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REVIEW

Effect of pH on the sonochemical degradation of organic pollutants

Zongsu Wei[1,2] · **Richard Spinney**[3] · **Runhui Ke**[4] · **Zhihui Yang**[1,5] · **Ruiyang Xiao**[1,5]

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Abstract An increasing number of organic compounds are manufactured, consumed, and discarded every year. Incomplete destruction of these compounds in wastewater treatment plants leads to pollution of natural waters, posing great health and ecological concerns. Ultrasound, as an emerging advanced oxidation technology, can quickly and effectively degrade organic pollutants in waters. To improve removal efficiency of organic pollutants in an ultrasonic system, operational parameters, especially pH, have been frequently evaluated and optimized. This review show that pH-induced changes in volatility, hydrophobicity and Coulombic force between the target compound and cavitation bubbles leads to higher degradation at acidic pH for most compounds. In addition, pH also changes free radical formation and reactivity in water during sonication, thereby altering degradation kinetics of target compounds. However, the influence of pH is not always consistent for various organic pollutants covering a broad range of physicochemical properties and reactivities. A systematic investigation on the pH effect is necessary to elucidate how pH alters cavitation bubble dynamics and collapse, radical yield and reactivity, distribution of target compounds in the vicinity of cavitation bubbles, water matrices transformation, and ultimately the degradation kinetics of organic pollutants. This first systematic review provides valuable insight into the pH effects on organic pollutant sonolysis, helps to improve our mechanistic understanding of the sonochemical system, and sheds light on future application of ultrasound in water engineering.

Keywords Ultrasound · Volatility · Hydrophobicity · Coulombic force · Free radical

List of symbols

C	Aqueous concentration of organic pollutants (M)
$\Delta_{\text{soln}}H$	Enthalpy of solution (kJ mol^{-1})
K	Specific heat ratio (unitless)
K_{H}	Henry's law constant (Pa m^3 mol^{-1})
K_{H}°	Henry's law constant at standard temperature (Pa m^3 mol^{-1})
K_{OW}	Octanol water partition coefficient (unitless)
p	Partial pressure of target compound in the aqueous solution (Pa)
P	Inside pressure of the bubble at its maximum size (Pa)
P_m	Pressure in liquid upon bubble collapse (Pa)
R	Universal gas constant (J K^{-1} mol^{-1})
t	Time (s)
T	Temperature (K)
T°	Standard temperature (K)
T_0	Ambient temperature (K)
$T_{\max}$	Maximum temperature for bubble collapse (K)

✉ Ruiyang Xiao
xiao.53@csu.edu.cn

[1] Institute of Environmental Engineering, School of Metallurgy and Environment, Central South University, Changsha 410083, China

[2] Grand Water Research Institute-Rabin Desalination Laboratory, Wolfson Faculty of Chemical Engineering, Technion-Israel Institute of Technology, 3200003 Technion City, Haifa, Israel

[3] Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210, USA

[4] China National Research Institute of Food and Fermentation Industries, Beijing 100015, China

[5] Chinese National Engineering Research Center for Control and Treatment of Heavy Metal Pollution, Changsha 410083, China

γ Surface tension (J m^{-2})
Γ Surface excess (M m^{-2})

Introduction

Organic pollutants in municipal wastewater consist of a wide range of synthetic chemicals, such as antioxidants, plasticizers, pharmaceuticals and personal care products. These pollutants are biologically active to some extent and pose a threat to the aquatic environment and human health (Daughton and Ternes 1999). To minimize the potential risk, efforts are underway to reduce the exposure of pollutants in waters. However, conventional wastewater treatment technologies, such as activated sludge treatment and sorption, do not necessarily achieve high removal efficiency for these emerging pollutants, especially trace organic chemicals, since they are hydrophilic, less volatile, and exhibit toxic effects to microorganisms (Oulton et al. 2010; Xiao et al. 2014a, b, c). Therefore, effluent from municipal sewage treatment plant is the major source for trace pollutants to enter natural waters.

Ultrasound is an emerging advanced oxidation process that can quickly and effectively degrade organic pollutants in waters. It has several unique advantages when compared to other conventional oxidation technologies, including lack of potentially harmful chemicals, ease of use, and short contact time (Adewuyi 2005a, b; Hoffmann et al. 1996). When water is exposed to ultrasound, acoustic pressure waves are generated. The acoustic pressure waves consist of compression and rarefaction cycles. In the rarefaction cycle of the acoustic pressure wave, it leads to the formation of bubbles from the gas nuclei that exist in water. In the compression cycle, the bubble volume decreases due to increasing pressure in the surrounding water (Mason and Lorimer 1988). Thus, bubbles grow and shrink in response to alternating acoustic pressures. Within several compression and rarefaction cycles, bubbles collapse when the ultrasonic intensity is beyond the cavitation threshold, known as cavitation bubbles (Suslick 1989).

The collapse of cavitation bubbles causes extreme conditions that are depicted by the hot spot theory, as shown in Fig. 1a (Suslick et al. 1986). In the center of collapsing bubble (i.e., gas region), the temperature and pressure are approximately 5000 K and 1000 atm, respectively (Flint and Suslick 1991). The high temperature leads to the breakdown of gaseous water molecule in the bubble to hydroxyl radicals ($^{\cdot}$OH) and hydrogen atoms ($^{\cdot}$H) (Flint and Suslick 1991):

$$H_2O \xrightarrow{(((} {}^{\cdot}OH + {}^{\cdot}H \qquad (1)$$

The temperature in the interfacial region surrounding the hot core is estimated to be 1900 K, and the $^{\cdot}$OH concentration is estimated to be up to 4 mM (Gutierrez et al. 1991). The thickness of the interfacial region is estimated to be 200 nm (Mason et al. 1990). The temperature of bulk phase surrounding the cavitation bubble is ambient. The $^{\cdot}$OH formed in the bubble core diffuses to the bubble–water interface and then to the bulk phase due to $^{\cdot}$OH concentration gradient, as shown in Fig. 1b (Adewuyi 2005a). Therefore, in a sonicated solution, an organic molecule undergoes degradation by two different pathways: decomposition by heat in the gas and interfacial regions of the cavitation bubbles and $^{\cdot}$OH oxidation in the gas, interfacial, and bulk regions, as indicated in the follow equation (Adewuyi 2001; Hoffmann et al. 1996; Mendez-Arriaga et al. 2008; Riesz et al. 1985; Weavers et al. 2005):

