Degradation of pentachlorophenol in aqueous solution by audible-frequency sonolytic ozonation

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Abstract

The degradation of pentachlorophenol (PCP) in aqueous solution by audible-frequency sonolytic ozonation was studied. The sonolysis of H_2O and PCP/H_2O solutions and the dissolution and decomposition of ozone under audible-frequency sonication were evaluated as well. The results showed that the ozone dissolution rate and PCP degradation rate were significantly enhanced by sonication in comparison to using mechanical stirring and O_3 bubbling alone. This enhancement is most likely attributed to the strong turbulence induced by sonication. The first-order rate constant of PCP degradation by ozonation with sonication is more than 15 times faster than that with bubbling ozone alone, while the rate constant with mechanical stirring is only four times faster. The influence of the ozone feed rate on PCP degradation and the degradation byproducts were examined as well. In addition, results showed that no H_2O_2 was generated by sonolysis of water with audible-frequency sonication and no PCP was degraded by sonolysis alone.
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Keywords: Sonication; Ozonation; Sonolysis; Pentachlorophenol; Degradation; Audible-frequency; Advanced oxidation process

1. Introduction

The contamination of pentachlorophenol (PCP) is of environmental concern due to its acute toxicity. PCP has been used extensively in agriculture and industry as an important component of fungicides, bactericides, herbicides, insecticides, molluscides, biocides, and wood preservatives [1]. Although the use of PCP is severely restricted nowadays, the widespread use and improper disposal practices in the past have led to its release into soil and groundwater, particularly at many wood preserving sites [2,3]. PCP is a priority pollutant listed by the United States Environmental Protection Agency (USEPA) and in many other countries [4]. Pentachlorophenol is a probable human carcinogen and its maximum contaminant level (MCL) for drinking water set by USEPA is 0.001 mg/L [5].

Degradation of PCP in aqueous solution by advanced oxidation processes (AOPs) using ozone has been studied by a number of researchers, which included traditional ozonation [6–11],

two-phase ozonation [12], ozonation with H_2O_2 [7], and ozonation with ultrasound [13]. Ozone-based AOPs for degradation of aqueous pesticide including PCP have been recently reviewed by Ikehata and El-Din [14]. The advanced oxidation processes involving ozone include mainly ozonation at high pH, ozonation combined with hydrogen peroxide, ozonation combined with UV, and ozonation combined with ultrasound. These ozonation processes are generally based on two major reaction pathways: reaction with molecular ozone and reaction with hydroxyl radicals which can be formed during the in situ decomposition of ozone [15]. For ozonation of PCP, both pathways were proposed in the literature [7,12]. If a particular ozonation process involves reactions with hydroxyl radicals, the combination of O_3 and ultrasound may be more effective since two $OH^\bullet$ molecules are formed per O_3 molecule consumed [13]. Furthermore, ultrasonication has been demonstrated to increase the mass transfer of ozone to aqueous solution, and different extents of efficiency improvement by sonolytic ozonation have been observed relative to ozone alone [15–17].

As a promising method for treating hazardous organic compounds, the coupling of ultrasound with O_3, H_2O_2, UV or ferrous ion is under active research and development, and

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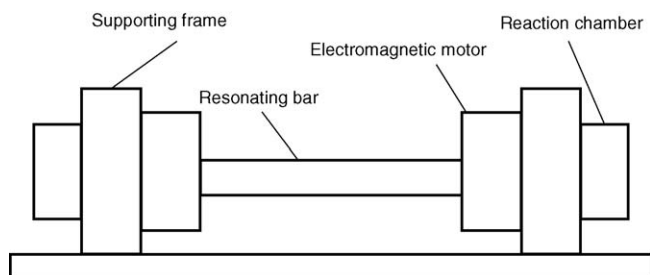*E-mail address:* lzeng@arc.ab.ca (L. Zeng).

Fig. 1. A schematic diagram of a horizontal audible-frequency sonicator.

the relevant applications in environmental remediation were reviewed by Adewuyi [18,19]. However, almost all sonication-involved AOPs are related to ultrasound with a frequency from 20 to 500 kHz. Up to date, little information is available for audible-frequency sonication-assisted ozonation. The sonochemical effect of audible-frequency sonication is unknown yet, although many characteristics of ultrasound in sonochemistry are well understood.

