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1	Sonochemical processes for the degradation of antibiotics in
2	aqueous solutions: a review
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14	
15	Abstract
16	Antibiotic residues in water are general health and environmental risks due to the
17	antibiotic-resistance phenomenon. Sonication has been included among the advanced
18	oxidation processes (AOPs) used to remove recalcitrant contaminants in aquatic
19	environments. Sonochemical processes have shown substantial advantages, including
20	cleanliness, safety, energy savings and either negligible or no secondary pollution. This
21	review provides a wide overview of the different protocols and degradation
22	mechanisms for antibiotics that either use sonication alone or in hybrid processes, such
23	as sonication with catalysts, Fenton and Fenton-like processes, photolysis, ozonation,
24	etc.
25	
26 27	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, cephalexin; 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

49 **1 Introduction**

Antibiotics were first discovered in 1928 by Alexander Fleming and the term was 50 first used in 1942 by Waksman and his collaborators [1, 2]. Initially, the classical 51 definition of antibiotics was: chemotherapeutic agents that can eradicate or restrain the 52 growth of microorganisms, including bacteria, fungi or protozoa [3, 4, 5]. Antibiotics 53 have been widely used for the treatment of infectious diseases in humans and animals 54 to the present day [4]. Macrolides, β -lactams, quinolones, tetracyclines, and 55 sulfonamides are the most consumed antibiotics [6]. Since the 1990s, however, 56 antibiotic residues have been broadly observed in aqueous matrices and soil as well as 57 in microorganism, animal and human bodies over the world thanks to the appearance 58 59 of the advance analytical technologies [5, 6].

The presence of antibiotic residues in the environment can either be caused by 60 their continuous discharge or inherent high persistence [7]. For example, CEFX and 61 CTX have attained levels surpassing 1000 µg/L in urban wastewater samples in Hong 62 Kong and Shenzhen, South China [8]. 11 antibiotics in hospital wastewater and sewage 63 treatment plants (STPs) have been identified in Beijing, China. Fluoroquinolones, in 64 particular, were found to be the most abundant, with a highest concentration of 16.8 65 μ g/L in the hospital samples. The maximum concentrations of antibiotics in STPs and 66 hospital wastewater were 1-3 orders of magnitude higher than those in the surface water 67 from the Wenyu River and groundwater [9]. 68

Antibiotic concentrations in wastewater and environmental water bodies are 69 obviously correlated with variations in annual consumption data [10]. Some antibiotics, 70 71 such as penicillins, are easily degraded, whereas others, such as fluoroquinolones (e.g. CIP), macrolides (e.g. TYL) and tetracyclines, are considerably more persistent, 72 resulting in their residues being found in the environment, spreading and accumulating 73 in organisms [10]. Antibiotic occurrence in water is generally in the range of a few to 74 hundreds ng/L [3, 5, 6, 10]. For examples, 77 antibiotics have been reported in 75 Danjiangkou Reservoir in China, but most were present at lower than 5.0 ng/L and 76

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

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

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

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

Due to the limitations of physical and biological processes, AOPs have gradually emerged as means for the degradation/mineralization of organic pollutants over recent decades [31]. As non-selective oxidation technologies, AOPs have attained the total removal of antibiotics, efficient reductions in toxicity and antimicrobial activity, and have also increased biodegradability [17, 31-38]. The generation of reactive oxygen species (ROS), such as 'O, 'O²⁻, 'OH, 'OOH, H₂O₂, etc., via various methods was the origin of AOPs [4, 10, 21, 22, 31, 33, 39-48].

Hydroxyl radicals ('OH) and other ROS are released by ozone (O₃) decomposition 118 in water during the ozonation process. Meanwhile, O3 often selectively reacts with 119 nucleophilic molecules. However, the high costs of equipment, maintenance and 120 operation, the high quantities of energy required, lower mass transfer, extreme pH-121 dependence and potential effluent ecotoxicity limit the application of ozonation [49, 122 123 50]. Photocatalysis has often been applied under ambient conditions and may gain energy from sunlight with the advantages of simple operation and scale-up applicability, 124 but it also suffers from mass-transfer limitations, and is affected by catalyst amount, 125 light wavelength, radiation intensity, pH and water quality. Additionally, the catalysts 126 consumed need to be specially treated or recycled, causing high overall costs [19-22, 127 26, 27, 30]. Electrochemical degradation is an effective, versatile, cost-effective, easy 128 and clean technology, and is suitable for the treatment of toxic wastewater that contains 129 high-concentration antibiotics and COD. However, the RE depends on the nature and 130 structure of the electrode material, electrolyte composition, the applied current and the 131 diffusion rates of substrates to the active sites of the anode. The low flow rates and high 132

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

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

In theory, a large variety of organic pollutants are capable of being degraded by sonication without additional chemicals. Thus, sonication is usually seen as a green and safe technique to perform wastewater treatment. However, the sonolysis of organic contaminants has limited efficiency and consumes considerable amounts of energy [23, 45, 68]. To improve the RE and reduce energy consumption, sonication-based combinations, such as sonocatalysis [69-73], Sono/Fenton [19, 21, 35, 43, 44, 74-77],
sonication-ozonation (Sonozonation) [78-81], sonication-persulfate (Sono/PS) [82],
sonophotocatalysis (Sono/Photo) [31, 39, 83-85], sonoelectrochemical degradation
[86-88], sonication-microwaves [89], sonication-hydrodynamic cavitation [90], and
ultrasound-assisted biological processes [91-93], have attracted great attention.

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

173 2

Antibiotic degradation by sonication alone

174 2.1 Mechanisms of sonolysis

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

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



199 200

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

However, the sonochemical degradation products were rarely mineralized. About 100% of 180 μ M 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 (BOD₅/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

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

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

Overall, two reaction mechanisms are presumably responsible for the sonolysis of antibiotics: pyrolysis and oxidation by the '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.



Figure 1 Schematic diagram of ultrasonic horn-type (a) and bath-type (b) setups for degradation. Reprinted from
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237

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

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

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

256

Antibiotics	s Fug/Pr Pug(W) t C./V pH RF (%) Other results		Rofs					
Anubiotics	(kHz/W)	1 US(**)	L	C ₀ / V	pn	KE (70)	Other results	Keis.
			(min)	(mg/L)/mL				
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	[124]
							cavitation bubbles.	
СРХ	24/200	17.3	60	20/50	6.5	~52	BOD ₅ /COD ratio was	[127]
							raised.	
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/	354/-	26.4	75-	40 µM/300	6.5	-	Hydrophobicity was	[129]
CPX/CDX/			120				critical.	
OXA/CLX								
CIP	520/-	13.8	120	15/150	3.0-	57	RE is pH-dependent.	[38]
					10.0			
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	3.0	100	~ 0 mineralization was	[130]
				mM/300			obtained.	
DXC	600/60	34.8	480	98.8/100	5.5	100	30% of COD was	[96]
							eliminated.	
SMZ	800/100	-	120	180 μM/-	-	100	8.31% TOC was reduced.	[41]

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

257 Note: Fus: ultrasonic frequency; PE: electrical power input; PUS: the power dissipated by the reactor (calculated using

the calorimetric method); t: sonication time; C₀: initial antibiotic concentration; V: volume of solution; RE: removal

259 efficiency; Refs.: references.

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

269 2.3 Role of effective factors

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

279 2.3.1 Effect of US frequency and power

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

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

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

2.3.2 Effect of Physicochemical properties of antibiotics

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

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

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

327 2.3.3 Effect of pH value

The effect of pH value on antibiotic degradation is also related to the properties of 328 antibiotics (i.e., ionic species or molecule states). Some antibiotics are more 329 sophisticated, being zwitterions (a molecule containing both a basic and an acidic 330 group). For example, LEV has two different acid-dissociation constant values (pKa 5.7 331 and 7.9) [124]. De Bel, et al. have explored the effect of pH on CIP sonolysis at 520 332 kHz [38]. The k_1 value (0.021 min⁻¹) at pH 3 is almost 4-fold higher than those at pH 7 333 (0.0058 min⁻¹) and pH 10 (0.0069 min⁻¹). The solution can even be considered readily 334 biodegradable after sonication at pH 3 ($BOD_5/COD > 0.4$) [38]. Degradation is clearly 335 faster when the main part of the CIP molecules carries an overall positive charge. These 336 positively charged molecules will accumulate at the negatively charged liquid-bubble 337 interface, where the concentration of ROS and the reaction temperature are higher. 338 Hence, degradation is faster [38]. Similarly, Villegas-Guzman, et al. have found that 339 the highest sonolysis of DXC was achieved under 600 kHz sonication at pH=3 [96]. 340 Acidic media also favour the sonochemical degradation of DXC (pH=3.0) [30], LEV 341

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

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

346 2.3.4 Effect of temperature

Generally, the degradation rate of antibiotics increases with increasing temperature 347 [33, 40, 125]. The influence of temperature on the sonodegradation of antibiotics is 348 complicated. As far as we know, high temperature usually results in a high solvent 349 vapour pressure, followed by the formation of more water-vapour-containing cavitation 350 351 bubbles, causing the cavitation bubbles to collapse less violently, which leads to reduced 'OH production. However, the reduction of the viscosity and surface tension at 352 353 high temperatures leads to a low threshold intensity for cavitation, which can increase the number of cavitation bubbles, and then promote the generation of 'OH and HOO'. 354 Moreover, the strengthened reactions of the hydroxyl radicals and mass transfer at high 355 temperatures are favourable to the removal of antibiotics [33, 40, 111, 125]. According 356 to De Bel et al., increased temperature (15-45 °C) leads to faster CIP degradation (k_1 357 was increased from 0.0055 to 0.0105 min⁻¹). The low apparent activation energy (17.5) 358 359 kJ/mol) suggests that the degradation of CIP is diffusion controlled (usually in the range of 12-15 kJ/mol) [125]. Higher temperature (in the range of 30-60 °C) facilitates the 360 removal of FLU by the Sono/H₂O₂ process [111]. 3% of FLU was removed from 200 361 mL of 1 mM aqueous FLU solutions for 120 min under 40 kHz and 120W sonication 362 at 60 °C and pH 4 in the presence of 20 mM H₂O₂. The activation energy for the 363 degradation of FLU was 6.510 kJ/mol [111]. 364

365 2.3.5 Effect of initial concentration of antibiotics

In general, low concentrations of antibiotics favour their sonochemical degradation; RE decreases with increasing initial concentration [30, 31, 36, 41, 69, 94-100]. The degradation of antibiotics is limited by the available surface at the bubble– liquid interface. According to the Arrhenius law, for example, the apparent activation energy for the sonochemical degradation of CIP has been determined to be 17.5 kJ/mol, which suggests that the degradation of CIP is diffusion controlled. A Langmuir-type heterogeneous-reaction-kinetics model could be used to explain why the k_1 value increases with decreasing initial CIP concentration from 0.0204 min⁻¹ (C_0 : 0.15 mg/L) to 0.0009 min⁻¹ (C_0 : 150 mg/L). According to the model, the molecules at the interface region of the cavitation bubbles can be readily oxidized by the formed 'OH [125].