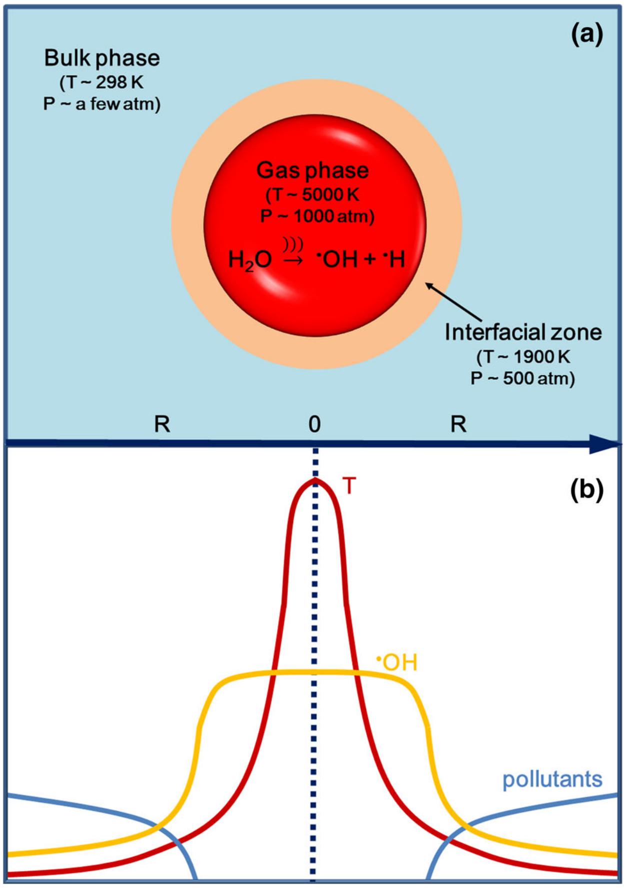

Fig. 1 Schematic diagrams of hot spot theory for a cavitation bubble (**a**) and corresponding spatial distributions of temperature (*T*), $^{\cdot}$OH, and organic pollutants surrounding the bubble (**b**; *vertical axis* is arbitrary). In the hot spot theory, the cavitation bubble is divided into three regions: gas phase, interfacial zone, and bulk phase. The temperature decreases rapidly from as high as 5000 K at the bubble core to ambient in the bulk solution. $^{\cdot}$OH is generated from thermolysis of water molecules in the gas phase and diffuses to the interface and bulk solution due to the concentration gradient. Organic pollutants undergo two major degradation pathways, thermolysis and radical oxidation, thereby exhibiting a increasing trend in spatial distribution as compared to temperature and $^{\cdot}$OH

$$\left(\frac{\mathrm{d}C}{\mathrm{d}t}\right)_{\mathrm{obs}} = k_{\mathrm{thermolysis}}[C] + k_{\cdot\mathrm{OH}}[C][{}^{\cdot}\mathrm{OH}] \quad (2)$$

where $\left(\frac{\mathrm{d}C}{\mathrm{d}t}\right)_{\mathrm{obs}}$ is the observed degradation rate of a given organic pollutant in the unit of M min^{-1}, $k_{\mathrm{thermolysis}}$ and $k_{\cdot\mathrm{OH}}$ are the thermolysis and $^{\cdot}$OH oxidation rate constants for the organic pollutant, respectively; $[C]$ and $[{}^{\cdot}\mathrm{OH}]$ represent the concentrations of the pollutant and $^{\cdot}$OH in solution, respectively.

In the past three decades, intensive efforts have been exerted to understand various factors determining the effectiveness of ultrasound in removing organic pollutants from waters. In general, three factors affect the removal efficiency of organic pollutants in waters, ultrasonic operational conditions (e.g., ultrasonic intensity, frequency, and mode), physicochemical properties of organic pollutants (e.g., surface excess, Γ, octanol–water partition coefficient, K_{OW}, Henry's law constant, K_{H}, and diffusivity, D), and solution chemistry (e.g., ionic strength and pH) (Adewuyi 2005a, b; Bolong et al. 2009; Brotchie et al. 2009; Colussi et al. 1999; Francony and Petrier 1996; Jiang et al. 2002; Mendez-Arriaga et al. 2008; Mizukoshi et al. 1999; Nanzai et al. 2008; Pee et al. 2015; Petrier et al. 1996; Xiao et al. 2013b). Studies on the impacts of solution chemistry on sonochemical degradation of contaminants have focused mainly on the pH (Chakinala et al. 2007; Ince et al. 2009; Jiang et al. 2002; Tauber et al. 2000; Uddin and Hayashi 2009), since it is considered the most practical and easiest adjustable parameter during treatment processes. These studies are vital for a better understanding of the application of ultrasound in drinking water and wastewater treatments, since water sources usually exhibit different pH values, depending on the geological conditions of groundwater or the origins of wastewaters (i.e., industrial or domestic wastewaters).

Although pH exerts a significant influence on removal efficiency of organic pollutants, the influence is not always consistent and there is lack of systematic investigation on the pH effect. The rationale for this review is to provide a comprehensive review to fulfill the knowledge gap in pH effects on sonochemical degradation of organic pollutants. In particular, we conducted a systematic literature investigation on pH effects, covering a temporal range from 1990s to 2010s, totaling 78 peer-reviewed literature, see Table 1. Among the list, combined systems such as ultrasound-UV, ultrasound-ozone, and ultrasound-Fenton are also included, as well as studies that include no or unclear explanations on the pH effects (Cyr et al. 1999; Goel et al. 2013; Goskonda et al. 2002; Hua et al. 1995; Okouchi et al. 1992; Shimizu et al. 2007; Shriwas and Gogate 2011; Suri et al. 1999; Wang et al. 2008; Wu et al. 1992, 2001b; Yoo et al. 1997; Zhang et al. 2007; Zhou and Ma 2006). We discuss how pH alters cavitation effects including collapse temperature and $^{\cdot}$OH formation, followed by pH-induced changes in physicochemical properties for organic pollutants, effects of coexisting species in water (i.e., water matrices), and consequent degradation kinetics of organic pollutants in the sonication system. To the best of our knowledge, this is the first summary of pH effects on the sonochemical degradation kinetics of organic pollutants.

pH effects on collapse temperature, radical yield and reactivity, and consequently degradation kinetics of organic pollutants

Collapse temperature

According to Eq. 2, collapse temperature of a cavitation bubble (i.e., $k_{\mathrm{thermolysis}}$), production of free radicals (i.e., $[{}^{\cdot}\mathrm{OH}]$), and their distribution surrounding the bubble all impact organic pollutant degradation kinetics to different extents (Fig. 1b). At collapse, the maximum temperature ($T_{\max}$, K) for cavitation bubbles is expressed as follows:

$$T_{\max} = T_0\left[(K-1)\frac{P_m}{P}\right] \quad (3)$$

where T_0 is the ambient temperature (K), K is the specific heat ratio (unitless), P_m is the pressure in liquid upon bubble collapse (Pa), and P is the pressure inside of the bubble at its maximum size (Pa). According to Eq. 3, the collapse temperature of cavitation bubbles depends on the saturation of different gases into solution (i.e., K) and ultrasonic operational parameters such as intensity and frequency that will alter P and P_m. The pH indirectly affects the collapse temperature of cavitation bubbles (case #1 and 2 in Table 1). For instance, Drijvers et al. (1996) observed that $\mathrm{CO_2}$ formed from mineralization of trichloroethylene during sonication diffuses into the gas phase at acidic pH, thereby reducing the specific heat ratio of vapor and thus the collapse temperature. They also attributed the unchanged sonochemical degradation kinetics of chlorobenzene at different pH to the low $\mathrm{CO_2}$ yield, thus fixing the specific heat index and consequent collapse temperature of cavitation bubbles (Drijvers et al. 1998).