The primary objective of this study was to investigate the degradation of PCP in aqueous solution by audible-frequency sonolytic ozonation. The audible-frequency sonicator used in the study could be operated under 500 Hz, a frequency much below ultrasound levels. The experimental work focused on sonolysis of H_2O and PCP/H_2O solutions, dissolution and decomposition of ozone, and ozonation of PCP under audible-frequency sonication. For comparison with sonolytic ozonation, degradation of PCP with ozone alone and with ozone plus mechanical stirring was also examined. The results obtained in this study would aid the development of an audible-frequency sonication process for destroying toxic organic pollutants from aqueous solution, and might advance our understanding on the difference between ultrasonication and audible-frequency sonication.

2. Materials and methods

2.1. Apparatus

The sonolytic ozonation apparatus consisted mainly of an audible-frequency sonicator and an ozone generator. A schematic diagram of a horizontal audible-frequency sonicator is shown in Fig. 1. The key component of the sonicator is a large steel bar that is vibrated at its lowest resonant frequency of up to 500 Hz, driven by three electromagnets spaced at 120° radially around the bar. The sonicator is symmetrically designed. Two cylinder-shaped chambers can be mounted on the two ends of the bar as sonolytic reactors. With the vibration of the bar, intense acoustic energy is created and transferred to the attached chambers. In the present experiments, a 20 kW (nominal power) sonicator with a steel bar being 25 cm in diameter by 150 cm long operated at 430 Hz and mounted with one 3-L steel chamber was used as the sonolytic reactor. The chamber had a gas inlet and outlet, a sampling valve, a thermocouple adapter, and a cooling water jacket. The maximum variation of solution temperature inside the chamber could be controlled within 3 °C over an experiment. The operation power requirement for this unit

at a power gain of 55% was about half of the nominal power. The acoustic power intensity in the reaction chamber was about 0.165 W/mL. To compare sonication with mechanical stirring, separate experiments were conducted in a mechanical stirred tank reactor, which consisted of an open cylindrical tank with 13.8 cm in diameter and 18 cm in height and a mechanical stirrer of about 1000 rpm.

2.2. Materials

Due to the insolubility of PCP in water, sodium pentachlorophenate (Na-PCP) was used in the experiments. A stock Na-PCP solution of 4000 mg/L PCP was prepared by dissolving pentachlorophenol (Aldrich, >99%) in deionized (DI) water and with NaOH in slight excess. A working Na-PCP solution (100 mg/L PCP) was obtained by dilution of the stock solution with DI water. The initial pH of the PCP working solution was adjusted by titrating diluted NaOH and HNO_3 solutions. Gaseous O_3 was generated on-site from compressed air with an ozone generator. Different concentrations of gaseous O_3 used in experiments were obtained by calibrating the ozone generator under various wattage and flow rate conditions. Pre-saturated aqueous O_3 solution was also used in ozonation experiments, which was produced by bubbling O_3 gas into DI water.

2.3. Experimental procedures

For sonolysis experiments, 2 L of DI water or PCP solution was sonicated in the sonolytic reactor in the presence of air or O_2 including pre-saturated, unsaturated, and continuously bubbling. Aqueous samples were immediately taken at the end of sonolysis for determination of H_2O_2 or PCP concentrations. For ozone dissolution and decomposition experiments, 2 L of deionized water was initially loaded in a sonolytic or mechanically stirred reactor, and then ozone gas at a concentration of 0.9% O_3 (by volume) in air was continuously bubbled through the water at a flow rate of 9.5 L/min. Samples were taken at time intervals during the experiments. The aqueous ozone sample was reacted with indigo solution immediately after being taken in order to eliminate errors from ozone decomposition after sampling.

For PCP degradation experiments using gaseous O_3, 2 L of 100 mg/L PCP solution was initially loaded in a sonolytic or mechanically stirred reactor. A constant ozone gas flow was bubbled through the solution. For PCP degradation experiments using pre-saturated aqueous O_3, 2 L of deionized water was first saturated with ozone in the reactor, and 50 mL of PCP stock solution (4000 mg/L) was quickly injected into the reactor to make the PCP concentration approximately 100 mg/L. Then air was continuously bubbled into the reactor to agitate the solution simultaneously with or without sonication. During both types of experiments, aqueous samples were taken at different time intervals to determine residual PCP and chloride concentrations. Due to the reactivity of most pH buffers with ozone or hydroxyl radicals [16], no attempt was made to add buffer solution for maintaining a constant pH in experiments. However, the pH was measured at the sampling time.