376

2.3.6 Effect of additives

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

Due to Ar's physical properties (e.g. solubility, thermal conductivity and specific 389 heat ratio), an Ar atmosphere favours sonolytic activity compared to diatomic gases [36, 390 109]. Gao, et al. have reported that the sonolytic degradation of SMZ is accelerated in 391 the presence of Ar or O₂, but inhibited by N₂ [41]. Meanwhile, the SMZ degradation 392 rate was slightly inhibited by NO_3^- , Cl^- and SO_4^{2-} , which is consistent with the 393 sonochemical degradation of TC [99], but significantly improved by HCO₃ and Br⁻ 394 [41]. The enhancement of TC degradation by adding HCO_3^- has also been 395 demonstrated [99], while a negligible influence was observed when adding mannitol or 396

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

Zhang, et al. have investigated the degradation of sulfa antibiotics by potassium 408 ferrate in combination with sonication (Sono/Fe(VI)) [75]. SDZ, SMR and SMX were 409 all well degraded by sonication, and the reaction process was in accordance with 410 pseudo-second order reaction kinetics; the REs of SDZ, SMR and SMX were 77.5, 82.5 411 and 82.5% for 30 min sonication, respectively. H₂O₂ was often added to the sonication 412 system to enhance antibiotic degradation [36, 99, 100, 132]. Matouq, et al. have 413 investigated AMX degradation at 2.4 MHz sonication, with the addition of H₂O₂ 414 415 providing a great increase to the RE of AMX [132]. The effect of adding H_2O_2 to the sonochemical degradation of antibiotics has been summarized in Table 2. 416

As seen in Table 2, the sonolysis of TC, LEV, NOR, MTZ, OFX and FLU, etc., has been conducted in a US-frequency range of (20-2400 kHz) and a US-power range of (100-750 W). Their REs are located in the range of 1.88%-81.00%, under sonication alone, and 0-30%, under oxidation alone with 0.29-333.00 mM H₂O₂ for 30-240 min. In some cases, significantly higher REs (5.9-93%) were given by sono/H₂O₂ processes than in those performed with sonication alone, or oxidation with H₂O₂ alone. In addition, 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	С _{н2О2}	F_{US}/P_E	t	C ₀ /V	pН	RE _{H2O2}	RE _{Sono}	RE _{Sono/H2O2}	Refs.
	(mM)	(kHz/W)	(min)	(mg/L)/mL		(%)	(%)	(%)	
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-	~30.0	-	70.0	[132]
					5.5				

425 Note: CH202: H2O2 concentration; FUS: ultrasonic frequency; PE: electrical power input; t: sonication time; Co: 426 initial antibiotic concentration; V: volume of solution; RE: removal efficiency; Refs.: references.

However, the addition of H₂O₂, used as a radical promoter, does not always 427 promote sonication processes [20, 32]. When sonication was applied without H_2O_2 , 428 degradation and mineralization (35.8 and 22.6%, respectively) were similar to the 429 results obtained in sono/H₂O₂ processes (36.5 and 24.4%, respectively) [32]. Therefore, 430 excess H₂O₂ can act as a 'OH scavenger and decrease the RE of antibiotics, resulting in 431 the presence of an optimal amount of H₂O₂ for the sonochemical degradation of the 432 target compounds. 433

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

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

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

449

3 Degradation of antibiotics by sonocatalysis

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

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

468 3.1 Mechanisms of sonocatalysis

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

- 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.





476

Figure 2 The mechanisms of antibiotic removal by sonocatalysis.

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

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

unsaturated species produced from the sonolysis of metal carbonyls are likelycandidates [37, 52].

494 On the other hand, solid catalyst particles may increase the density of microbubbles, meaning that more ROS will be produced during bubbles collapse. H₂O₂ 495 formation is significantly increased due to the dispersion of catalysts under sonication, 496 indicating that the dispersed catalyst particles can act as additional nuclei for the 497 pyrolysis of water molecules and the formation of 'OH [40]. As a result, increased 498 radical transfer from cavitation bubbles to the interface and bulk solution is promoted, 499 and with it the RE of antibiotics [37, 52, 126]. In homogeneous systems, catalysts, such 500 as Fe^{2+} , promote radical formation via the decomposition of H_2O_2 , formed under 501 502 sonication, to enhance and accelerate the degradation of antibiotics [137, 138]. For example, the sonolysis of SMZ was accelerated in the presence of ferrous ion. The 503 synergetic effect was mainly attributed to the production of additional 'OH via Fenton 504 chemistry [41]. 505

506 3.2 Application of sonocatalysis in antibiotic degradation

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

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

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

Antibiotics	Catalyst	F_{US}/P_E	t	C ₀ /V	рН	RE _{Catal} .	REsono	RE _{Sono/Catal}	SF	Refs.
		(kHz/W)	(min)	(mg/L)/mL		(%)	(%)	(%)		
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	35/65	120	10/100	6.0	<25.0	8.1	65.0	~2.0	[135]
	TiO ₂ /Montmorillonite									
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	37/256	15	50/50	7.0	28.2	12.8	87.6	2.1	[104]
	ZnO/nano-cellulose									
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/LZrO 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	40/300	80	47.6/100	6.5	32.6	6.8	97.6	2.5	[102]
	double hydroxide									
NOR	0.3 g/L multilayer	40/200	80	2.0/50	7.5	19.2	6.4	47.5	1.9	[140]
	ZnO nanoflowers									
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-	40/300	45	20/100	5.5	15.1	10.4	96.1	3.8	[103]
	biochar									
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]

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

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 = *REsono/Catal/(REsono+REcatal)* [71, 81, 109];
529 Refs.: references.

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

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

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

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

558 3.3 Role of effective factors

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

564 3.3.1 Effect of US frequency

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

580 3.3.2 Effect of pH value

Hoseini, *et al.* have investigated the effect of pH on TC degradation using sonocatalysis with TiO_2 nanoparticles, and it was found that an increase in pH attenuated TC degradation [105]. The relatively high *RE* values of sonocatalytic degradation for PG using MgO and SMX, with SWCNs nanoparticles, were also obtained under acidic conditions at pH 3.0 and pH 3.5, respectively [40, 141]. Seid-Mohammadi, *et al.* have found that pH value clearly affects the removal of CPX in sono/H₂O₂/NiO hybrid process, and that process efficiency was reduced at pH 9, with pH 3 giving the highest RE (93.8%) [74].

589

3.3.3 Effect of temperature

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

603 3.3.4 Effect of initial concentration

Hoseini, *et al.* have investigated the effect of initial TC concentration on its degradation by sonocatalysis using TiO_2 nanoparticles, and it was found that an increase in initial TC concentration attenuated TC degradation [105]. Similarly, the *RE* values of NOR and AMP also decreased with increased initial concentrations [101, 107].

608 3.3.5 Effect of catalyst amount

Gao, *et al.* have found that increases in both the MnSO₄ concentration of the wet
impregnation solution and the catalyst dosage enhanced the sonocatalytic degradation
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 RE, while the presence of inorganic and organic scavengers suppresses the performance 615 of the sonocatalytic removal of antibiotics [71, 102, 135]. Furthermore, the degradation 616 mechanisms, namely the interactions between 'OH and the antibiotics, can be 617 demonstrated [71]. For example, the presence of ethanol suppressed SSZ degradation 618 due to the quenching of 'OH, while the addition of K₂S₂O₈ and H₂O₂ increased the RE 619 due to the formation of SO_4^{\bullet} and extra OH, respectively [52, 54, 73, 74, 97, 111, 126, 620 128]. 621

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

In addition, Dehghan, *et al.* have investigated the effect of adding IO_4^- on the sonocatalytic degradation of AMX with a ZnO@Fe₃O₄ magnetic nanocomposite. It was observed that the degradation rate was accelerated in the presence of IO_4^- , showing the greater oxidation potential compared to the other oxidant agents [134]. Moreover, peroxydisulfate (S₂O₈²⁻) has been extensively investigated as a means to enhance the sonocatalytic degradation of antibiotics [109, 140], which is discussed particularly in chapter 5.

638

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

with CeO_2/Fe_3O_4 , and it was found that the addition of O_2 and Ar improved the RE of OTC by up to 78 % and 76 %, respectively [106]. The enhancement of adding gases on RE is attributed to an increase in the number of nucleation sites in aqueous media, and enhancements in the pressure and temperature of collapsing cavitation bubbles [103].

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

651 3.3.7 Reusability of catalysts

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

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

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

4.1 Mechanisms of sono/Fenton processes

Fenton oxidation is one of the AOP techniques that has been most widely applied 672 for antibiotic removal [17, 32-35]. So far, the Fenton processes that have been applied 673 to the degradation of antibiotics can be divided into: classic homogeneous Fenton 674 processes; and heterogeneous Fenton processes or Fenton-like processes. The classic 675 Fenton reaction usually occurs in acidic homogeneous systems where Fe²⁺, or other 676 metal ions (Cu^{2+} , Zn^{2+} , etc.), and H_2O_2 exist simultaneously. By contrast, Fenton-like 677 reactions generally occur in acidic heterogeneous systems where solid catalysts (Fe⁰, 678 Fe₃O₄, etc.) and H₂O₂ exist simultaneously. 679

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

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
(1)

685

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + OOH^-$$
 (2)

$$Fe^{3+} + OOH \rightarrow Fe^{2+} + O_2 + H^{+-}$$
(3)

In sono/Fenton processes, the radical reactions near the hotspots and/or in the bulk liquid dominate the degradation of antibiotics [96]. One the one hand, sonication can improve mass transfer, thus enhancing the generation of 'OH and reducing the consumption of chemicals [47, 48]. On the other, adding the right amount of Fe^{2+} (e.g., 691 1.0 mM) can also enhance 'OH production via the reactions between Fe^{2+}/Fe^{3+} and H_2O_2 ,

including H_2O_2 that is formed *in situ* [17, 30, 34, 41, 43, 46, 69, 95, 96, 97, 139].