Radical yield

For the radical oxidation, the degradation kinetics of organic pollutants are controlled by both radical reactivity (i.e., $k_{\cdot\mathrm{OH}}$) and quantity (i.e., $[{}^{\cdot}\mathrm{OH}]$), as shown in Eq. 2. Many studies (case #3–18 in Table 1) observed decreasing degradation kinetics of organic pollutants with increasing pH and cited three explanations for the $^{\cdot}$OH yield: (1) $^{\cdot}$OH self-combines to form $\mathrm{H_2O_2}$ at high pH; (2) $^{\cdot}$OH is scavenged by the buffer solutions, such as $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$ at

Table 1 Literature summary of pH effects on sonochemical degradation of organic pollutants

No.	Reference	pH range	Saturation gas	Frequency[a]	Process	Organic pollutants	Observation	pK_a	Explanation
1	Drijvers et al. (1996)	4.7–10	Air	20, 520	US[c]	Trichloroethylene	Degradation rate increases with pH	No	Formed CO_2 at acidic condition diffuses into gas phase reducing the specific heat ratio of vapors and thus cavitation
2	Drijvers et al. (1998)	4.7–10	Air, Ar	520	US	Chlorobenzene	No impact on degradation kinetics is observed at tested pH range	No	CO_2 is too low to influence specific heat index and subsequent collapse temperature of cavitation bubbles at different pH values
3	Poon et al. (1999)	3–11	Air	NR[b]	US/UV/ H_2O_2	Cuprophenyl yellow RL	Degradation rate increases with pH	NR	H_2O_2 decomposition increases at alkaline pH resulting in higher degradation
4	Fung et al. (2000)	5–11	Air	NR	US/UV/ H_2O_2	Reactive red 120	Degradation rate increases with pH	NR	H_2O_2 decomposition increases at alkaline pH resulting in higher degradation
5	Adewuyi and Appaw (2002)	8–11	Air, Ar, NO	20	US	Carbon disulfide	Degradation rate decreases with pH	No	$^{\cdot}OH$ dissociates at high pH resulting in reduced degradation
6	Yim et al. (2002)	4–12.5	Air	200	US	Phthalic acid esters	Degradation rate remains stable before pH 11, but increases above pH 11	Yes	Radical oxidation is independent on pH, but hydrolysis reaction for phthalic acid esters at pH above 11 results in a faster degradation
7	Ince and Tezcanli-Guyer (2004)	3–9.5	Air	300	US	Acid orange 7, reactive orange 16	Degradation rate decreases with pH	Yes	$^{\cdot}OH$ recombination to form H_2O_2, $^{\cdot}OH$ scavenging by added HCO_3^- buffer, and ionized forms of dye all lead to the reduced degradation rate at high pH
8	Svitelska et al. (2004)	4–12	Air	20	US	Grape condensed tannin	Degradation rate remains stable before pH 8, but increases above pH 8	Yes	More radicals are formed at higher pH resulting in higher degradation rate
9	He et al. (2007a)	2–12	Air	20	US/ ozone	Reactive yellow 84	Degradation rate increases then decreases with pH	NR	$^{\cdot}OH$ formation increases with pH but $^{\cdot}OH$ is scavenged by CO_3^{2-} at alkaline pH
10	He et al. (2007b)	7–12	Air	20	US/ ozone	*p*-aminophenol	Slight increase in degradation rate is observed at higher pH values	Yes	Stability of O_3 decreases with pH resulting in more $^{\cdot}OH$ yield and thus higher degradation at high pH
11	Liang et al. (2007)	2–5.6	Air	28, 50, 100, 200, 600	US/ Fenton-like	2-Chlorophenol	Degradation linearly decreases with pH	Yes	Dissolved Fe facilitated $^{\cdot}OH$ formation at acidic pH, while Fe concentration is quite low at high pH resulting in low $^{\cdot}OH$ yield
12	Hamdaoui and Naffrechoux (2008)	5.5–12.7	Air	516	US/UV	4-Chlorophenol	Degradation rate decreases with pH	Yes	Rapid dissociation of $^{\cdot}OH$ in alkaline solutions and ionized forms of 4-chlorophenol lead to the reduced degradation at high pH

Table 1 continued

No.	Reference	pH range	Saturation gas	Frequency[a]	Process	Organic pollutants	Observation	pK_a	Explanation
13	Mendez-Arriaga et al. (2008)	3–11	Air	300	US	Ibuprofen	Degradation rate decreases with pH	Yes	$^{\cdot}$OH recombination to form H_2O_2 and ionized forms of ibuprofen lead to the reduced degradation at high pH
14	Ghodbane and Hamdaoui (2009)	1–11.8	Air	22.5, 1700	US	Acid blue 25	Degradation rate decreases from pH 1 to 5, then increases from 5 to 11.8	NR	$^{\cdot}$OH recombination to form H_2O_2 leads to the low degradation at pH 5 to 8, while the neutral forms of dye at acidic and alkaline pH results in high degradation
15	Quan and Chen (2011)	3.3–10.1	Air	NR	US/ozone	2,4-Dichlorophenoxyacetic acid	Degradation rate linearly increases with pH	Yes	More $^{\cdot}$OH is formed at high pH resulting in higher degradation rate
16	Uddin and Hayashi (2009)	2–11	Air, Ar, N_2, O_2	489	US	2,4-Dichlorophenol	Degradation increases then decreases with pH except for N_2 saturated solution	Yes	Hydrophobicity dominates degradation; radical scavenging by phosphoric acid at acidic pH results in low degradation
17	Katsumata et al. (2011)	2.5–5.4	Air	200	US/UV/Fenton	Linuron	Degradation rate decreases with pH	Yes	Higher concentration of dissolved Fe at acidic pH yields more $^{\cdot}$OH as compared to that at high pH
18	Cai et al. (2016b)	2–7	Air	No	HC/Fenton	Azo dyes Orange G	Degradation rate decreases with pH	Yes	Higher concentration of dissolved Fe at acidic pH yields more $^{\cdot}$OH resulting in higher degradation
19	Kotronarou et al. (1991)	3–12	O_2	20	US	*p*-nitrophenol	Degradation rate decreases with pH and remain stable at high pH	Yes	Increased stability of the nitrophenoxide ion and ionized forms of compound lead to the reduced degradation at high pH
20	Park et al. (2000)	2–12	Ar	20	US	Methylnaphthalene	Degradation rate decreases with pH	No	Oxidation potential of $^{\cdot}$OH radical decreases with pH (2.7 V in acidic solution, 1.8 V in neutral solution)
21	Gaddam and Cheung (2001)	3.96–12.5	Air	20	US	1,1,1-Trichloroethane	Degradation rate increases then decreases with pH	No	Dipole of free radical determines degradation kinetics at different pH values, and $^{\cdot}$OH decomposes to oxide ion at pH > 11
22	Tezcanli-Guyer et al. (2003)	3–4.72	Air	300	US	Reactive blue 19, basic blue 16, basic brown 4	Degradation rate increases with pH	No	High concentration of H^+ at low pH inhibits the degradation rate
23	Nakui et al. (2007)	0.8–9	Air	200	US	Hydrazine	Degradation rate decreases with pH and remain stable at pH from 2 to 7, then increases at higher pH	Yes	Hydrazine changes from $N_2H_6{}^{2+}$ to $N_2H_5{}^{+}$ to N_2H_4 with pH, and $k_{N_2H_6^{2+}} > k_{N_2H_4} > k_{N_2H_5^{+}}$