2.4. Analytical methods

PCP was analyzed by a HP5890II gas chromatograph with a DB-5 column and a flame ionization detector (GC-FID). Prior to analysis, the Na-PCP samples were acidified with concentrated HCl and extracted with hexane (EM Science, >99.99%). The PCP standards were prepared by directly dissolving PCP in hexane solution. For analyses of low concentrations of PCP and other chlorinated organic compounds, a HP5890II gas chromatograph with an electron capture detector (GC-ECD) was used. Chloride (Cl^-) was determined by a Dionex ion chromatograph with an Ion Pac AS4A column and a conductivity detector. Other analytical methods included sodium thiosulfate titration of iodine for gaseous ozone [20], indigo dye method for aqueous ozone [20], and ceric sulfate ($Ce(SO_4)_3$) titration for determination of hydrogen peroxide (H_2O_2) in water with a detection limit of about 3 ppm [21].

3. Results and discussion

3.1. Sonolysis of water

It is widely recognized that sonolysis of water under ultrasound produces H_2O_2 and H_2 [19,22–24]:

$$H_2O \rightarrow OH^\bullet + H^\bullet \rightarrow H_2O_2 + H_2 \tag{1}$$
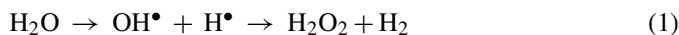
However, the frequency of ultrasound has a significant effect on H_2O_2 generation from water. Petrier et al. [24] demonstrated that the rate of production of peroxide was faster at the higher frequency (500 kHz) than that at the lower frequency (25 kHz). Based on the mathematical model calculations, Margulis et al. [25] proposed that the hydrogen peroxide yield was much larger for 1 MHz than for 22 kHz, and, in turn than for audible frequencies.

A series of experiments for sonolysis of water with audible-frequency sonication were performed at a temperature of 15–20 °C and a sonolysis time of 15–30 min in the presence of air or oxygen including pre-saturated, unsaturated, and continuously bubbling. No H_2O_2 was detected under any mentioned experimental conditions.

The above results of no peroxide/hydroxyl radicals generated under the audible-frequency sonolytic conditions are generally consistent with the findings of the frequency effect on sonolysis of water [24,25]. It can be explained by the theory of free radical generation that at a low frequency the lifetime of the cavitation bubbles is longer than that of the oxidative species, which cannot escape from the bubbles, while at higher frequencies a much faster cavitation bubble collapse releases these species into the solution [24]. An alternative explanation is based on the smaller recombination coefficient of $H^\bullet$ and $OH^\bullet$ radicals. The lessening of the recombination coefficient under low frequencies depends on the growth of the resonance radius of the cavitation bubble and the corresponding decrease in the local concentration of radicals in the bubble under low frequencies [25].

3.2. Sonolysis of PCP solution

PCP can be degraded by ultrasonic irradiation [26]. Therefore, it is necessary to verify this phenomenon under audible-frequency sonolysis. Two experiments on sonolysis of 20 mg/L PCP solution at an initial pH 7.5 for 40 min were conducted with sonication only and sonication plus air bubbling. The results revealed that audible-frequency sonolysis of aqueous PCP solution with or without air bubbling does not yield any detectable reduction in PCP concentration within the analytical errors. These results were confirmed by analyzing chloride ion. None of above experiments showed any Cl^- increase during this audible-frequency sonolysis. Assuming that a radical reaction is responsible for cleavage of C–Cl bonds in PCP during ultrasonic sonolysis of PCP solution as proposed by Petrier et al. [26], there are likely very little oxidative radicals generated by means of this audible-frequency sonication because no C–Cl bond cleavage was found. This is consistent with the previous results that no oxidative radicals were detected during audible-frequency sonolysis of water.