Unfortunately, excessive H_2O_2 and Fe^{2+} negatively influence the degradation of 693 antibiotics [30, 34, 96], since large doses of Fe^{2+} and H_2O_2 can act as scavengers for 694 'OH in aqueous matrices [34, 41, 95, 96]. In addition, the pH value of solutions 695 significantly affects the degradation of antibiotics [111]. For pH > 4, the total 696 concentration of Fe^{2+} and Fe^{3+} decreases considerably as their complexes and 697 hydroxides are formed in solution. At pH < 2, Fe^{2+} and Fe^{3+} exists as $[Fe(H_2O)_6]^{2+}$ and 698 $[Fe(H_2O)_6]^{3+}$ respectively, and the regeneration of Fe^{2+} in the form of $[Fe(H_2O)_6]^{2+}$ from 699 $[Fe(H_2O)_6]^{3+}$ is slow. Meanwhile, H₂O₂ forms oxonium ions (H₃O₂⁺). These are more 700 stable than H₂O₂ and their reactivity with ferrous ions decreases. In addition, the 701 scavenging effect of 'OH by H^+ is enhanced at pH < 2 [111]. Therefore, the optimal pH 702 range for classic Fenton reactions is 2-4 [21, 22, 41,111]. Also, the pH value affects the 703 chemical structures of the antibiotics, thus influencing REs in sono-Fenton process [96, 704 99]. 705

4.2 Application of sono/Fenton processes on antibiotic degradation

Wang, *et al.* have reported the degradation of 50 mg/L TC via sonication at 20 kHz and 100 W US in 1 L solution at pH 6, in the presence of 0.2 mM Fe²⁺ and 2.0 mM H₂O₂ [34]. Consequently, an RE of 91.3% was achieved in 60 min using this sono/Fenton process, which is higher than the sum of those obtained under Fenton (70.2%) and sonication alone (6.7%). Meanwhile, mineralization reached 45.8% in the sono/Fenton process, resulting in the toxicity of the TC solution being significantly decreased [34].

Labrada, *et al.* have studied CIP degradation in wastewater using a homogeneous sono/Fenton process at high frequency [32]. 100 mg/L CIP was sonicated with 580 kHz and 30.6 W US in a 250 mL solution at pH 3, in the presence of 2.4 mM Fe²⁺ and 14.2 mM H₂O₂. An RE of about 98.4% was achieved using this sono/Fenton process in 15

min. However, the RE obtained by sono/Fenton is lower than the sum of those obtained 718 under Fenton and sonication alone (96.4% and 9.3%). However, the mineralization 719 reached 60% using the sono/Fenton process after 60 min [32]. Ammar et al. have 720 investigated the degradation of 500 mg/L MTZ by sonication at 20 kHz US in a 200 721 mL solution at pH 3.0 in the presence of 3 mM Fe^{2+} and 60 mM H_2O_2 [113]. The results 722 indicate that 98% of MTZ was removed using the sono/Fenton process in 180 min at 723 30 °C, which is higher than those obtained by sonication alone (42%) and Fenton 724 725 process alone (90.0%), but is lower than sum of REs of the two individual processes [113]. At 40 kHz, 261.2 mg/L FLU was sonicated with 120 W US in a 200 mL solution 726 at pH 4.0 in the presence of 4 mM Fe^{2+} and 20 mM H_2O_2 [111] As a result, an RE of 727 93% was achieved using the sono/Fenton process in 120 min at 60 °C, which is 728 obviously higher than that (73%) obtained by the Fenton process alone [111] 729

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

4.3 Mechanisms of sono/Fenton-like processes

The Fenton process requires a large amount of Fe^{2+} and acidic conditions, which 734 requires neutralization with alkaline, resulting in large-scale sedimentation and high 735 costs. With the development of Fenton-like technologies, the drawbacks of the 736 conventional Fenton process have been overcome to some extent [44]. Fe^0 , Fe_3O_4 737 particles and their nanoparticles are important catalysts to promote the decomposition 738 of H₂O₂ for the formation of 'OH [21, 22, 33, 43, 44]. Unfortunately, the solid catalysts 739 may be poisoned during Fenton reactions, nano-catalysts particles can aggregate and 740 solid-catalyst passivation can occur, thus decreasing the degradation rate and limiting 741 potential applications [21, 22, 33, 119]. Therefore, sonication has been applied in the 742 Fenton-like process to maintain the activity of catalysts and improve antibiotic removal. 743 744 The mechanism of sono/Fenton-like processes is shown in Figure 3.



745

Figure 3 Mechanism schematic of sono/Fenton-like processes. Reprinted from ref. [33] Copyright (2016), with
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As shown in Figure 3, solid-liquid interfacial iron corrosion, bulk homogenous oxygen activation and Fenton reactions are the main reaction pathways in sono/Fenton processes, during which sonication plays both mechanical and chemical roles [35]. The antibiotics and intermediates adsorbed onto the Fe₃O₄ surface are oxidized preferentially [33]. 'OH, 'O₂ and H₂O₂, formed *in-situ* on the catalyst surface, have been identified as the dominant reactive species in Fenton-like processes [21, 22, 33, 35, 44].

755 Figure S2 exhibits the LC/MS analysis of the intermediate formation during the degradation of LEV in a sono/H₂O₂/Fe₃O₄ (magnetic nanoparticles) process [43]. The 756 degradation pathway of LEV is shown in Scheme 2. The formation of isatin and 757 anthranilic acid analogues is attributed to the oxidation of LEV by 'OH. The 758 demethylation of the piperazinyl ring and the degradation at the oxazinyl group result 759 in the generation of the other two intermediates [43]. Unfortunately, this study does not 760 provide the mineralization data of LEV and toxicity variation of LEV solutions by the 761 treatment. 762



763 764 <u>Sche</u>

765

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

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

767 degradation

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

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

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

CLA	0.3 g/L ZnS	20/75	60	10/100	3.0	31.4	~8.0	61.2	~1.56	[119]
	quantum									
	dots/SnO ₂ , 6									
	$mM \ H_2O_2$									
RXM	0.3 g/L ZnS	20/75	60	10/100	3.0	36.4	~12.0	65.5	~1.35	[119]
	quantum									
	dots/SnO2, 6									
	$mM \; H_2O_2$									
NOR	0.25 g/L	20/240	30	5/200	7.0	46.7	<5.0	91.5	>1.77	[20]
	nano-Cu ⁰ or									
	micro-Cu ⁰ , 20									
	$mM \; H_2O_2$									
CEX	7.5 mg/L NiO,	40/-	90	40/<500	3.0	-	-	93.0	-	[74]
	$30\ mL/L\ H_2O_2$									
CLM	0.2 g /L Fe ⁰ , 1	130/500	150	45/-	3.0	~40.0	~30.0	95.0	~1.36	[21]
	$M \; H_2O_2$									
TNZ	0.2 g /L Fe ⁰ , 1	130/500	150	45/-	3.0	~20.0	-	93.0	-	[22]
	$M H_2O_2$									

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

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

Ma, *et al.* have investigated the degradation of NOR via the ultrasound-enhanced nanosized zero-valent copper (Cu^0) activation of hydrogen [20]. Compared with the silent degradation system, significantly enhanced NOR removal was obtained in the sono/Fenton-like process. The Cu^+ released during Cu^0 dissolution was the predominant copper species that activated H_2O_2 , yielding 'OH in the sono/Cu⁰/ H_2O_2 system. According to radical quenching experiments and electron paramagnetic resonance technique, free 'OH in solution was verified as the primary reactive species, and superoxide anion radicals ('O₂) were regarded as the mediator for copper cycling, via the reduction of Cu²⁺ to Cu⁺ [20].

Importantly, the toxicity of the solution increased during the first 60 min and then decreased with treatment time for the degradation of TC in a sono/Fenton-like process with a Fe_3O_4 catalyst [33]. In general, an increase in the biodegradability of wastewater has been demonstrated after antibiotic degradation by sono/Fenton and sono/Fentonlike processes [32], indicating that these processes are suitable for the treatment of wastewater that contains highly toxic and bio-recalcitrant compounds [113].

806 4.5 Role of effective factors

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

813 4.5.1 Effect of Fenton-Reagent dose

In general, a larger amount of catalyst increases the sites for H₂O₂ decomposition 814 and the production of more ROS, resulting in higher antibiotic RE [21]. Gholami, et al. 815 and Rahmani, et al. have investigated the effects of catalyst amount on the degradation 816 of CLM and TNZ using sono/Fenton-like processes with nanoscale Fe⁰, respectively 817 [21, 22]. The REs increased with increasing Fe⁰ nanoparticle dosage, and the highest 818 REs (93%-95%) were observed in a 130 kHz sonochemical system with 0.2 g/L Fe⁰ 819 nanoparticles and 1 mM H_2O_2 [21, 22]. It was speculated that the increasing nano-Fe⁰ 820 dosage results in an increase in total surface area and therefore increased adsorption 821

onto active sites. Over 0.2 g/L Fe^0 nanoparticles, the RE values reached a plateau due to the agglomeration of Fe⁰ nanoparticles and the scavenging of 'OH in undesirable reactions [21, 22].

Wei, *et al.* have reported the effect of Fe₃O₄ magnetic-nanoparticle amount on the removal of LEV in a sono/Fenton-like process [43]. As the amount of Fe₃O₄ magnetic nanoparticles increased from 0 to 1.0 g/L, the k_1 value increased from 4.69 × 10⁻³ to 21.3 × 10⁻³ min⁻¹ in the 20 kHz sonication system. The higher catalyst dose favoured LEV removal due to higher number of nucleation sites for the generation of 'OH [43].