Table 1 continued

No.	Reference	pH range	Saturation gas	Frequency[a]	Process	Organic pollutants	Observation	pK_a	Explanation
24	Wang et al. (2009)	2–10	Air	No	HC[d]	Rhodamine B	Degradation rate decreases with pH	Yes	Oxidation potential of ${}^{\cdot}$OH radical and H_2O_2 quantity both decreases with pH, and radical is scavenged by buffer (i.e., $CO_3{}^{2-}$, $HCO_3{}^{-}$) at higher pH leading to the reduced degradation
25	Patil and Gogate (2012)	2.2–8.2	Air	No	HC	Methyl parathion	Degradation rate increases then decreases with pH	Yes	The faster radical yield and higher oxidation potential of ${}^{\cdot}$OH at acidic condition result in higher degradation
26	Banerjee et al. (2013)	1.5–13.5	Air	50	US	Rhodamine 6G	Degradation rate decreases then increases with pH	Yes	The faster radical yield and higher oxidation potential of ${}^{\cdot}$OH at acidic condition result in higher degradation, while degradation of rhodamine 6G in neutral form is favored at alkaline pH
27	Xu et al. (2013)	2–11	Air	400	US	Dimethyl phthalate	Degradation rate increases then decreases with pH	No	Radical scavenging by hydrogen sulfate ion at acidic pH results in the low degradation, while decreased oxidation potential of ${}^{\cdot}$OH and scavenging of ${}^{\cdot}$OH by OH^- depresses the degradation at alkaline pH
28	Lin et al. (1996)	3–11	O_2	20	US/H_2O_2	2-Chlorophenol	Degradation rate linearly decreases with pH	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high thermolysis and radical oxidation at low pH
29	Ku et al. (1997)	3–11	O_2	20	US	2-Chlorophenol	Degradation rate decreases with pH	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high degree of thermolysis and radical oxidation at low pH
30	Ashokkumar et al. (1999)	3–12	Air	515	US	*n*-propanoic acid, *n*-butanoic acid, *n*-pentanoic acid, *n*-propylamine, *n*-butylamine, *n*-pentylamine, and *β*-alanine	Degradation rate decreases with pH for propanoic, butanoic and pentanoic acids, increases then decreases for propylamine, butylamine, pentylamine, and no impact is observed for alanine	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high thermolysis and radical oxidation at low pH
31	Lin and Ma (1999)	3–11	Air	20	US	2-Chlorophenol	Degradation rate decreases with pH	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high degree of thermolysis and radical oxidation at low pH

Table 1 continued

No.	Reference	pH range	Saturation gas	Frequency[a]	Process	Organic pollutants	Observation	pK_a	Explanation
32	Ashokkumar et al. (2000)	2–12	Air	515	US	1-Propanoic and 2-chloropropanoic acids, 1-butanoic and chlorobutanoic acids, phenol and aniline	Degradation rate decreases with pH and remains stable at high pH for propanoic chloropropanoic, butanoic, and chlorobutanoic acids, remains unchanged then decreases for phenol, increases and then remains stable for aniline	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high degree of thermolysis and radical oxidation at low pH
33	Tauber et al. (2000)	4–10	Ar	321	US	4-Nitrophenol	Degradation rate decreases with pH	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high degree of thermolysis and radical oxidation at low pH
34	Price et al. (2002)	2–10	Air	20, 515	US	Acrylic acid, methacrylic acid	Degradation rate decreases with pH and remains stable at high pH for 515 kHz, no impact by pH for 20 kHz	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high degree of thermolysis and radical oxidation at low pH
35	Singla et al. (2004)	2.5–6.5	Ar	355	US	Benzoic acid	Degradation rate decreases with pH	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high degree of thermolysis and radical oxidation at low pH
36	Guo et al. (2005)	2–8	Air	20	US	2,4-Dinitrophenol	Degradation rate decreases with pH	Yes	High Henry's law constant of compound in neutral form results in high thermolysis and radical oxidation at low pH
37	Sivakumar et al. (2002)	3–7	Air	25, 40	US	*p*-nitrophenol	Degradation rate linearly decreases with pH	Yes	High Henry's law constant/hydrophobicity of compound in neutral form results in high degree of thermolysis and radical oxidation at low pH
38	Serpone et al. (1992)	3–12	Air	20	US	Phenol	Degradation rate decreases with pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
39	Cost et al. (1993)	NR	Air	20	US	*p*-nitrophenol	Degradation kinetics is slow at higher pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation

Table 1 continued

No.	Reference	pH range	Saturation gas	Frequency[a]	Process	Organic pollutants	Observation	pK_a	Explanation
40	Peller et al. (2001)	2.2–11.8	Ar, O_2	640	US	2,4-Dichlorophenoxyacetic acid	Degradation rate decreases with pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
41	Wu et al. (2001a)	3–11	Air	30	US/UV	Phenol	Degradation rate decreases with pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
42	Okitsu et al. (2005)	2–6.5	Ar	200	US	Methyl orange	Degradation rate is slow at higher pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
43	Ozen et al. (2005)	3–6.1	Air	300	US	Acid orange 7 acid orange 8	Degradation rate decreases with pH	NR	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
44	Shemer and Narkis (2005)	3–10	Air	20	US	Trihalomethane	Little effect in trihalomethane degradation is observed at tested pH range	No	Trihalomethane without pK_a values have no ionized form and therefore no variance in degradation at different pH values
45	Weavers et al. (2005)	2.8–7.4	Air	20, 354	US	Octylbenzene sulfonic acid, octylphenoxy polyethoxyethanol	No impact on degradation is observed at tested pH range	No	Surfactant is always transphilic no matter what pH is, so no variance in degradation kinetics is observed
46	Song et al. (2006)	2.3–9.7	Air	640	US	Microcystin-LR microcystin-RR	Degradation rate decreases with pH, and then remains stable	NR	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
47	Chakinala et al. (2007)	4.2–11	Air	20	US	Salicylic acid	Degradation rate decreases with pH	Yes	Hydrophobicity dominate degradation, but not fully applicable to all pH range
48	Vajnhandl and Le Marechal (2007)	2–10	Ar	20, 279, 817	US	Reactive black 5	Degradation rate decreases with pH	NR	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation

Table 1 continued

No.	Reference	pH range	Saturation gas	Frequency[a]	Process	Organic pollutants	Observation	pK_a	Explanation
49	Wang et al. (2007)	2–8	Air	20	US	Methyl orange	Degradation rate decreases with pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
50	Behnajady et al. (2008)	2–10	Air	35	US	Rhodamine B	Degradation rate decreases with pH, then remains stable	NR	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
51	Gultekin and Ince (2008)	3–10.5	Air	300	US	Bisphenol-A	Degradation rate remains same at acidic and neutral pH, then decreases in alkaline solution	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
52	Okitsu et al. (2008)	2–6	Air	45, 200	US	Methyl orange	Degradation rate is slow at higher pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
53	Ince et al. (2009)	3–10.8	O_2	20, 861	US	4-*n*-nonylphenol	Degradation rate decreases then increases with pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation. The hydrophobic alkyl chain and hydrophilic phenol moiety at high pH results in faster decomposition at the interface
54	Chen and Huang (2011)	0.2–2	Air	20	US/TiO_2	Dinitrotoluenes trinitrotoluene	Degradation rate decreases with pH	No	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
55	Saharan et al. (2012)	2–11	Air	No	HC	Acid red 88	Degradation rate decreases with pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
56	Dalhatou et al. (2013)	3–10.8	Air	278	US	Naphthol blue	Degradation rate decreases with pH	NR	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation

Table 1 continued

No.	Reference	pH range	Saturation gas	Frequency[a]	Process	Organic pollutants	Observation	pK_a	Explanation
57	Yang et al. (2013)	3–11	Air	600	US/UV	Perfluorooctane sulfonate	Degradation rate decreases with pH and remains stable at high pH	Yes	High hydrophobicity of compound in neutral form at low pH results in high degree of accumulation at the bubble–water interface, thus fast degradation
58	Kim et al. (2001)	3–9	Air	20	US	Dibenzothiophene	Degradation rate increases with pH	No	Dibenzothiophene intermediates become increasingly charged at higher pH resulting increased degradation rates
59	Kaur and Singh (2007)	3.5–9	O_2	47	US/UV/ TiO_2	Reactive red 198	Degradation rate decreases with pH	Yes	Positively charged TiO_2 in acidic pH attracts more dye adsorbed on its surface resulting in high degradation rate
60	Cheng et al. (2010)	3–11	Ar	612	US	Perfluorooctane sulfonate, perfluorooctanoate	Degradation rate is high at $pH < 4$, but remains stable at $pH > 4$	Yes	Bubble surface is increasingly positively charged at acidic pH, thereby attracting more contaminants with opposite charge
61	De Bel et al. (2009)	2–11	Air	520	US	Ciprofloxacin	Degradation rate decreases with pH, then remains stable	Yes	Ciprofloxacin with higher charge at low pH is more easily attached to negatively charged bubble resulting in higher degradation rate
62	Anju et al. (2012)	3–11	Air	40	US/UV/ ZnO, TiO_2	Phenol	Degradation rate increases then decreases with pH	Yes	pH alters the surface charge of metal oxides and thus adsorption and degradation of phenol
63	Jiang et al. (2002)	2.2–8.8	O_2	610	US	4-Nitrophenol, aniline	Degradation rate of 4-nitrophenol decreases with pH; degradation of aniline increases with pH then remains stable after pH 7	Yes	Charge and hydrophobicity dominant degradation for 4-nitrophenol; high reaction rate constant leads to high degradation rate for aniline
64	Kidak and Ince (2006)	2–10	Air, Ar	20, 300, 520	US	Phenol	Degradation rate decreases with pH	Yes	Phenolate at high pH repulses with negatively charged bubble resulting in low degradation rate, and high hydrophobicity of neutral form phenol results in high degradation rate at low pH
65	Okouchi et al. (1992)	1–12	Air, He, N_2, O_2	200	US	Phenol	Degradation rate increases then decreases with pH	Yes	No explanation is given
66	Wu et al. (1992)	4–10	Air	20	US	Carbon tetrachloride	Degradation rate increases with pH	No	No explanation is given
67	Hua et al. (1995)	3–8	Ar, He, Kr	NR	US	*p*-nitrophenyl acetate	No significant difference in degradation kinetics is observed at tested pH range	Yes	No explanation is given

Table 1 continued

No.	Reference	pH range	Saturation gas	Frequency[a]	Process	Organic pollutants	Observation	pK_a	Explanation
68	Yoo et al. (1997)	3.8–10.6	Air	200	US	*n*-valeric acid	Degradation rate decreases with pH	Yes	No explanation is given
69	Cyr et al. (1999)	3.1–11	Air	20	US	Trichloroethylene	No significant difference in degradation kinetics is observed at tested pH range	No	No explanation is given
70	Suri et al. (1999)	3–11	Air	20	US	Trichloroethylene	No significant difference in degradation kinetics is observed at tested pH range	No	No explanation is given
71	Wu et al. (2001b)	1.12–11.2	Air	30	US/UV	Trichloroacetic acid	Degradation rate increases with pH	Yes	No explanation is given
72	Goskonda et al. (2002)	1–10	Air	20	US	4-Chlorophenol	Degradation rate increases with pH then remains stable	Yes	No explanation is given
73	Zhou and Ma (2006)	3–6.39	Air	20	US	Polysaccharide from Porphyra yezoensis	Degradation rate decreases with pH	NR	No explanation is given
74	Shimizu et al. (2007)	3–12	Air	39	US/ H_2O_2/ TiO_2	Methylene blue	Degradation rate remains stable at acidic and neutral pH, but increases in alkaline solution	Yes	No explanation is given
75	Zhang et al. (2007)	2–7	Air	20	US/ Fenton	Reactive black 8	Degradation rate decreases with pH	NR	No explanation is given
76	Wang et al. (2008)	2–12	Air	20	US	Reactive brilliant red K-BP	Degradation rate decreases from pH 2 to 8, then increases from 8 to 12	NR	No explanation is given
77	Shriwas and Gogate (2011)	2.5–9.3	Air	20	US	Methyl parathion	Degradation rate linearly decreases with pH	No	No explanation is given
78	Goel et al. (2013)	3–11	Ar, N_2, O_2	20	US/ ozone	Eosin B	No significant difference in degradation kinetics is observed at tested pH range	Yes	No explanation is given

[a] Frequency is in the unit of kHz

[b] NR denotes not reported

[c] US denotes ultrasound

[d] HC denotes hydrodynamic cavitation

high pH; and (3) $^{\cdot}$OH deprotonates at pH > 11 (Adewuyi and Appaw 2002; Ghodbane and Hamdaoui 2009; Ince and Tezcanli-Guyer 2004; Mendez-Arriaga et al. 2008; Svitelska et al. 2004; Uddin and Hayashi 2009; Yim et al. 2002). However, in synergistic systems combining ultrasound, UV, ozone, and H_2O_2, the effect of pH on radical yield and consequent organic pollutant degradation kinetics is more complex. Particularly, ultrasound-ozone combination exhibited increased degradation kinetics with an increase in pH (He et al. 2007a, b; Quan and Chen 2011; Sierka 1984). Elovitz et al. (2000) attributed the enhanced degradation kinetics to the OH^- initiated decomposition of ozone and possible high $^{\cdot}$OH yield at high pH in the ultrasound-ozone system. The ultrasound-UV–H_2O_2 system has the same trends as seen in the ultrasound-ozone system (Fung et al. 2000; Poon et al. 1999). In the combined system of ultrasound-Fenton, acidic condition was favorable for degradation since dissolved iron facilitates $^{\cdot}$OH formation at low pH through Fenton reaction, while iron concentration is quite low at high pH (Cai et al. 2016a, b; Katsumata et al. 2011; Liang et al. 2007).