3.3. Ozone dissolution and decomposition

For ozonation of aqueous solutions, ozone must be dissolved before it can react with any substance in the liquid phase. The experiments of ozone dissolution were performed with continuous feed of 0.9% O_3 (by volume) at 116 mg/min under conditions of sonication, absence of sonication, and mechanical stirring. As shown in Fig. 2, in the absence of sonication, the aqueous ozone concentration gradually approached to its saturation point (at 10 °C and a gaseous ozone concentration of 1%, the saturated O_3 concentration is 6.5 mg/L [27]). The O_3 dissolution curve in the absence of sonication shown in Fig. 2 is similar to the one obtained by Kuo and Yocum [28]. However, with sonication, the aqueous ozone concentration rapidly jumps to a level close to its saturation point. With mechanical stirring, the dissolution curve shows an analogous trend to that without sonication except for a minor increase on the dissolution rate. A slight decrease of
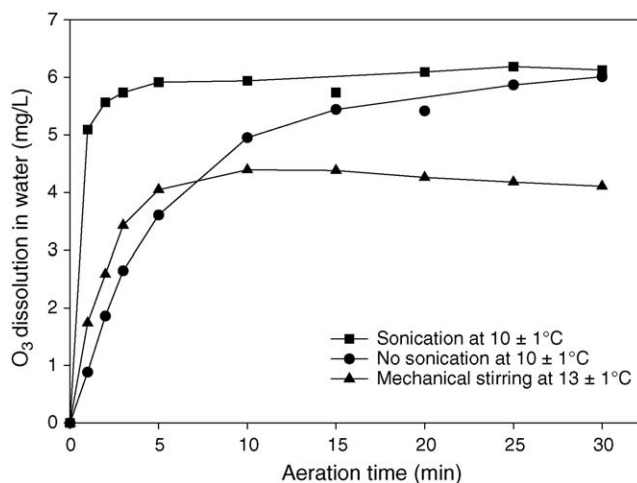
Fig. 2. Comparison of ozone dissolution in water with sonication, no sonication, and mechanical stirring.

ozone dissolution after 10 min in the experiment with mechanical stirring is due to an increase of temperature from 11 to 13 °C, since the ozone solubility is strongly temperature-dependent.

The significant increase of the ozone dissolution rate under the present sonication condition indicated an enhanced mass transfer during ozone dissolution with audible-frequency sonication. This is similar to the results obtained by Weavers and Hoffmann [15] with ultrasonication that increased mass transfer rates for ozone dissolution in water. Dissolution of ozone in the water solution by means of mechanical stirring is a diffusion-limiting mass transfer process [28], whereas the gas–liquid interface diffusion limitation appears to be much smaller under the present audible-frequency sonication conditions. Reasonably, this might be attributed partially to the strong turbulence induced by sonication. It is most likely that the large size fed gas bubbles are dispersed into micron size bubbles by sonication that then act as cavitation nuclei. Consequently, the cavitation bubbles provide a dramatically increased interfacial zone for mass transfer between gas–liquid phases, resulting in rapid ozone transfer to the liquid phase. It is also interesting to note that under the present audible-frequency sonication, the saturation concentration of dissolved ozone is similar to that observed without sonication. However, it was reported [17,29] that with ultrasound, the saturation concentration of dissolved ozone was lower than that achieved in the absence of sonication, even though the dissolution rate was increased by means of ultrasound.

The ultrasonic enhancement of ozone decomposition rate has been reported by different authors [15–17,30]. Under the present conditions, two experiments of ozone decomposition with and without sonication were conducted with an initial aqueous ozone concentration of about 6.5 mg/L at 10 ± 1 °C. The results shown in Fig. 3 indicate that ozone decomposition is approximately first-order with respect to dissolved O_3 regardless of whether or not sonication is used, which is in agreement with the results obtained with or without ultrasound [16,17]. Following first-order reaction kinetics, the ozone decomposition can be expressed as:

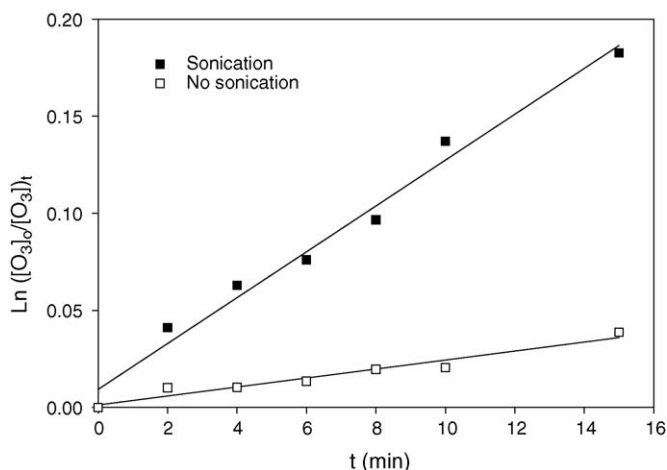$$\frac{-d[O_3]}{dt} = k_{app}[O_3] \qquad (2)$$

where k_{app} is the apparent rate constant of O_3 decomposition. Under sonication conditions, k_{app} can be expressed as:

$$k_{app} = k_{oz} + k_{son} \qquad (3)$$

where k_{oz} is the O_3 decomposition rate constant without sonication and k_{son} is the sonolytic enhanced decomposition rate constant. From the curve slopes in Fig. 3, k_{oz}, k_{app}, and k_{son} can be calculated as 0.0023, 0.012, and 0.0097 min^{-1}, respectively. These three rate constants are almost one order of magnitude smaller than those obtained with and without ultrasound by Olson and Barbier [16] and Dahi [17]. This is likely due to the fact that ozone decomposition in the present experiments was conducted at a temperature about 10 °C lower and there was more than 1 L of head space filled with O_3/air mixture above the aqueous ozone solution in the nearly closed reactor.