4.5.2 Effect of H_2O_2 concentration

Without H_2O_2 present initially, the RE of LEV was approximately 30%, which is mostly attributed to the adsorption of LEV onto the catalyst. As H_2O_2 concentration increased from 1.5 to 15.0 mM, the *RE* of LEV increased until it reached a peak. The results are mainly related to the adsorption amount of H_2O_2 onto the catalyst [43]. During the degradation of CLM and TNZ in a sono/Fenton-like process with nanoscale Fe⁰, the RE increased with increasing H_2O_2 concentration due to the increase of 'OH formed. The system had the highest efficiency with 1 mM H_2O_2 [21, 22].

However, excessive amounts of H_2O_2 adversely affected the REs [82], as the excess H_2O_2 consumes the 'OH formed *in situ* and inhibits iron corrosion. In the chemical reaction of 'OH with the nanoparticle, hydroxyl ions are produced, which are less active than 'OH and reduced system efficiency [21, 22].

842 4.5.3 Effect of pH value

In general, the pH value can affect the surface-charge properties, adsorption behaviour and electron-transfer ability of the catalyst, which all affect catalytic degradation. Thus, it is necessary to study the effect of the pH value on RE and degradation kinetics in a wide range of pH conditions [44]. The acidic condition (pH 2-4) has been demonstrated to be suitable for the Fenton reaction. Gholami, *et al.* and Rahmani, *et al.* have investigated the effect of pH on the degradation of CLM and TNZ,
using a sono/Fenton-like process with nanoscale Fe^0 [21, 22]. Over the pH range of 3-9, the system had the highest efficiency under acidic conditions (pH 3), as Fe^0 corrosion and the reactivity of 'OH were greatly influenced by H⁺ concentration [21, 22].

Guo, et al. have reported the effect of pH value on the degradation of LEV in a 852 sono/Fenton-like process with Fe₃O₄ magnetic nanoparticles [43]. Over the pH range 853 of 4-9, the k_l values of LEV degradation were calculated to be 2.13×10^{-2} , 2.85×10^{-2} 854 and 1.26×10^{-2} min⁻¹ at pH 4, pH 8 and pH 9, respectively. It seems that pH 8 is the 855 optimal condition. LEV exists as different species depending on pH value. At 5.7≤ pH≤ 856 7.9, LEV mainly exists in its zwitterion form in solution, while at pH > 7.9 and <5.7, 857 LEV exists in its cationic or anionic form in solution, respectively. Therefore, the 858 859 hydrophilicity and solubility of LEV at different pH values play the critical role in its oxidative degradation by 'OH. In addition, pH value affects not only LEV adsorption 860 onto the catalyst, but also the heterogeneous Fenton-like reaction on the catalyst surface. 861 The enhanced degradation of LEV over the wide range $4.0 \le pH \le 8.0$ occurred due to 862 nucleation sites on the catalyst for the formation of cavities. At pH 9.0, the decrease of 863 RE was partly due to the decrease in H₂O₂ adsorption onto the catalyst, which was 864 covered with $Fe(OH)_6^{3-}$, and the self-decomposition of H_2O_2 , resulting in the low 865 availability of H_2O_2 and a low yield of 'OH [43]. 866

20 mg/L MNZ has been degraded with 157.4 mM H₂O₂ and 500 mg/L nano-Fe₃O₄ 867 at 30 °C within a wide pH range, from 3 to 9, and the REs were considerably enhanced 868 by sonication [44]. The RE reached its highest value (98%) after 5 h at pH 3, and the k_1 869 was 1.4×10^{-2} min⁻¹. k_1 decreased to 1.25×10^{-2} , 7×10^{-3} , 6×10^{-3} and 3.1×10^{-3} min⁻¹ at 870 pH 5.00, 5.79, 7.00 and 9.00, respectively. This dependence on pH is similar to that of 871 the traditional Fenton reaction, and was attribute to a sharp decrease in the 872 concentration of Fe in the oxidation state Fe²⁺ with increasing pH value, thus hindering 873 the activity of the catalyst [44]. 874

875 4.5.4 Effect of temperature

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

4.5.5 Stability of catalysts

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

Fe⁰ particles can be reused in the relative long-term and not lead to high 888 concentration levels of dissolved iron in the treated effluents (<0.6 mg/L) [35]. A 889 consecutive triplicate-repeated sono/Fe⁰/tetrapolyphosphate experiment was conducted 890 to examine the reusability of Fe^0 particles for NOR degradation. The k_1 for the three 891 repeated runs were 0.039, 0.032 and 0.029 min⁻¹, respectively. This indicates that 892 sonication is able to effectively clean and refresh the surface of used Fe⁰ particles over 893 a long-term treatment schedule. The Sono/Fe⁰/tetrapolyphosphate system only led to 894 acceptable levels of dissolved iron in the effluents even after repeated runs. 895

896 5 Degradation of antibiotics by sonication with

897

peroxydisulfate (PS) and peroxymonosulfate (PMS)

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 radicals (SO4[•], SR) can be formed by the activation of persulfate salts (PS, SO5²⁻ or S₂O₈²⁻) or peroxymonosulfate (PMS, HSO5⁻) via multiple approaches, including heat, UV, sonication, alkaline pH and transition metal ions [21, 119, 144-146]. The triple salt KHSO5·0.5 KHSO4·0.5 K₂SO4 (Oxone) is a form with higher stability [147]. SR-AOP appears to be more advantageous, efficient and powerful than 'OH-based AOPs [143, 145], as SR appears to be more stable than 'OH in reacting with target antibiotics and is able to oxidize antibiotics efficiently over a wide pH range of 2-8 [148, 149].

In general, 'OH is a powerful oxidant with a redox potential of 1.89-2.8 V [150, 908 151]. In comparison, SR has an equal or even higher redox potential (1.81–3.1 V), 909 depending on activation method [113, 146, 150, 152]. SR is generated from PS, which 910 has a higher standard redox potential (2.01 V) than PMS (1.81 V) [145, 150]. Therefore, 911 the RE order of acid orange 7 by heat activation is $PS \gg PMS > H_2O_2$, but by UV 912 activation, the RE order of acid orange 7 becomes $PS > H_2O_2 > PMS$ [153, 154]. Under 913 sonication activation, the REs of 25 mg/L furfural with PS or PMS reached 95.3% or 914 915 58.4%, respectively [155]. However, the REs of SMX by UV activation were observed to follow a different order: PMS > PS > H₂O₂ [156]. Even with a TiO₂ catalyst, k_1 by 916 UV activation still shows the same order: $PMS > PS > H_2O_2$ [157]. A similar order was 917 observed during the degradation of rhodamine B by Fe²⁺/PMS or PS/MoS₂ [158]. 918 Therefore, the oxidation potential of PS and PMS was affected by the whole oxidation 919 system rather than by one factor. 920

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

925
$$S_2O_8^{2-} + OH \rightarrow HSO_4 + SO_4 + 0.5 O_2$$
 (4)

926
$$HSO_5^- + US \rightarrow SO_4^{-} + OH$$
 (5)

927
$$HSO_5^- + SO_4^- \to SO_5^- + SO_4^{2-} + H^+$$
 (6)

928
$$S_2O_8^{2-} + US/thermal \rightarrow 2 SO_4^{--}$$
 (7)

929
$$\operatorname{SO_4^{\bullet}} + \operatorname{OH} \to \operatorname{HSO_4^{\bullet}} + 0.5 \operatorname{O_2}$$
 (8)

930
$$S_2O_8^{2-} + SO_4^{-} \rightarrow SO_4^{2-} + S_2O_8^{2-}$$
 (9)

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

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





944

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

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



Figure 4 SMT degradation by different processes: US, PMS and US/PMS systems. Reprinted from ref. [82]
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So far, the sonochemical degradation of antibiotics, such as CAP, CIP, TC, SMZ,
SDZ, etc., with PS in aqueous solution have been studied. 5-100 mg/L of antibiotics
has been sonicated for 30-240 min with 1-200 mM PS or Oxone in 50-1000 mL of
aqueous solution. The application of sonication for the degradation of antibiotics with
PS or Oxone has been summarized in Table 5.

954

Antibiotics	C _{PS}	F _{US} /P _E (kHz/W)	t	C ₀ /V	pН	RE _{PS}	RE _{Sono}	RE _{Sono/PS}	SF	Refs.
	(mM)		(min)	(mg/L)/mL		(%)	(%)	(%)		
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]

⁹⁶² *Table 5 Summary of the degradation of antibiotics by sonication with PS or Oxone.*

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-	-	9.7	13.7	-	[76]
					7.0					
SMZ	1	40/60	60	5/500	7.0	-	1.6	7.2	-	[161]
SMZ	Oxone	20/600	30	50/<100	7.5	54.3	8.6	99.6	1.58	[82]
	2									

964

Note: CPS: PS concentration; FUS: ultrasonic frequency; PE: electrical power input; C0: initial concentration of 963 antibiotic solution; V: the volume of antibiotic solution; RE: removal efficiency; SF: synergy factors = REsono/PS/(REsono+REPS) [71, 81, 109]; Refs.: references. 965

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

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

To effectively remove antibiotics from aqueous solutions using sono/PS, PMS or 975 Oxone, catalysts have been added to enhance RE [149, 163]. For example, Fe^0 or PS 976 alone cannot cause significant SDZ degradation, and sonication alone only led to 977 marginal degradation of SDZ after 1 h treatment (9.7% RE). Moreover, the RE of SDZ 978 reached only 9.8% and 13.7% in 1 h using a combination of two factors, such as 979 sono/Fe⁰ and sono/PS, respectively. By contrast, 45.5% of SDZ was removed in 1 h 980 using the Fe⁰/PS combination due to the catalytic decomposition of PS by Fe⁰ and 981 higher SR formation. However, surface passivation prevented the dissolution of Fe⁰ and 982 the release of Fe^{2+} , hampering the continuous degradation of SDZ. Therefore, 983 sonication was used to remove the passivation film and improve mass transfer, inducing 984 an SDZ RE of 95.7% in 1 h in the sono/Fe⁰/PS reaction system [76]. Similarly, it is also 985

