS under more powerful sonication. For example, the
1712 k_l values of SMX degradation reached 0.25, 0.26 and 0.30 min⁻¹ at 400, 600 and 800
1713 W/L of power density in a sonozonation system, respectively [79]. Moreover, the TC
1714 degradation rate increased with increasing power density, and the k_l values of TC
1715 degradation reached 0.57, 0.71, 0.90, 1.04, 1.74 and 2.60 min⁻¹ at 0, 85.3, 125.4, 142.8,
1716 169.8 and 218.6 W/L of power density, respectively [80].

1717 7.3.5 Other concerning issues

1718 The chemical structures and hydrophobicity of antibiotics generally influence their

1719 degradation kinetics and efficiency [120]. Little competitive oxidation of SMX,
1720 diclofenac and carbamazepine has been observed in a mixing solution under
1721 sonozonation, showing that the simultaneous presence of SMX, diclofenac and
1722 carbamazepine is not an obstacle for degradation via sonozonation [120].

1723 This indicates that the oxidation of TC by $\cdot\text{OH}$ that are generated *in situ* dominates
1724 the degradation of TC by sonozonation. By contrast, the addition of the radical
1725 scavenger *t*-butanol can accelerate the SMX degradation rate [79], and it has been
1726 speculated that the direct oxidation of SMX by O_3 molecules is the dominant pathway
1727 in the sonozonation system. The presence of H_2O_2 improved the TC degradation rate
1728 when the H_2O_2 concentration did not exceeded 10 mM, while the presence of *t*-butanol
1729 inhibited the TC degradation rate to some extent [80].

1730 Alkalinity and humic acid species reduced the RE (50% decrease) by sonication
1731 alone as radical reactions control the degradation of AMX [78]. However, the addition
1732 of alkalinity, humic acid and both did not significantly change the removal rate of AMX
1733 during both ozonation and sonozonation, since, in this case, the reaction of AMX with
1734 O_3 molecules controls the degradation [78].

1735 Besides enhancing the degradation of antibiotics by ozonation, sonication can
1736 simultaneously promote the mineralization and detoxification of antibiotics in aqueous
1737 solutions. The Microtox toxicity test has been used to find the concentration value of
1738 the treated effluents that affects 50% of the microorganisms in a solution (EC50), and
1739 thus to assess the toxicity of solutions. The initial AMX solution shows high toxicity
1740 with a EC50 value of 14% [78]. Under sonozonation (250 mL of 25 mg/L AMX, 575
1741 kHz, 75 W/L US power, 0.13 mg/L O_3 , pH 10.0, 90 min treatment), the EC50 value
1742 decreased to 10.87% and 13.59% after treatment with sonication and ozonation alone,
1743 respectively, showing that the intermediates with higher toxicity were formed during
1744 the degradation of AMX. By contrast, the EC50 value increased to 67.48% under
1745 sonozonation, indicating that fewer intermediates were formed with a higher
1746 mineralization degree [78]. For the degradation of 100 mg/L SMX by sonozonation,

1747 with 20 kHz, 600 W/L US and 5.0 g/h O₃ at pH 7.0 for 30 min, the BOD₅/COD ratio
1748 increased from 0 to 0.54 after sonozonation treatment and the biological toxicity of the
1749 solution was reduced [79].

1750 During the degradation of 400 mg/L TC by sonozonation with 20 kHz and 142.8
1751 W/L of US at pH 7, Wang *et al.* found that the COD removal reached 91% after 90 min
1752 treatment, while very low COD removal was obtained by sonication alone, due to the
1753 lower production of free radicals by sonication at 20 kHz. 76% of COD removal was
1754 achieved by ozonation alone at a gas flow rate of 35 L/h, which contained 45.6 mg/L
1755 O₃ [80]. The initial TC solution resulted in 24% death of the crustaceans after 24 h of
1756 exposure. However, the acute toxicity reached its maximum after 10 min of
1757 sonozonation treatment, and the mortality was as high as 95%. The acute toxicity then
1758 gradually decreased to 80% in 70 min and 60% in 90 min of treatment [80].

1759 Finally, it should be mentioned that most of the reported work, whether it used
1760 sonication alone or hybrid processes, made use of standard solutions and simulated
1761 wastewater to investigate the removal of antibiotics. Only a few studies have focused
1762 on the comparison of simulated and actual wastewater. Higher degradation rates (R_d)
1763 have been found for AMP in simulated urine than in distilled water ($\rho > 1$, $\rho = R_d$ in
1764 matrix/R_d in distilled water), which indicates that sonochemical processes are suitable
1765 for the removal of antibiotics in complex matrices [46]. OXA was difficult to mineralize
1766 (360 min) under sonication, while it can be completely mineralized using non-adapted
1767 microorganisms from a municipal wastewater treatment plant, which demonstrates that
1768 the sonication process transformed the antibiotic into substances that are bio-treatable
1769 using a typical aerobic biological system [128]. Furthermore, the highest (the most
1770 hydrophobic, i.e., CLX) and lowest (the most hydrophilic, i.e., CPD) R_d of antibiotics
1771 were observed in simulated hospital wastewater and seawater. A higher degradation rate
1772 for CLX was obtained in simulated hospital wastewater and seawater than in distilled
1773 water ($\rho > 1$), probably due to the salting-out effect exerted by matrix components. The
1774 moderate inhibition of CPD removal in hospital wastewater and seawater, compared to

1775 distilled water, has been attributed to competition by $\cdot\text{OH}$ with the other substances in
1776 the matrices [129]. Compared with synthetic water, the RE of CIP for 15 min and
1777 mineralization for 60 min in real wastewater from a municipal wastewater treatment
1778 plant was decreased by 13.6 and 18.9% respectively, which illustrates that the treatment
1779 of CIP and TOC by the sono/ Fe^{2+} / H_2O_2 process is significantly hampered in a real
1780 matrix [32].

1781 Another important factor to consider is the fact that almost all research on the the
1782 removal of antibiotics by US involves processes that are performed on a bench scale,
1783 thus further pilot-scale investigations are recommended. Factors that should be
1784 considered when using pilot-scale systems include energy consumption by US, mass
1785 transfer, pH adjustment and application in real wastewater samples, temperature
1786 controls, *et al.*

1787

1788 **Declaration of Competing Interest**

1789 The authors declare that they have no known competing financial interests or
1790 personal relationships that could have appeared to influence the work reported in
1791 this paper.

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1797

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