On the other hand, different free radical formation and reaction pathways at various pH result in different quantities of oxidative radicals during sonication, thereby altering the degradation kinetics of organic pollutants (Adewuyi and Appaw 2002; Bielski et al. 1985; Buxton et al. 1988; Czapski and Dorfman 1964; Ross and Ross 1977; Fung et al. 2000; He et al. 2007a, b; Kotonarou et al. 1992; Matheson and Rabani 1965; Orzechowska et al. 1995; Pang et al. 2011; Poon et al. 1999; Sehested et al. 1968; Sierka and Amy 1985; Svitelska et al. 2004; Weavers et al. 2000; Yu 2004). However, very few studies have quantitatively investigated oxidative radicals at different pH during sonolysis. Therefore, it is necessary to revisit this issue and scrutinize the potential influence of free radicals (e.g., hydroperoxyl radical, $^{\cdot}HO_2^-$) on organic pollutant degradation.

Radical reactivity

The reactivity of $^{\cdot}$OH (i.e., $k_{\cdot OH}$ in Eq. 2) is also used to explain the sonochemical degradation trend of organic pollutants at different pH values (case #19–27 in Table 1). For example, different degradation rates of non-ionizable chemicals were attributed to the higher oxidation potential of $^{\cdot}$OH in acidic solutions ($E° = 2.78$ V) than that in neutral and basic solutions ($E° \leq 1.80$ V) (Park et al. 2000). The oxidation potential of $^{\cdot}$OH was also considered to contribute the varied degradation kinetics of rhodamine B and methyl parathion in a pH-dependent manner in ultrasonic systems (Patil and Gogate 2012; Wang et al. 2009). Nakui et al. (2007) correlated hydrazine degradation kinetics to reaction rate constants at different pH values, confirming varied $^{\cdot}$OH reactivity in the presence H^+ and OH^-.

pH effects on physicochemical properties of target organic pollutants and their degradation kinetics

In Eq. 2, the proportion of each pathway (i.e., $k_{\mathrm{thermolysis}}$ or $k_{\cdot OH}$) to the whole degradation is dependent on the physicochemical properties of organic pollutants (Adewuyi 2001; Hoffmann et al. 1996; Xiao et al. 2014b). Usually, pH affects degradation kinetics of non-ionizable organic pollutants by altering quantity and reactivity of free radicals. For acidic or basic organic pollutants, pH controls the protonation of organic acids and bases and thus their degradation kinetics, as shown in Fig. 2. In particular, the pH-dependent protonation or deprotonation results in changes in volatility of a compound described by Henry's law constants (K_H) (Ashokkumar et al. 1999, 2000; Guo et al. 2005; Ku et al. 1997; Lin et al. 1996; Lin and Ma 1999; Price et al. 2002; Singla et al. 2004; Sivakumar et al. 2002; Tauber et al. 2000), hydrophobicity described by octanol–water partition coefficient (K_{OW}) (Behnajady et al. 2008; Chakinala et al. 2007; Chen and Huang 2011; Cost et al. 1993; Dalhatou et al. 2013; Gultekin and Ince 2008; Ince et al. 2009; Okitsu et al. 2005, 2008; Ozen et al. 2005; Peller et al. 2001; Saharan et al. 2012; Serpone et al. 1992; Shemer and Narkis 2005; Song et al. 2006; Vajnhandl and Le Marechal 2007; Wang et al. 2007; Weavers et al. 2005; Wu et al. 2001a; Yang et al. 2013), and Coulombic interactions between the compound and the cavitation bubbles

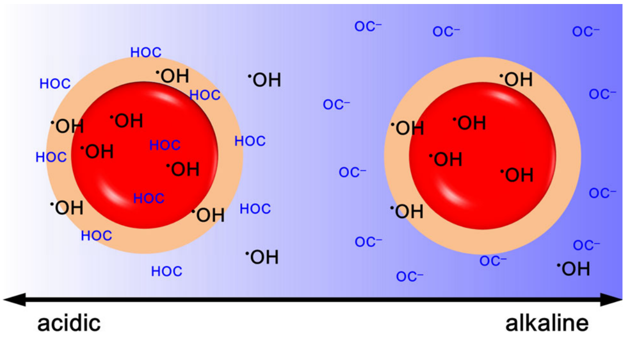

Fig. 2 Speciation, location, and degradation of a hypothetical acidic organic compound ($HOC = OC^- + H^+$) from acidic to alkaline condition in a sonicated solution. Note the HOC in neutral form at acidic pH accumulates on the bubble–water interface and diffuses into bubble core resulting in intensive radical oxidation and thermolysis reaction, while OC^- in deprotonated form at alkaline pH remains in the bulk solution, where radical oxidation is the major reaction pathway

(Anju et al. 2012; Cheng et al. 2010; De Bel et al. 2009; Jiang et al. 2002; Kaur and Singh 2007; Kidak and Ince 2006; Kim et al. 2001).

Volatility

The volatility of an organic compound in aqueous solution is described by the Henry's law constant of K_{H} (Pa m^3 mol^{-1}), which is a measure of the partition of a compound between the gas and water phases defined by Eq. 4:

$$K_{\mathrm{H}} = \frac{p}{[C]} \tag{4}$$

where p is the partial pressure of target compound in the aqueous solution (Pa). Similar to any other thermodynamic properties, K_{H} is dependent on temperature, as indicated by Eq. 5:

$$K_{\mathrm{H}} = K_{\mathrm{H}}^{\circ}\exp\left(\frac{-\Delta_{\mathrm{soln}}H}{\mathrm{R}}\left(\frac{1}{T}-\frac{1}{T^{\circ}}\right)\right) \tag{5}$$

where $\Delta_{\mathrm{soln}}H$ is the enthalpy of solution (J mol^{-1}), R is the universal gas constant (J K^{-1} mol^{-1}), T° is the standard temperature (K), and K_{H}° is the Henry's law constant at T°. Therefore, temperature control for the bulk solution is critical for sonolysis experiments to minimize the changed volatility of an organic compound due to the temperature increase during sonication.