3.4. Effect of sonication on PCP degradation

In order to compare audible-frequency sonication with other techniques for the degradation of aqueous PCP by ozone, several ozonation experiments with 100 mg/L PCP initially at pH 9.4 were conducted under three conditions: with sonication, without sonication (bubbling only), and with mechanical stirring. As shown in Fig. 4, in approximately 2 min, 90% of PCP was degraded by ozone with sonication. Mechanical stirring achieved a similar degradation over 8 min, whereas only 60% degradation was obtained without sonication after 10 min. This is indicative of strong enhancement in PCP degradation with ozone by audible-frequency sonication.

The pH monitoring showed that the pH in the above experiments dropped significantly from 9.4 to about 3. In particular, under the sonolytic ozonation, the pH decreased to 3.6 after 1 min and to a final value of 2.8 after 10 min. The formation of HCl as well as some organic acid intermediates during PCP degradation is likely a major cause for this dramatic pH decrease, which was also noticed by other researchers [26,31]. The low final pH during ozonation of PCP resulted in approximately 10 ppm of PCP remaining in the treated solution regardless of

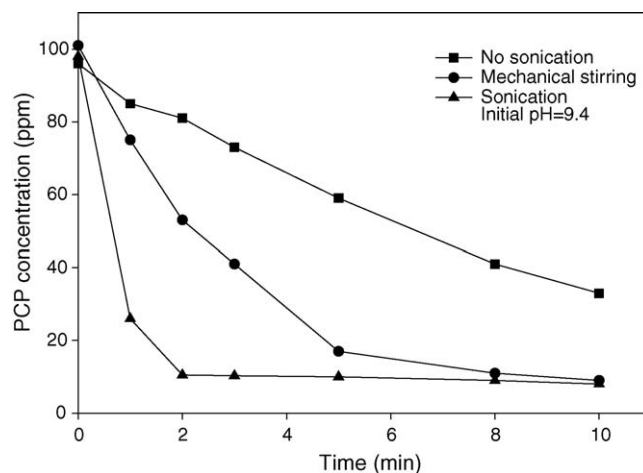Fig. 3. Ozone decomposition with and without sonication at 10 ± 1 °C.

Fig. 4. Effect of mixing methods on PCP degradation at an initial pH of 9.4, ozone feed of 24 mg/min, and reaction temperature of 13–16 °C.
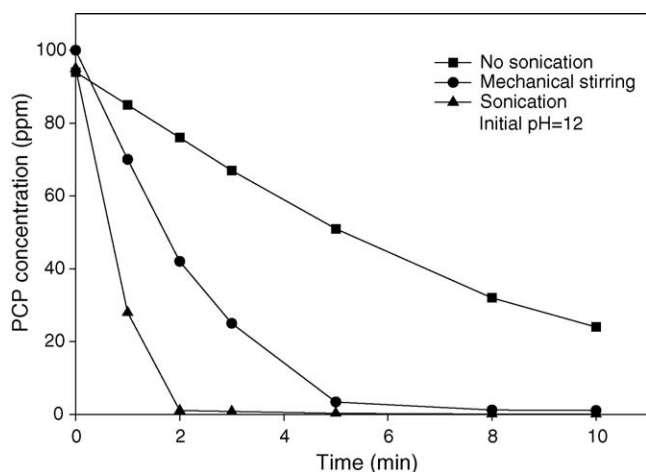
Fig. 5. Effect of mixing methods on PCP degradation at an initial pH of 12.0, ozone feed rate of 24 mg/min, and reaction temperature of 15–18 °C.

Fig. 6. Effect of sonication on PCP degradation in an aqueous ozone solution with an initial ozone concentration of 7.6 mg/L.

the reaction time in experiments. This observation was attributed to the insolubility of PCP (pK_a = 4.7) in a low-pH acidic solution. Apparently due to the mass transfer limitation, the aqueous ozone cannot attack the suspended particles of PCP even with sonication. Benítez et al. [9] also demonstrated a much higher PCP degradation rate constant at pH 9 than that at pH 2.5 for ozonation of PCP.