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

Fe⁰ [76, 161], ZnO [104], Fe²⁺ [111, 113], Co²⁺ [145, 162], Ag [150], Fe₃O₄ [163], 995 etc. can enhance the activation of PS, PMS or Oxone in sonication systems. Obviously, 996 transition metals or their ions and oxides were the important catalysts for the activation 997 of PS, PMS or Oxone to generate SR [19, 76, 140, 145, 149, 150, 159, 161, 162]. The 998 cavitation effects mean that sonication not only induces the release of SR from PS or 999 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 degradation mechanisms of SDZ by sono/Fe⁰/PS are shown in Scheme 4 [76]. 1002



1003



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As shown in Scheme 4, sonication played important roles in the Fe⁰/PS system, including producing radicals, enhancing iron-corrosion reactions and accelerating the radical reactions in the bulk liquid [76, 149]. The microstreaming or microjets, shockwaves, and turbulence generated by sonication promoted mixing at the solidliquid interfaces and the continuous cleaning of the solid catalyst surface, which favour 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 oxidation of the amine group (α -position in the benzene ring) by SR to generate the 1014 nitro-SD derivatives. SR then further attacks the nitro-SD derivatives (the C-N bonds 1015 on the γ -position in the heterocyclic ring), leading to ring opening. Another degradation 1016 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 products, 2-aminopyrimidine and sulfanilic acid. Furthermore, the low molecular 1019 weight organic acids (formate and acetate), inorganic ions (nitrate, nitrite and sulfate) 1020 1021 were examined using an ion chromatograph, which demonstrated the mineralization of SDZ [76]. Unfortunately, this study does not provide the variation of TOC and toxicity 1022 of the SDZ solutions by the treatment. 1023

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

1031 Moreover, Hu, *et al.* have demonstrated that the sonocatalytic degradation of NOR 1032 is principally induced by 'OH and SR in the system with PS and multilayer flower-like 2nO [140]. Soltani, *et al.* have also demonstrated that 'OH-mediated oxidation was the main mechanism in the decomposition of TC, and that PMS led to the more significant enhancing effect on the removal of TC, compared with percarbonate, PS and periodate [104]. Guo, *et al.* have reported that the reactive radicals were generated through the Co₃O₄-mediated activation of PMS during the sonocatalytic degradation of AMX using Co₃O₄-catalyzed PMS [159]. Furthermore, the sonocatalytic degradation of CAP was accelerated remarkably by adding PS and Co²⁺ simultaneously [145].



1041 Scheme 5 Proposed SDZ degradation pathways in the sono/Fe⁰/PS system. Reprinted from ref. [76] Copyright
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1040



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 antibiotic degradation. For example, the elimination of FLU was significantly 1046 accelerated and the RE increased when 1.0 mM PS was added to a sono/Fenton system. 1047 As a result, 98% of FLU elimination was achieved in 80 min [111]. Roy, et al. have 1048 investigated SDZ degradation in a sono/Fenton-like process with PS and yolk-shell 1049 Fe_3O_4 (*a*) hollow (*a*) mSiO₂ nanoparticles [164]. The faster leaching of Fe^{2+}/Fe^{3+} ions from 1050 the metal core of the Fe₃O₄@hollow@mSiO₂ particles, due to micro-convection 1051 generated by sonication, enhanced SDZ degradation [164]. 1052

Rahmani, et al. have reported the sonocatalytic degradation of CIP associated with 1053 PS and Zn⁰ under 40 kHz and 350 W sonication [19]. With 4.4 mM PS and 1.84 mM 1054 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 1055 mg/L CIP solution, which was much higher than those (39.7, 18.5, 9.9, 7.5, 3.3 and 1056 2.5%) obtained by PS/Zn^0 , sono/PS, sono/Zn⁰, PS, Zn⁰ and sonication alone. 1057 respectively [19]. This indicates that the production of $^{\circ}OH$, activation of PS and Zn^{0} 1058 dispersion in solution were enhanced by sonication [19]. In the presence of 10 mM 1059 PMS, periodate, PS and percarbonate, the sonocatalytic RE of TC reached 99.6, 94.2, 1060 90.4 and 98.2% in 50 mL of 50 mg/L TC solutions with 0.5 g/L ZnO/nano-cellulose at 1061 pH 4.0 for 30 min, respectively, under 37 kHz and 256 W sonication, which are higher 1062 than that of the sono/ZnO/nano-cellulose process (87.6%) [104]. 1063

Besides the removal of antibiotics, the mineralization of antibiotic solutions can be significantly enhanced by sonication with PS, PMS and catalysts. Su, *et al.* have investigated the sonocatalytic degradation of AMX and the removal of COD with Co^{2+} and Oxone [162]. The REs of COD were in the order of: Oxone < Oxone/Co²⁺ < Sono/Oxone < Sono/Oxone/Co²⁺. More than 98% of COD removal was achieved by 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 Co ²⁺ [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 Co^{2+} 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 Co^{2+} without sonication [162]. In addition, 89% of COD was
1083	removed as the RE of TC reached 93% under sono/PS/Fe ₃ O ₄ nanoparticles [163].

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

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

 $\label{eq:solution} 1085 \qquad \text{Note: } F_{\text{US}:} \text{ ultrasonic frequency; } P_{\text{E}:} \text{ electrical power input; } C_0: \text{ initial antibiotic concentration; } V: \text{ the volume of } P_{\text{E}:} \text{ of } P_{\text{E}:}$

antibiotic solution; RE: removal efficiency; SF: synergy factors = RE_{Sono/PS/Catal}/(RE_{Sono}+RE_{PS/Catal}) [71, 81, 109];
Refs.: references.

46

1088 5.5 Role of effective factors

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

The sonocatalytic degradation of antibiotics, such as TC [31], AMX [159, 162], 1096 etc., with PS or PMS generally follows PFO kinetics [131]. For example, a k_1 value for 1097 20 mg/L SDZ in a 400 mL solution was measured to be about 0.057 min⁻¹ at pH 7 and 1098 room temperature under 20 kHz and 40 W sonication with 0.92 mM Fe⁰ and 1.84 mM 1099 PS [76]. In general, initial antibiotic concentration, catalyst dosage, PS and PMS 1100 concentration, and the initial pH value of the solution, temperature and US frequency 1101 1102 and power affect the degradation kinetics [112, 131, 149, 160]. At lower US power ranges, the RE increased with increased US power [76, 112, 148, 149, 161], but the 1103 benefits of increasing US power over an optimal power value were not observed [149]. 1104 In addition, RE increased with an increase in temperature [131, 160, 162], while RE 1105 decreased with an increase of the initial antibiotic concentration [76, 131, 140, 149, 162, 1106 163]. However, the amount of antibiotics removed increased with increasing initial 1107 concentration. For example, 45.9, 88.9 and 121.9 mg/L TC were oxidized by sonication 1108 with Fe₃O₄/PS when its initial concentrations were 50, 100 and 200 mg/L, respectively 1109 [149]. The effects of catalyst dosage, PS or PMS concentration, pH value, and other 1110 additives, on the degradation of antibiotics using sono/PS or PMS/ and catalyst are 1111 discussed below. 1112

1113 5.5.1 Effect of catalyst dosage

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

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

Based on the sonocatalytic degradation of SMZ with pre-magnetized Fe⁰/PS, Pan, 1119 et al. have demonstrated that the degradation rate of SMZ is mainly determined by the 1120 amount of Fe²⁺ produced from Fe⁰ [161]. The SMZ removal at 60 min was 84.8%, 1121 96.1%, 97.8%, 100% and 99.3% at 0.05, 0.1, 0.2, 0.4 and 0.8 mM Fe⁰, respectively. 1122 Thus, the removal of SMZ increased with increasing Fe⁰ doses over the above range. 1123 Meanwhile, k_l value increased from 0.028 min⁻¹, at 0.05 mM Fe⁰, to 0.176 min⁻¹ at 1124 0.40 mM Fe⁰, but slightly decreased at 0.80 mM Fe⁰ (0.143 min⁻¹) due to the 1125 consumption of SR by excess Fe^{2+} . Thus, 0.40 mM Fe^{0} was noted to be the optimum 1126 dosage and the optimum ratio of Fe^{0}/PS was denoted as 2/5 [161]. 1127

Hou, et al. have concluded that initial degradation rates increase with various doses 1128 of Fe₃O₄, in the range from 0 to 2.0 g/L, in the sonocatalytic degradation of TC with 1129 Fe₃O₄/PS [149]. As an initiator, Fe₃O₄ activates PS to generate SR, and then accelerates 1130 the decomposition of TC. However, the final RE was similar, as a result of the same 1131 concentration of PS, since the SR yield is dependent on PS concentration [149]. In 1132 addition, the degradation rate of TC increases with increasing martite nanoparticle 1133 dosage, and the sonocatalytic RE of 100 mg/L TC reached 87% with 0.5 g/L martite 1134 (Fe₂O₃)/3 mM Oxone at pH 4 for 60 min [112]. 1135

1136 5.5.2 Effect of PS or PMS concentration

In general, the degradation rate of antibiotics increases with increased initial PS concentration [149, 160]. During the sonocatalytic degradation of TC with Fe₃O₄/PS, the RE of TC increased with increasing PS concentration from 20 to 200 mM [149]. However, when the PS concentration was over 200 mM, the RE decreased as excessive amounts of PS produced sulfate anions rather than active SR. It is also speculated that the SR formed could be scavenged by excess PS, thus inhibiting the generation of 'OH,
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 on the sonocatalytic degradation of TC with martite nanoparticles and Oxone [112]. 1145 The results revealed that increasing the Oxone dosage from 1 to 7 mM increases the 1146 decomposition rate from 0.0282 to 0.0588 min⁻¹. Similarly, excessive amounts of 1147 Oxone (5 and 7 mM) led to insignificant improvements in the decomposition rate of 1148 TC. It was assumed that the excessive amounts of HSO₅⁻ react with SR to form SO₅⁻, 1149 which has lower oxidation potential than SO_4 , leading to poorer decomposition of TC. 1150 In addition, the reaction between sulfate radicals intensified when the Oxone 1151 concentration was excessive, leading to the generation of PS ions. Subsequently, the 1152 addition of extra amounts of Oxone not only causes the scavenging of SR, but also 1153 generates the less reactive species [112]. 1154

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.