Many studies have investigated the influences of K_{H} on sonochemical degradation kinetics (Ayyildiz et al. 2007; Colussi et al. 1999; De Visscher 2003; Nanzai et al. 2008; Petrier et al. 1998, 2010). The ionized form of a volatile or semi-volatile compound (e.g., phenol) at higher pH remains in the bulk phase during sonication, but at lower pH the neutral species with high Henry's law constant diffuses onto the bubble–water interface and evaporates into the gaseous phase, where intensive thermolysis and oxidation occur (Mason and Tiehm 2001; Mason and Lorimer 2002; Suslick 1989, 1990; Suslick et al. 1986). As shown in Table 1 (case #28–37), a decrease in degradation rates was observed for volatile or semi-volatile organic pollutants, such as chlorophenol and nitrophenol, with an increase in pH at various ultrasound frequencies (20–1000 kHz) and purging gases (i.e., air, argon and oxygen). All pK_{a} values fall into the tested pH range in each study to assure the protonation state of the organic pollutants. Since not all organic molecules diffuse into gas phase of cavitation bubbles, hydrophobicity-induced accumulation of organic pollutants onto bubble–water interface also accounted for the enhanced degradation for neutral form species as compared to the ionic species.

Hydrophobicity

Octanol water partition coefficient, K_{OW}, is a physicochemical property that is a measure of the hydrophobicity of a compound (McNaught and Wilkinson 2000), as indicated in the following equation:

$$K_{\mathrm{OW}} = \frac{[C]\text{ in octanol phase}}{[C]\text{ in water phase}} \tag{6}$$

Many studies have evaluated the effect of K_{OW} on the sonolytic degradation of organic contaminants (Emery et al. 2005; Fu et al. 2007; Nanzai et al. 2008; Park et al. 2011; Wu and Ondruschka 2006). Particularly, faster sonolytic kinetics of non-volatile acidic organic pollutants were observed at low pH, because the increased hydrophobicity of protonated species resulted in more molecules accumulating and degrading at the interface of cavitation bubbles, the site of reactivity (Mason and Tiehm 2001; Mason and Lorimer 2002; Suslick 1989, 1990; Suslick et al. 1986). As shown in Table 1, cases #38–57, the majority of these studies reported reduced degradation of organic pollutants in ionized form at high pH. For example, Jiang et al. (2002) studied the sonolysis of 4-nitrophenol ($\mathrm{NP} = \mathrm{NP}^- + \mathrm{H}^+$, p$K_{\mathrm{a}} = 7.08$) and aniline ($\mathrm{ANI}^+ = \mathrm{ANI} + \mathrm{H}^+$, p$K_{\mathrm{a}} = 4.6$) with pH ranging from 2 to 9. They observed that the degradation rate of 4-nitrophenol decreased with an increase in pH, but the degradation rate of aniline increased with an increase in pH. They attributed the faster degradation rates of neutral 4-nitrophenol and aniline over their ionic forms to the protonation of phenoxide group for 4-nitrophenol at acidic pH and deprotonation of ammonium group for aniline at alkaline pH, respectively. The higher hydrophobicity of neutral form than the ionic form results in a higher degree of accumulation at bubble–water interfaces for the neutral species. It is worth mentioning that hydrophobicity was also the predominant factor that has been frequently used to account for organic pollutant degradation in ultrasound-UV, ultrasound-$\mathrm{TiO_2}$, and hydrodynamic cavitation systems (Chen and Huang 2011; Wu et al. 2001a; Yang et al. 2013).

Since surfactants always stay transphilic in different pH solutions due to a polar head and hydrophobic tail structure, no impact on the surfactant sonolysis was observed (Weavers et al. 2005). On the other hand, compounds without pK_{a} values such as trihalomethane have no ionized form and little degradation variance for trihalomethane was observed in tested pH range (Shemer and Narkis 2005). These unchanged degradation kinetics further confirms the hydrophobicity explanation for pH effects.

Charge

Watmough et al. (1992) used a 1 kV potential electrode to record the dye (i.e., methylene blue and sky blue dye) deposition on paper in a sonicated solution. Their results implied that the ultrasound-induced gas bubbles carry a negative electric charge with a field charge of about 7×10^5 V m^{-1}. Therefore, the electrostatic attractive force between the positively charged organic molecule and the negatively charged bubble–water interface was reported to contribute to the altered degradation kinetics at different pH values (case #58–64 in Table 1). De Bel et al. (2009) reported that the sonochemical degradation rate constants for zwitterion ciprofloxacin ($pK_{a1} = 3.64$, $pK_{a2} = 5.05$, $pK_{a3} = 6.95$ and $pK_{a4} = 8.95$) was almost four times larger at pH 3.0 than those at pH 7.0 and 10.0. They explained that the electrostatic attractive force between the positively charged ciprofloxacin molecule (+3 charged at pH < 3.64; +2 charged between pH 3.64 and 5.05; +1 charged between pH 5.05 and 6.95; 0 charged between pH 6.95 and 8.95; and −1 charged at pH > 8.95) and the negatively charged bubble–water interface resulted in a faster degradation kinetics under acidic condition than neutral and alkaline pH (De Bel et al. 2009). In addition, Kim et al. (2001) stated that dibenzothiophene during sonolysis became increasingly charged at higher pH resulting in increased degradation rates.

Other researchers have come up with alternate explanations. For example, Cheng et al. (2008) monitored degradation of perfluorooctane sulfonate and perfluorooctanoate at different pH values and attributed the fast kinetics at low pH to interactions of protons with the bubble–water interface. They suggested that the bubble–water interface became increasingly positively charged as pH decreased below 4 and therefore attracted more contaminants with opposite charge (Cheng et al. 2010). Likewise, Jiang et al. (2002) and Kidak and Ince (2006) both claimed hydrophobicity and charge of 4-nitrophenol and phenol molecules as reasons for decreasing degradation with respect to pH values (Jiang et al. 2002; Kidak and Ince 2006). In sonocatalysis systems, pH altered the surface charge of metal oxides and thus adsorption of phenol and reactive red dye 198 onto the oxide surface leading to varied degradation (Anju et al. 2012; Kaur and Singh 2007).

Many of these studies have utilized combinations of explanations for organic pollutant sonolysis at different pH in the heterogeneous cavitational system. For example, Mendez-Arriaga et al. (2008) observed that the initial degradation rate at pH 3.0 was significantly higher than those at pH 5.0 and 11.0 during sonolysis of ibuprofen. They explained that the protonation of the carboxylic group of ibuprofen at pH values lower than its pK_a, 4.9, led to a faster degradation rate because the increased hydrophobicity of protonated ibuprofen results in more ibuprofen molecules accumulating and degrading at the interface of the cavitation bubble (Mendez-Arriaga et al. 2008). Additionally, they also discussed that $^{\cdot}OH$ recombined to form H_2O_2 at high pH resulting in a low radical yield that further slowed down the degradation process of ibuprofen. Since the sonochemical process involves thermolysis, $^{\cdot}OH$ oxidation, and formation of byproducts in gas, interfacial, and bulk regions of cavitation bubbles, a single physicochemical property of organic pollutants may have limited capability to accurately govern the complex kinetics, especially when the compound covers a diversity of structures and a wide range of physicochemical properties.

pH effects on water matrices and subsequent organic pollutant degradation kinetics