To exclude the influence of the solubility on PCP degradation, three similar experiments were carried out with an initial pH 12.0 that resulted in a final pH of about 11.7 at the end of the degradation experiments. The superiority of sonication to mechanical stirring and ozone bubbling alone for degradation of PCP by ozone was further demonstrated as shown in Fig. 5. It can be seen that 99% of PCP was degraded within 2 min by sonolytic ozonation. Ozonation with mechanical stirring obtained a similar degradation over 8 min, while only 74% PCP was degraded with bubbling ozone alone for 10 min. It was also found that the initial degradation rates were almost identical for experiments with initial pH 9.4 and 12 (Figs. 4 and 5). This result indicated that if pH is controlled in such a value that can maintain PCP soluble in aqueous solution during ozonation, then pH does not affect the PCP degradation rate. Kuo and Huang [6] reported a similar observation that there are little differences in the PCP degradation rates by ozone in the pH range of 5.25 to around 7.0, due to the complete dissociation of PCP.

To further investigate the effect of sonication on PCP degradation by ozone, two sets of ozonation experiments were carried out with and without sonication using a pre-saturated aqueous ozone solution at initial pH 12 and 7.5. As shown in Fig. 6, the PCP degradation is markedly enhanced with sonication compared to without sonication. Surprisingly, a higher initial pH apparently resulted in a lower PCP degradation efficiency. This is likely attributed to the fact that more ozone was lost under higher pH, due to the increased decomposition rate of ozone with increasing pH [32,33]. This result implied that the PCP degradation through ozonation regardless of sonication or non-sonication most likely follows a direct pathway involving reactions with molecular ozone. At least, any indirect pathway involving reactions with hydroxyl radicals is not a dominant
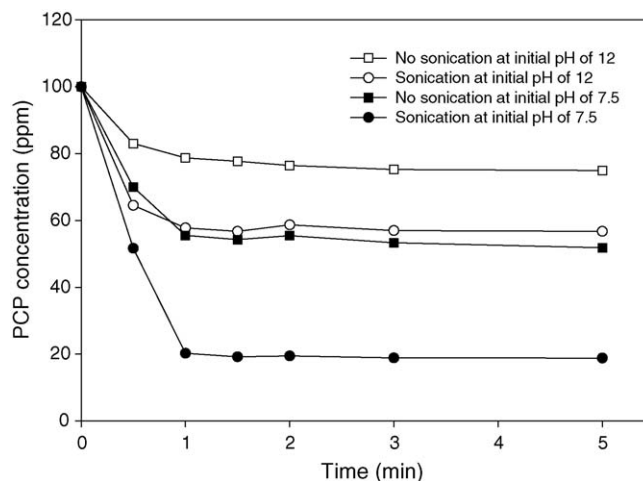
mechanism for PCP degradation through ozonation, since more hydroxyl radicals should be produced during the ozone decomposition by increasing pH [32,33]. Kim and Moon [7] also reported that PCP degradation by ozone was a direct reaction between O_3 and PCP, since their PCP ozonation experiments with addition of H_2O_2 did not show any meaningful increase in the degradation reaction rate compared to ozone alone. However, the audible-frequency sonochemical enhancement of PCP degradation by ozone can be considered through enhancement of both ozone dissolution rate and PCP degradation reaction rate under the strong turbulence produced by sonication.

3.5. Rate constants of PCP degradation by ozone

Assuming that ozonation of PCP follows a pseudo first-order reaction as:

$$\ln[PCP]_0/[PCP]_t = k_{PCP}t \tag{4}$$

where $[PCP]_0$ and $[PCP]_t$ denote the initial PCP concentration and its concentration at any time t, respectively. The rate constant k_{PCP} were obtained by reprocessing the kinetic data in Fig. 5 through linear regression as shown in Table 1. Since the PCP degradation rate significantly slowed after the PCP concentration approached a very low level ($\sim$1 mg/L), only the data with a PCP concentration above a few mg/L were used for the present rate constant regression.