In homogeneous systems, antibiotics such as TC exist in the molecular form under 1161 acidic conditions, resulting in higher affinity to the cavitation bubbles where oxidation 1162 with higher concentration 'OH and the pyrolysis of molecules can occur [34]. Thus, 1163 higher RE has been achieved under acidic conditions. For example, 90.5%-91.3% of 50 1164 mg/LTC degradation and 25.7%-28.3% of TOC removal were achieved in 1 L solutions 1165 at pH 3 to pH 6 in 60 min under 20 kHz and 100 W sonication with 2 mM Fe²⁺ and 2 1166 1167 mM PS. However, the differences in the REs at the various pH values under acidic conditions are not significant. Therefore, it is not necessary to adjust the initial pH to a 1168 very low level, and an initial pH of 6 is an optimal pH condition [34]. Similarly, the 1169

sonocatalytic degradation of 20 mg/L CAP has been carried out in 50 mL solutions by 22 kHz and 200 W sonication for 240 min with 5 mM PS and 0.1 mM Co²⁺ [145]. The results revealed that the RE of CAP decreases with increasing pH value, while k_1 values are higher under acidic solutions (pH 1.0-3.3) than those obtained in neutral or basic solutions (pH 5.0-10.0) [145].

In heterogeneous systems, such as sono/Fe⁰/PS, the efficient degradation of SDZ 1175 (95.7%–98.4%) has been achieved at a pH range of 3.0–7.0 [76], but the performance 1176 was greatly slowed (35.7%) at pH 10.0. Acidic conditions favour the corrosion of Fe⁰ 1177 and produce more soluble Fe²⁺, while alkaline conditions cause the precipitation of 1178 soluble iron ions and the passivation of the Fe⁰ surface, resulting in a low production 1179 of oxidative radicals, both SO₄⁻⁻ and 'OH. Moreover, the SO₄⁻⁻ formed reacts with H₂O 1180 and OH⁻ under neutral or alkaline conditions, and also inhibits the reactivity of 'OH. 1181 [76]. 1182

Furthermore, a gradual decrease in solution pH was observed during the 1183 degradation of antibiotics at an initial pH 3.0-7.0; the formation of carboxyl acid 1184 products and the decomposition of PS led to this pH decrease. At an initial pH of 10.0, 1185 the pH value decreased to 6.5 by the end of degradation [76]. Pan et al. have found that 1186 pH value decreases faster with reaction time during the degradation of SMZ in a 1187 sono/premagneted-Fe⁰/PS system than in other systems [161]. As pH dropped quickly, 1188 Fe²⁺ was produced faster, leading to the formation of more SO₄⁻, a higher RE of SMZ, 1189 and better synergistic effects in the sono/premagnated-Fe⁰/PS system [161]. 1190

1191 5.5.3.2 Insignificant effect of pH value

Hou, *et al.* have found that the TC degradation rate increases with decreasing pH value in a system of Sono/Fe₃O₄/PS, but the REs were all similar after 1.5 h sonication [149]; the finial REs were 89%, 86% and 85% at pH 3.7, 7.0 and 9.0, respectively. This 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 and 9.00 to 2.66, 2.63 and 2.68 after 1.5 h reaction, respectively. This is probably the
reason why similar REs were achieved by the end of the reactions at various initial pH
values [149]. Similarly, the pH value decreased from 4.0 to 3.4, from 7.0 to 5.8 and
from 10.0 to 7.3 during TC degradation via sono/PS in the absence of a buffer solution
[160].

1203 5.5.3.3 RE increased under alkaline conditions.

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

1207 TC is an amphoteric molecule with *pKa* values of 3.3, 7.7 and 9.7. TC molecules are predominantly neutral and positively charged at pH = 4 and negatively charged at 1208 pH= 9. The negatively charged TC molecules tend to attract reactive species such as 1209 'OH because of the high electrical density on ring system, which resulted in an 1210 acceleration in the degradation of TC [160, 165]. Moreover, alkaline-activated PS is 1211 primarily responsible for the production of SO_4^{-} , O_2^{-} and 'OH at pH \geq 10. Furthermore, 1212 SR can react with OH⁻ to generate 'OH under alkaline conditions [160, 165]. Therefore, 1213 increasing pH enhances the decomposition of PS to form 'OH and SR. 1214

1215
$$S_2O_8^{2^-}+2H_2O \xrightarrow{OH^-} HO_2^-+2SO_4^{2^-}+3H^+$$
 (10)

1216
$$HO_2^-+S_2O_8^{2-} \rightarrow SO_4^{-+}+SO_4^{2-}+H^++O_2^{--}$$
 (11)

1217
$$SO_4^{\bullet} + OH^{\bullet} \rightarrow SO_4^{2-} + OH$$
 (12)

SR is the predominant species responsible for TC degradation at pH 4, whereas TC degradation was caused by both SO_4^{-} and 'OH at pH 7. Thus, the competing reactions between SR and 'OH, and TC reduce the TC degradation rate at pH 7 [160].

Similarly, TC degradation under a sono/martite/oxone process has been studied at initial pH values of 4, 7 and 9, and the k_1 values were 0.0481, 0.0545 and 0.0641 min⁻¹ , respectively [112]. On the one hand, the scavenging of SR and disintegration of the active species by H^+ was thought to cause slight decreases in the TC degradation rate under acidic conditions. The increased degradation rate with increased initial pH can be explained by the conversion of SO₄⁻⁻ and 'OH in the presence of OH⁻⁻ under alkaline conditions. On the other hand, the reaction between 'OH and SR leads to the production of HSO₄⁻⁻ in the bulk solution, and then the dissociation of HSO₄⁻⁻ into sulfate ions releases H⁺ ions, decreasing the pH of the solution [166]. Therefore, an insignificant increase in the degradation rate was observed with increasing initial pH value [112].

1231 5.5.4 Effect of temperature

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

1236
$$S_2O_8^{2-} \longrightarrow 2SO_4^{-}$$
 (13)

The k_{obs} of SDZ increased $(3.56-27.39 \text{ h}^{-1})$ with increased bulk temperature (10-1237 50 °C) in the sono/Fe⁰/PS system. The pseudo activation energy was 38.2 kJ/mol, 1238 demonstrating that higher temperature was beneficial to the removal of SDZ and 1239 verifying that thermal treatment can also be a persulfate activator. The activation energy 1240 obtained in sono/Fe⁰/PS was approximately one order of magnitude lower than that 1241 obtained in the heat/PS system and Fe⁰/PS system, which indicates that the effective 1242 removal of SDZ can also be achieved by sono/Fe⁰/PS processes even at a low bulk 1243 temperature (10 °C) [76]. Upon increasing the temperature from 25 to 65 °C, the 1244 degradation rate constant increased from 0.0229 to 0.1042 min⁻¹ under the sono/ $S_2O_8^{2-}$ 1245 process [131]. Complete TC degradation occurs after 40, 60 and 75 min of reaction at 1246 65, 55 and 45 °C respectively. The low activation energy (32.01 kJ/mol) indicates that 1247 the degradation of TC by $sono/S_2O_8^{2-}$ is thermodynamically feasible [131]. Increasing 1248 temperature (25-65 °C) enhanced the TC degradation rate constant (0.0175 to 0.1573 1249 min⁻¹) during the sono/S₂O₈²⁻ process. TC was completely removed after 60, 90 and 1250

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 H_2O_2 is a common oxidant and also the precursor to producing 'OH, which is frequently used to accelerate the degradation of organic pollutants [113]. Under 1259 sonication, the formation of extra 'OH, from H₂O₂ decomposition, enhanced MTZ 1260 removal [113]. In a homogenous Fe²⁺/PS (3 mM/1 mM) system, the RE of 500 mg/L 1261 MTZ in 200 mL solution reached 97% at pH 3 in 90 min of sonication with 20 kHz and 1262 1263 the addition of 60 mM H₂O₂, as compared to an RE of 72% in the absence of PS [113]. In another homogenous Fe^{2+}/PS (4 mM/1 mM) system, the RE of 261 mg/L FLU in 1264 200 mL solution reached 98% at pH 4 after 80 min of sonication with 40 kHz and the 1265 1266 addition of 20 mM H₂O₂, compared to an RE of 73% in sono/H₂O₂ [111].

In a heterogeneous martite/Oxone /(0.5 g/L/3 mM) system, the RE of 100 mg/L 1267 TC in 100 mL solution reached 87% at pH 4 in 60 min under 37 kHz and 320 W 1268 sonication with martite-nanoparticle-activated Oxone, compared to an RE of 78% in 1269 unmilled martite (sono/unmilled martite/Oxone) [112]. Only 6.5% of TC was removed 1270 by the adsorption process, while the decomposition of TC by Oxone alone was lower 1271 than 44%. As a result, when the H_2O_2 concentration rose from 10 to 40 mM, the k_1 value 1272 increased from 0.0533 to 0.0907 min⁻¹. However, increasing H₂O₂ concentration up to 1273 1274 50 mM caused a substantial drop in the decomposition rate of TC [112].

1275 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, O_2 ' and SO_4 ' 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 SO_4^{-} and 'OH are the major radicals for the degradation 1280 of TC. In theory, EtOH is a scavenger of SO_4^{-} and can also react with 'OH, and the 1281 reaction constants of EtOH with SO_4^{-} and OH are $1.6-7.7 \times 10^7$ and $1.2-2.8 \times 10^9$ M⁻¹S⁻ 1282 ¹, respectively [149].

In order to investigate the role of O_2^{-} , 1,4-benzoquinone was used as an O_2^{-} quencher in a TC degradation via a sono/Fe₃O₄/PS process [149]. The addition of 0.021 M 1,4-benzoquinone did not significantly affect the TC degradation in the initial stages. However, the suppression became significant after 30 min, indicating the delayed formation of O_2^{-} during the reaction [149].

t-BuOH is generally used as an OH scavenger and the reaction constant is 3.8-7.6×10⁸ M⁻¹S⁻¹. Excess t-BuOH (1.05 M) was added to the solution to check the contribution percentage of 'OH [149].