In addition to the physicochemical properties of organic pollutants, solution chemistry including both inorganic and organic matrices in waters is a critical factor in determining the final degradation kinetics by altering [$^{\cdot}OH$] and [C] in Eq. 2. Generally, inorganic matrices can change the sonochemical degradation of contaminants through two mechanisms: competing for $^{\cdot}OH$ and altering the accumulation of organic compounds at the bubble–water interface through salting-out effects. Studies on effects of inorganic scavengers on organic pollutant degradation kinetics in different pH solutions are mostly focused on buffer ions, such as HCO_3^-, CO_3^{2-}, HPO_3^{2-} and SO_4^{2-}. At acidic conditions, SO_4^{2-} and HPO_3^{2-} are reported to scavenge $^{\cdot}OH$ (Uddin and Hayashi 2009; Xu et al. 2013), whereas HCO_3^- and CO_3^{2-} consumed the free radical in bulk solution at alkaline pH (He et al. 2007a; Ince and Tezcanli-Guyer 2004; Wang et al. 2009). Cheng et al. (2010) investigated the effect of specific anions on sonolysis of perfluorooctane sulfonate and perfluorooctanoate at the frequency of 612 kHz. They observed the role that anions played on the degradation kinetics followed the Hofmeister series: $ClO_4^- > NO_3^- > Cl^- > SO_4^{2-}$. They speculated that the coordinating structure of water clusters at the bubble–water interface may be forced to transform due to the presence of these ions and alter water vapor transported into the bubble, resulting in a decreased collapse temperature.

On the other hand, the natural organic matters, such as Suwannee River fulvic and humic acid, have been selected as representative organic matrices to examine their influence on sonochemical degradation of organic pollutants (Cheng et al. 2008; Laughrey et al. 2001; Lu and Weavers 2002; Taylor et al. 1999; Xiao et al. 2013a, 2014a). Reduced sonochemical degradation of target contaminants, such as 4-chlorobiphenyl (4-CB) (Lu and Weavers 2002) and polycyclic aromatic hydrocarbons (Taylor et al. 1999) by natural organic matters have been reported. Both attribute the reduced degradation kinetics to two effects: (1) natural organic matters competes with target contaminants for $^{\cdot}$OH, potentially hindering the degradation process; and (2) Suwannee River fulvic acid alters the threshold of transient cavitation via surface tension (γ, J m^{-2}) changes, reducing the bubble–water interfacial temperatures and ultimately degradation rates. However, some studies suggest that the presence of natural organic matters has no impact on the sonochemical degradation of contaminants, such as methyl tert-butyl ether (Kang et al. 1999). Examining the pH effects on sonochemical removal of organic pollutants in the presence organic matrices is a more complex process, since any change in a single parameter results in an alteration in both target compounds and organic matrices. So far, there is a lack of systematic studies exploring the impact of organic matrices on organic pollutant sonolysis under different pH conditions.

Conclusion

In the present review, several common explanations were summarized for the pH effects on sonochemical degradation: volatility and hydrophobicity of the target compound, Coulombic interactions between compound and cavitation bubble, and radical quantity and reactivity in different pH solutions, as tabulated in Table 2. The physicochemical property, pK_a value of ionizable organic pollutants seems to be one of the most critical factors in determining sonochemical degradation kinetics at different pH. Volatility, hydrophobicity and Coulombic interactions are the most widely used explanations for sonochemical degradation of organic pollutants with pK_a values. However, these explanations are not sufficient to explain the degradation variance at different pH for organic pollutants without ionizable groups (e.g., PAHs and carbamazepine), since they do not protonate or deprotonate with pH. Instead, the oxidation potential and quantity yield of $^{\cdot}$OH with respect to pH was proposed to account for the degradation kinetics of organic pollutants during sonication.

Although the proposed explanations are valid in each individual case, they are not necessarily valid in all cases implying further study is required for clear interpretation of pH effects in sonochemical processes, as cavitation bubble dynamics, molecular properties of organic pollutants, and solution matrix all contribute to the complexity of sonochemical responses (e.g., radical quantity, bubble charge, and number of organic molecules accumulated on bubble–water interface). In particular, identifying and elucidating radical reaction pathways in the ultrasonic or combined systems is crucial to determine the radical yield and related degradation variance with respect to pH. In addition, the potential interference of coexisting buffer ions (e.g., $H_2PO_3^-$, HPO_3^{2-}, HCO_3^-, and CO_3^{2-}) to radical quantification needs to be addressed. Further, the charge of cavitation bubbles needs to be verified and quantified with more concreted evidence. Winter et al. (2009) summarized the surface-selective photoelectron spectroscopy results and molecular dynamics simulations and concluded that the air–water interface was more positively charged than the bulk due to the presence of hydronium ion in acidic solution. This conflicts with observations from Watmough et al. (1992) that cavitation bubbles are negatively charged. Although these studies confirmed that the surface charge on bubbles changes with pH, it is controversial whether the charge becomes more positive or negative as pH changes.

In addition, due to the limited knowledge of fluid and bubble dynamics in ultrasonic reactors, it is quite difficult to fully understand the characteristics of ultrasonic systems and combined effects of the thermodynamics and kinetics of target contaminants. In particular, bubbles in the ultrasound field are subjected to high velocity oscillations and translations (Leighton 1994). These phenomena significantly affect the fluid dynamics in the reactor (Wei et al. 2015; Wei and Weavers 2016), resulting in a more complex factor to take into consideration when it comes to prediction of the degradation kinetics using a single physicochemical property of an organic pollutant. In

Table 2 Summary of existing explanations for pH effects on sonochemical degradation of organic pollutants

Organic pollutants	Dominant factor	Explanations	
With pK_a	Physicochemical properties	K_H or K_{OW}	Increased hydrophobicity of neutral form results in accumulation and degradation at the bubble interface or thermolysis in the gas phase for volatile compounds
		Charge	The opposite electrostatic charge between ionized form and cavitation bubble surface affects distribution of organic pollutants in vicinity of bubbles and thus degradation kinetics
Without pK_a	Free radical	Quantity	Enhanced $^{\cdot}$OH production accelerates degradation kinetics based on the reaction rate law
		Reactivity	Higher reactivity (e.g., oxidation potential) of $^{\cdot}$OH at acidic pH than that at neutral and basic pH increases degradation kinetics

combined systems such as ultrasound-ozone, it is obviously more problematic to correlate the bubble and fluid dynamics to degradation kinetics, especially for the determination of radical reaction pathways and free radical quantity in the presence of ozone or catalytic UV processes.

In summary, it is of particular interests and importance to conduct the following future studies to clarify the pH effects in ultrasonic systems: (1) quantifying free radical yield and concentration distribution, molecule accumulation on bubble water surface, and electrostatic interaction between compounds and bubbles to evaluate the relative contribution of each mechanism; (2) investigating the bubble and fluid dynamics at different pH conditions to reveal their influence to organic pollutant degradation; (3) improving or designing new analytical technique to overcome the low detection limit of free radicals (e.g., $^{\cdot}HO_2^{-}$) in the presence of other radicals and species for current instruments; and (4) examining the influence of composition and concentration of water matrices, especially organic matrix, on the sonochemical treatment of wastewater under different pH conditions.

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