It can be seen from Table 1 that the ozonation rate of PCP with sonication is more than 15 times faster than that with bubbling ozone alone, while this rate with mechanical stirring is only four

Table 1
Rate constants for pseudo first-order ozonation of PCP at pH of 12

Ozonation system	Reaction time (min)	Rate constant k_{PCP} (min^{-1})	Correlation coefficient R^2
Bubbling O_3 alone	10	0.14	0.998
Mechanical stirring	8	0.60	0.985
Sonication	2	2.23	0.968

times faster. Weavers et al. [13] also found that both ozonation and ultrasonolytic ozonation of PCP follow the pseudo first-order reaction kinetics. Interestingly, the first-order rate constant for PCP degradation by bubbling ozone obtained in the present study is very close to the rate constant ($0.15\,\mathrm{min}^{-1}$) reported by Freshour et al. [31] for an aqueous phase ozonation system that was operated with 400 mL of 100 mg/L PCP solution at an initial pH of 10.3 with an ozone charge rate of 56.5 mg/min.

3.6. Effect of ozone feed rate on PCP degradation

To evaluate the effect of the O_3 feed rate on PCP degradation in the sonolytic reactor, experiments of sonolytic ozonation with an initial PCP concentration of 100 mg/L were carried out at three different gaseous O_3 feed rates (12.5, 24, and 116 mg/min). The results are shown in Fig. 7, where the PCP degradation efficiency was expressed as a ratio of the remaining PCP concentration over the initial PCP concentration (C_A/C_{Ao}). It can be seen that the PCP degradation efficiency significantly increased when the O_3 feed rate increased from 12.5 to 24 mg/min. However, this efficiency increased only a little when the O_3 feed rate further increased to 116 mg/min. The degradation efficiency achieved 99% in 5 min at the O_3 feed rate of 12.5, while in about 2 min at the O_3 feed rate of 24 mg/min or higher. These results indicated that there exists an optimum gaseous O_3 feed rate for PCP degradation, which is subject to the enough supply of O_3 to degrade PCP and its intermediates. In the present experiments, the optimum O_3 feed rate is approximately 24 mg O_3/min. Below this optimum rate, the PCP degradation efficiency increases with the feed rate, while over the optimum rate, the PCP degradation efficiency would not be further improved. Accordingly, an O_3 feed rate higher than the optimum value could result in unreacted O_3 being released from the system. The optimum ozone feed rate should be determined by the required O_3/PCP ratio for complete destruction of PCP. The required O_3/PCP ratio apparently relates to the PCP concentration and O_3 consumption by PCP degradation. Under audible-frequency sonication, as discussed previously, the ozone dissolution rate is significantly enhanced

and the ozone saturation point can be rapidly achieved without altering its saturation value. Thus, the optimum O_3 feed rate should be dependent mostly on the PCP concentration and its degradation rate. The actual optimum ozone feed rate or required O_3/PCP ratio should be determined by experiments for individual treatment systems.

3.7. Byproduct and intermediate formation

With the C–Cl bond breakage during degradation of PCP, Cl^- is expected to form. Fig. 8 shows results of PCP disappearance and Cl^- release during sonolytic ozonation of PCP solution. For a sonolytic ozonation experiment with a PCP degradation efficiency of 99% at the initial pH of 12 and the final pH of 11.7, it was observed that 91% of the theoretical amount of chlorine from PCP was accounted in the solution as chloride ions. For a similar experiment at the initial pH of 9.4 and the final pH of 3, only 52% of the theoretical amount of chlorine from PCP was released as chloride ions, although about 92% of PCP was degraded. It was further observed from Fig. 8 that the PCP disappearance rate was clearly greater than the Cl^- release rate. Over 98% of PCP was degraded after 2 min, but less than 60% Cl^- was released in the experiment with a higher final pH. In the experiment with a lower final pH, 89% of PCP degraded in 2 min resulted in only 36% of the theoretical chlorine being recovered as Cl^-. This is strongly indicative of the formation of chlorinated intermediates. Gas chromatographic analysis showed that about 20–30 ppm of 2.3.4.6- or 2.3.4.5-tetrachlorophenol was formed during PCP degradation in a sonolytic ozonation experiment with a final pH about 3, but no tetrachlorophenol was detected in experiments under completely alkaline conditions (initial pH 12.0 and final pH 11.7). This result suggested that tetrachlorophenol should probably form at the acidic conditions during sonolytic ozonation of PCP. This is presumably the reason why much less Cl^- is released in the experiments with a lower final pH of 3. Another degradation byproduct from ozonation of PCP detected by different groups of researchers [7–10,13,31] is
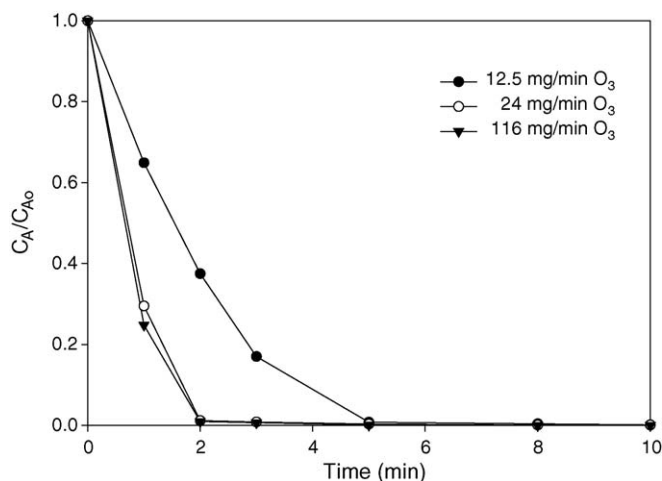