Zhou, *et al.* have demonstrated that SDZ degradation is inhibited by SO_4^{2-} , NO^{3-} , 1291 HCO^{3-}/CO_{3}^{2-} and $H_2PO_{4}^{-}$ to different extents in a sono/Fe⁰/PS system [148]. Such 1292 inorganic anions would mainly react with SO4⁻ and/or 'OH to form sub-radicals of 1293 less oxidative potential, which was also proven by the sonocatalytic degradation of SDZ 1294 in a sono/yolk-shell Fe₃O₄@ hollow@ mSiO₂ nanoparticle/PS system [164]. The 1295 1296 inhibition effect was revealed to be probably due to the stronger metal ion complexation and radical scavenging in the hollow core of the yolk-shell nanoparticles [164]. 1297 Moreover, the presence of carbonate and even persulfate ions suppressed the 1298 sonocatalytic degradation of TC with martite nanoparticles and Oxone [112]. However, 1299 Cl⁻ enhanced the SDZ degradation with a low dose (5 mM), but inhibited it at a high 1300 dosage (100 mM) [148]. Moreover, the enhanced effects of chloride and carbon 1301 tetrachloride have also been demonstrated in the sonocatalytic degradation of TC [112]. 1302

At pH 3 and 5 with a buffer solution, the REs of SDZ reached 54.6% and 58.4%, respectively, which were lower than in the un-buffered systems. It was also speculated that the additional phosphate species (mainly HPO_4^{2-} and $H_2PO_4^{-}$ at pH 3.0–5.0) play the scavenging role for SR via complexion of the phosphate species. It also indicates
that the soluble iron ions inhibit SDZ degradation. As the predominant oxidant under
stable neutral or alkaline conditions, 'OH was strongly scavenged by phosphate species,
and significant inhibition of SDZ degradation was therefore found at pH 7 and 10 with
a buffer solution [76].

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

1316 5.5.6 Stability of catalysts

In the heterogonous sonocatalytic system with martite nanoparticles and Oxone, 1317 the decomposition rate of TC dropped by only 10.8% after four consecutive 1318 experimental runs, indicating the appropriate reusability potential of martite 1319 1320 nanoparticles [112]. In a sonocatalytic system with Fe₃O₄ and PS, the RE of TC reached 89% in 1.5 h in the primary experiment, and then the RE decreased to 73.5% after three 1321 repetitive experiments. A low dissolved iron concentration (<0.2 mM) was detected in 1322 1323 the solution. It was speculated that Fe(III)-bearing iron oxides formed on the surface of the catalyst, which may be more soluble, less active and stable, and thus cause the RE 1324 decline. As for effect of sonication on the catalyst particle size distribution, the particle 1325 size distribution of the used catalysts is similar to that of the fresh catalysts, indicating 1326 that Fe₃O₄ is stable under sonication [149]. 1327

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,

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

Sonophotocatalysis has attracted much attention because it is generally considered 1341 to be an applicable and environmentally friendly process [114]. The synergistic effect 1342 of sonocatalysis and photocatalysis generates a large number of ROS, and thus 1343 enhances the oxidation process to remove organic contaminants [84]. The cavitation 1344 effects induced by sonication eliminate the defects of photocatalysis, including the 1345 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 sonophotocatalysis are shown in Figure 5. 1348

1349



1350

1351Figure 5Degradation mechanisms of TC by sonophotocatalysis. Reprinted from ref. [31] Copyright (2019), with1352permission from Elsevier.

1353 6.2 Application of sonophotocatalysis in antibiotic degradation

Vinesh, et al. have investigated the degradation of TC by sonophotocatalysis under 1354 simulated visible light with a reduced graphene-oxide (rGO) supported electron-1355 deficient B-doped TiO₂ (Au/B-TiO₂/rGO) nanocomposite synthesized via the 1356 hydrothermal method [117]. The RE of TC under sonolysis, photocatalysis and 1357 sonophotocatalysis was found to be 25, 65 and 100%, respectively, when the reaction 1358 was performed in the presence of sonolysis and photocatalysis under 40 kHz, 600 W 1359 US, 300 W of visible light power with 0.25 g/L Au/B-TiO₂/rGO in 60 min (40 mL, 15 1360 mg/L). The enhanced sonophotocatalytic activity (SF: ~1.3) observed was attributed to 1361 the generation of more ROS by the combination of sonication and photocatalysis [117]. 1362 According to trapping tests, holes, 'OH and ' O_2 ' contributed to the degradation process 1363 [31]. 1364

The application of sonophotocatalysis for the degradation of antibiotics ha sbeensummarized in Table 7.

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AB	Catalysts	$\lambda_{UV/vis}\!/P_U$	F_{US}/P_E	t	C ₀ /V	рН	REPh	RE _{Sono}	RE _{Sono/}	SF	Refs.
Х		V/vis	(kHz/W)	(min	(mg/L)/		oto	(%)	Photo		
		(nm/W))	mL		(%)		(%)		
OF	1 g/L	350-400	20/192*	120	10/300	6.0	85.0	15.0	~100.0	~1.0	[85]
Х	TiO ₂	/3.2									
		W/m ²									
TC	0.3 g/L	254/6	20/40	60	30/<500	5.5	47.4	2.1	59.2	1.2	[31]
	TiO ₂ /MAC										
	@T										
TC	0.25 g/L	-300	40/600	60	15/40	-	65.0	25.0	100.0	1.3	[117]
	Au/B-TiO ₂										

1371 *Table 7 Degradation of antibiotics by sonophotocatalysis.*

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

1372 Note: ABX: Antibiotics; $\lambda_{UV/vis}$: wavelength of light; P_{UV} :light power; W/m²: light power intensity; Fus: ultrasonic 1373 frequency; P_E: electrical power input; C₀: 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, TiO_2 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

TiO₂ is a common catalyst for promoting the photocatalytic degradation of organic 1380 contaminants. Hapeshi, et al. have investigated the degradation of OFX by 1381 1382 sonophotocatalysis with TiO₂ (Conditions: 300 mL of 10 mg/L OFX, pH 6.0, 1.0 g/L catalysts, 20 kHz, 640 W/L US power, 350-400 nm UV, 3.2 W/m² UV power, 120 min 1383 treatment at 27 ± 2 °C) [85]. The working solution, containing 10 mg/L OFX, was 1384 prepared by spiking the appropriate mass of the compound in the secondary treated 1385 wastewater (collected from the urban wastewater treatment plant (UWTP) of Limassol, 1386 Cyprus) and then performing the necessary dilutions. The results revealed that the 1387 sonophotocatalytic degradation of OFX follows PFO kinetics. The k_1 values were 1388 0.1054, 0.0713, 0.0203 and 0.0131 min⁻¹ for sono/Photo/TiO₂, photo/TiO₂, sono/TiO₂ 1389 and sonication alone, respectively. The REs of OFX for 120 min reached 15, 62, 85 and 1390

1391 $\sim 100\%$ 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.

Table 8 REs of TC for 60 min under various sonication and photocatalytic processes (Conditions: <500 mL of 30
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].

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

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

1419 6.2.2 Fenton and Fenton-like reactions

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

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

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

1461 6.2.3 Other nano-composites

Khataee, et al. have investigated the degradation of MOX by the 1462 sonophotocatalytic method using a NiFe-layered double hydroxide/reduced graphene 1463 oxide (NiFe-LDH/rGO) nanocomposite [118]. The RE of MOX (90.4%) by 1464 sonophotocatalysis under the used conditions - 100 mL of 20 mg/L MOX, pH 8.0, 1.0 1465 g/L catalysts, 36 kHz, 150 W US power, 10 W UV power, 60 min treatment - was higher 1466 than the REs of sonocatalysis (72.4%) and photocatalysis (62.7%), but lower than their 1467 sum. The results revealed that 'OH and ' O_2^- radicals play the dominant role in MOX 1468 1469 degradation.

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

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

Ghoreishian, et al. have investigated the degradation of TC by sonophotocatalysis 1482 with flower-like rGO/CdWO₄ hierarchical structures that were synthesized using a 1483 facile wet-chemistry method without any calcination [84]. rGO/CdWO₄ exhibited 1484 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]. Thus, the higher catalytic activity of rGO/CdWO₄ is attributable to rGO, which catches 1488 TC residuals from aqueous solution and acts as a charge acceptor to promote the 1489 separation of photo-generated carriers via its π - π conjugated structure. 1490

1491 6.3 Other concerning issues

1492 6.3.1 Effective factors

Due to the emerging nature of sonophotocatalysis, little has been reported on the effects of critical factors. The performance of sonophotocatalytic systems is influenced by various parameters, such as US and UV conditions, catalyst dosage, pH value, initial antibiotic concentration, additives, etc. [31, 83-85]. In general, the RE of antibiotics 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 factor for the degradation of antibiotics [116]. As discussed above, sonocatalysis or 1506 photocatalysis alone are not adequate to effectively remove antibiotics from aqueous 1507 solutions, but the addition of either H₂O₂ or PS significantly enhances the RE, while 1508 RE increases with increasing concentration of additives [20, 163]. For example, OFX 1509 degradation increases slightly upon increasing the H_2O_2 concentration, but with an 1510 optimum level of H₂O₂ concentration at 0.14 mM. [85]. Zeng, et al. have investigated 1511 1512 the degradation of LEV by visible-light-driven sonophotocatalysis and PS activation over 3D urchin-like MoS₂/C nanoparticles [100]. The radical species 'OH and SO₄' 1513 were accelerated, while O_2 was limited in this coupled system, which largely 1514 facilitates its excellent degradation performance with a synergistic effect [167]. 1515

By contrast, the addition of inhibitors decreases the degradation of antibiotics as a means to probe the role of 'OH that is formed *in situ*. For example, the inhibitory effect of different inorganic salts on NOR degradation in a sono/nano-Cu⁰/H₂O₂ system followed the sequence: Na₂SO₄ > NaNO₃ >≈ no salt > NaCl > NaHCO₃ [20]. However, a contradictory result has been observed, in which a decreasing sequence of the inhibitory effect of anions towards TC degradation in a sono/photo/MAC@T process 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

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

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

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

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

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

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

1562 7.1 Mechanisms of sonozonation

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

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

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





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

degradation of TC by sonozonation, indicating the degradation pathway of TC (Scheme 6) [80]. As shown in Scheme 7, Product 1 was generated by an initial 1,3-dipolar cycloaddition towards the C_{11a} - C_{12} double-bond and a rearrangement with the hydroxyl at position C_{12} . Subsequently, Product 2 was formed via the further oxidization of the double-bond C_2 - C_3 in Product 1. Product 3 was finally synthesized by O_3 or 'OH by successively attacking ring D (bearing hydroxyl group) of Product 2. Therefore, 'OH dominates the degradation of TC in the sonozonation system [80].