Fig. 7. Effect of the ozone feed rate on PCP degradation during sonolytic ozonation of 100 mg/L PCP at initial pH 12 and 13–15 °C.
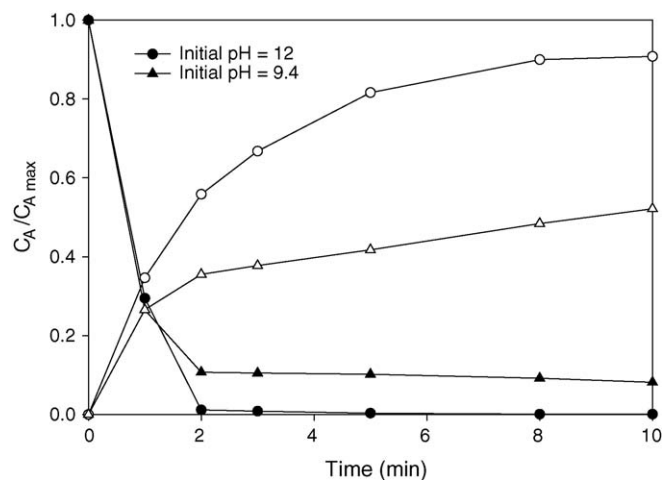

Fig. 8. PCP degradation and dechlorination during sonolytic ozonation of 100 mg/L PCP at an ozone feed rate of 24 mg/min. C_{Amax} is C_{Ao} (initial concentration) for PCP (solid symbols) and $5C_{Ao}$ for chloride (open symbols).

oxalic acid measured by HPLC. This analysis was not used in the present study. However, there may be a fraction of the chloride tied up in some other intermediates not yet identified. These intermediates probably cause Cl^- to continue increasing even after PCP drops to zero because the chlorine in the intermediates can be further ozonated to release Cl^-. Freshour et al. [31] found 100% chloride formation during PCP degradation with a continuous supply of ozone over an extended amount of time. Weavers et al. [13] observed that ozonation and ultrasonolytic ozonation of PCP resulted in the complete release of Cl^- in 30 min with sonolytic ozonation releasing Cl^- more rapidly than ozonation alone.

4. Conclusions

This study investigated sonolysis of H_2O and PCP/H_2O solutions, dissolution and decomposition of ozone, and ozonation of PCP under audible-frequency sonication. The ozone dissolution rate was largely increased by sonication with achieving the same ozone saturation concentration. The ozone decomposition was enhanced by sonication in a lesser extent as was for dissolution. Either with continuous feed of O_3 or in an O_3 saturated aqueous solution, PCP degradation by ozonation was faster by means of sonication and was not greatly affected by pH provided such a pH is maintained to ensure PCP to be completely dissolved. A first-order reaction rate constant for ozonation of PCP with sonication was $2.23 \, min^{-1}$, whereas a similar rate constant was only $0.14 \, min^{-1}$ without sonication and $0.6 \, min^{-1}$ with mechanical stirring. An increase in the O_3 feed rate during sonolytic ozonation increased PCP degradation only when the feed rate was below an optimum value. Analytical results show that the PCP degradation rate under sonolytic ozonation was greater than the Cl^- release rate. 2.3.4.6- or 2.3.4.5-Tetrachlorophenol was the identified chlorinated intermediate from sonolytic ozonation of PCP at a low-pH of 3. However, no H_2O_2 was generated by audible-frequency sonolysis of water and no PCP was degraded by sonolysis. These are the major differences found so far between audible-frequency sonication and ultrasonication. The enhancement of the ozonation process by audible-frequency sonication is likely primarily due to the increased mass transfer under strong turbulence induced by sonication.

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