1600 Scheme 7. The degradation pathway of TC in the sonozonation system. Reprinted from ref. [80] Copyright (2012),
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Recently, we have reported the mechanisms, reactors and effective factors of sonozonation for organic degradation [81]. In this review, the applications of sonozonation and the roles of effective factors on antibiotic degradation are discussed.

1605 7.2 Application of sonozonation on antibiotic degradation

1599

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 (EC₅₀% = 67.5) were achieved, compared with those obtained by sonication alone $(k_1 = 0.04 \text{ min}^{-1} \text{ and } 10\% \text{ of TOC removal})$ and ozonation alone $(k_1=1.97 \text{ min}^{-1} \text{ and } 32\% \text{ of TOC removal and } \text{EC}_{50}\%=13.6)$ [78]. Based on the k_1 values obtained by the various processes, the synergistic factor of sonozonation for AMX degradation was calculated to be 1.24.

Naddeo *et al.* have investigated the degradation of SMX using sonozonation with 20 kHz and 370W/L US [120]. 61% of SMX was removed from 200 mL of a 10 mg/L SMX solution, with 3.3 g/h of O₃ dose, after 40 min in the sonozonation system, while 51% SMX was removed by ozonation alone [120]. The enhancement of SMX degradation by sonozonation can reduce the consumption of chemicals, which is particularly interesting for performing the scale-up of sonozonation process [120].

Guo *et al.* have also investigated the degradation of SMX by sonozonation with 20 kHz and 600W/L US [121]. A 100 mg/L (0.5 mM) SMX solution was treated in a 1.5 L-reactor with 3.0 g/h of O₃ dose, and about 95% of SMX was removed after 5 min treatment in the sonozonation system, while only 3% and about 85% SMX was 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 O₃ 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 O₃ concentration, flowrate and dosage

In general, O_3 concentration in a gas increases with the yield or dosage of O_3 production under an identical gas flowrate. Naddeo *et al.* have noted that the degradation of SMX was enhanced by increasing ozone flows in the sonozonation system, which was attributed to improved O_3 mass transfer [120]. Guo *et al.* have found that the RE of SMX doubled as O_3 dosage increased from 2 to 5 g/h, because the 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 O_3 concentration increase the 1639 amount of O_3 molecules and 'OH that were available to react with antibiotics in solution 1640 [79].

Wang et al. have also demonstrated that the RE of TC increases with increasing 1641 gaseous O_3 concentration and gas flowrate in a sonozonation system [80]. On the one 1642 hand, k_1 values were 0.42, 0.66, 0.85 and 1.34 min⁻¹ at 30, 35, 40 and 50 L/h of gas 1643 flowrate, respectively. The increasing gas flowrate increases the net surface area and 1644 improved O3 mass transfer from the gas phase to aqueous phase, thus increasing the 1645 volumetric mass transfer coefficient of O_3 [80]. On the other hand, k_1 values reached 1646 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 1647 1648 concentration, respectively. This suggests that the increasing gaseous O₃ concentration increased the equilibrium O₃ concentration in the aqueous phase, according to Henry's 1649 law. The increasing equilibrium O₃ concentration also improved O₃ mass transfer from 1650 the gas phase to the liquid phase [80]. 1651

1652 7.3.2 Effect of pH value

The pathways of ozonation generally include direct oxidation by O₃ molecules, 1653 which is more selective and predominant under acidic conditions, and the indirect 1654 oxidation by 'OH that is formed in situ, which is non-selective and predominant under 1655 alkaline conditions [79, 80]. Therefore, the predominant reaction and reaction rate 1656 during ozonation can be controlled by adjusting pH value, which is also considered a 1657 critical factor for the efficiency of sonozonation [79]. The increase of reaction rate 1658 means that a shorter reaction time is required to complete the degradation of antibiotics, 1659 1660 while O_3 consumption and operation costs are reduced [121].

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

protonated form is the predominant form at pH < 7, and is less susceptible to O₃ attack 1665 than the deprotonated form, leading to lower k_l values under acidic conditions (0.29) 1666 min⁻¹ at pH 3; 0.30 min⁻¹ at pH 5). At pH 7, SMX molecules were converted into the 1667 completely deprotonated form, which had a higher reactivity towards O₃ molecules. 1668 Under basic conditions, the oxidation of SMX was enhanced due to the generation of 1669 numerous 'OH species (0.42 min⁻¹ at pH 7; 0.50 min⁻¹ at pH 9). Consequently, the 1670 degradation rate of SMX under basic conditions was higher than under acidic 1671 1672 conditions [79].

Furthermore, the enhancement of sonication on SMX degradation by ozonation 1673 varied by 6-26% under different pH values, and the highest enhanced effect was 1674 observed at pH 5 [121]. This suggests that sonication promoted the diffusion of O₃ 1675 molecules in water under acidic conditions and increased the contact area between O₃ 1676 and SMX, resulting in increased RE of SMX by direct-oxidation with O₃ molecules. 1677 Under neutral and alkali conditions, sonication increased the degradation rates of SMX 1678 1679 by only 6-7%. This indicates that sonication slightly enhanced O₃ decomposition and 1680 the yield of 'OH, which is responsible for the indirect-oxidation [121].

TC degradation rate has also increased as the pH value increased from 3 to 9 in a 1681 sonozonation process [80]. Similarly, there are four different species of TC molecule, 1682 TCH_3^+ , TCH_2 , TCH^- and TC^{2-} , in which the protonation-deprotonation reactions 1683 depend on pH value. The deprotonated TC with a positively charged group at higher 1684 pH values is more easily attacked by O₃ molecules and/or 'OH than TC itself. Thus, the 1685 TC degradation rate increases with increasing pH [80]. Likewise, AMX is a hydrophilic 1686 and weak polyprotic acid with three *pKa* values of 2.67, 7.11 and 9.55 at 37 °C. At pH 1687 10, dissolution is favoured for the more degradable forms of AMX when the amine is 1688 deprotonated and a pair of electrons is available for electrophilic attack, while the 1689 increased solubility of AMX at pH 10 leads to higher reaction rates in the presence of 1690 the readily abundant radicals formed in the 575 kHz US field [78]. 1691

1692 7.3.3 Effect of initial antibiotic concentration

Since the concentrations of O₃ and 'OH available are almost identical under the 1693 same operation conditions in a sonozonation system, and are independent of the initial 1694 antibiotic concentrations, the degradation rate decreases mostly with increasing 1695 antibiotic concentration. For example, the k_1 value of SMX degradation decreased 1696 three-fold (from 0.37 to 0.09 min⁻¹) as SMX concentration increased from 50 to 400 1697 mg/L in a sonozonation system. The additional reason for this is the fact that the 1698 competing reactions between SMX and its degradation products gradually turned 1699 predominant with the increasing initial SMX concentration. Such competing reactions 1700 reduced the reaction rates of SMX with O₃ and 'OH [79]. Similarly, the TC degradation 1701 rate also decreased with increasing initial TC concentration in a sonozonation system, 1702 and the k_1 value decreased from 0.92 to 0.59 min⁻¹ when TC concentration increased 1703 from 200 to 800 mg/L [80]. 1704

1705 7.3.4 Effect of power density of US

1706 Increasing US power density can generally enhance the turbulence effect, resulting in increased antibiotic degradation rates, as the enhanced turbulence favours O₃ mass 1707 transfer from the gas to liquid phase [79]. It has been speculated that powerful 1708 sonication enhances mechanical mixing, making O₃-containing bubbles smaller and 1709 1710 reducing the thickness of liquid films [80]. In addition, more O_3 molecules can be decomposed to generate more ROS under more powerful sonication. For example, the 1711 k_l values of SMX degradation reached 0.25, 0.26 and 0.30 min⁻¹ at 400, 600 and 800 1712 W/L of power density in a sonozonation system, respectively [79]. Moreover, the TC 1713 degradation rate increased with increasing power density, and the k_l values of TC 1714 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, 1715 169.8 and 218.6 W/L of power density, respectively [80]. 1716

1717 7.3.5 Other concerning issues

1718 The chemical structures and hydrophobicity of antibiotics generally influence their
degradation kinetics and efficiency [120]. Little competitive oxidation of SMX, diclofenac and carbamazepine has been observed in a mixing solution under sonozonation, showing that the simultaneous presence of SMX, diclofenac and carbamazepine is not an obstacle for degradation via sonozonation [120].

This indicates that the oxidation of TC by 'OH that are generated *in situ* dominates the degradation of TC by sonozonation. By contrast, the addition of the radical scavenger *t*-butanol can accelerate the SMX degradation rate [79], and it has been speculated that the direct oxidation of SMX by O₃ molecules is the dominant pathway in the sonozonation system. The presence of H_2O_2 improved the TC degradation rate when the H_2O_2 concentration did not exceeded 10 mM, while the presence of t-butanol inhibited the TC degradation rate to some extent [80].

Alkalinity and humic acid species reduced the RE (50% decrease) by sonication
alone as radical reactions control the degradation of AMX [78]. However, the addition
of alkalinity, humic acid and both did not significantly change the removal rate of AMX
during both ozonation and sonozonation, since, in this case, the reaction of AMX with
O₃ molecules controls the degradation [78].

Besides enhancing the degradation of antibiotics by ozonation, sonication can 1735 1736 simultaneously promote the mineralization and detoxification of antibiotics in aqueous solutions. The Microtox toxicity test has been used to find the concentration value of 1737 the treated effluents that affects 50% of the microorganisms in a solution (EC50), and 1738 thus to assess the toxicity of solutions. The initial AMX solution shows high toxicity 1739 with a EC50 value of 14% [78]. Under sonozonation (250 mL of 25 mg/L AMX, 575 1740 kHz, 75 W/L US power, 0.13 mg/L O₃, pH 10.0, 90 min treatment), the EC50 value 1741 1742 decreased to 10.87% and 13.59% after treatment with sonication and ozonation alone, respectively, showing that the intermediates with higher toxicity were formed during 1743 the degradation of AMX. By contrast, the EC50 value increased to 67.48% under 1744 1745 sonozonation, indicating that fewer intermediates were formed with a higher mineralization degree [78]. For the degradation of 100 mg/L SMX by sonozonation, 1746

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

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

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

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

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

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Declaration of Competing Interest

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

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