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Sonolysis and mineralization of pentachlorophenol by means of varying parameters

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Abstract: Degradation effect of organic pollutant on pentachlorophenol(PCP) is researched by ultrasound. PCP is treated by low frequency(16 kHz) and high frequency(800 ± 1 kHz), and bi-frequency. The results of investigation on the ultrasonic destruction of PCP showed that the rate of PCP degradation at the same conditions is the highest at bi-frequency, and the lowest at 16 kHz. In the presence of Fenton type reagent the degradation rate of PCP is the highest at bi-frequency(20.93 times) as compared to the stirring system. This ratio is 4.91 and 1.06 at 800 kHz and 16 kHz, respectively. The studies showed the bi-frequency is an effective method for pollutants degradation, but it is need make further study. Taking 800 kHz for example, under the same conditions, the smaller pH of the solution, the higher is the reaction rate. A similar situation applied to TOC, but the TOC removal lags behind degradation of PCP. This indicated the PCP is not completely mineralized. The ultrasound is somewhat enhanced for degradation of PCP and mineralization with only addition of $CuSO_4$, but the combination of ultrasound and Fenton type reagent is effective method for PCP degradation and mineralization. The rate of PCP degradation and TOC removal appeared to follow pseudo-first-order reaction kinetic law.

Keywords: sonochemistry; Fenton type reagent; bi-frequency; pentachlorophenol; hydroxyl radical

Introduction

The presence of human-derived or naturally occurring volatile or novolatile toxic organic compounds in drinking water have become a problem of a major national and international concern. The presence of toxic organic compounds in a few parts per billion is enough to render a water supply unpotable for reasons of long-term health risks, even though the water may have no discernible taste and odor, so waste water must be treated. In relationship with water treatment, there are several reports in early literature (Okouchi, 1992; Terese, 1994; Wu, 1992; Ingale, 1995; Drijvers, 1998) which describe the power ultrasound which destruct organic compounds in water. However, the present knowledge about the mechanism of sonochemical breakdown of organic compounds is limited. Two reaction mechanisms have mainly been proposed to explain the chemical and kinetic data.

The first mechanism is pyrolysis in the cavitation bubbles. The second mechanism is the generation of OH radicals in the cavitation bubbles. Cavitation is a source of radicals, especially the hydroxyl radical, ·OH, the very strong and nonspecific oxidizing species which escapes out of the bubble and reacts rapidly with compounds in solution.

Recent decade, Petrier and co-workers(Petrier, 1994; 1998) have studied in detail ultrasonic degradation of organic compounds at low frequency and high frequency. The results showed that treatment effect is better at high frequency than low frequency. As for study of the combination of two frequencies(i.e. bi-frequency) on pollutants decomposition, this aspect report is scarce. Inez Hua and co-workers(Hua, 1995) first researched *p*-NP degradation by combination of 16 and 20 kHz. After that, the organic compound degradation has not been studied with bi-frequency. Pentachlorophenol(PCP) belongs to the class of aromatic halides that have to be removed from waster water. By itself, it is still a widely used compound for wood treatment and it exhibits a high toxicity(Petrier, 1992a). Petrier *et al*. (Petrier, 1992a) only described the degradation at 530 kHz of PCP in aqueous solutions saturated with different gases and had not studied degradation of PCP as compared to low frequency, not to speak of bi-frequency combination. In this work, our aim is to study degradation of PCP at 800 kHz, 16 kHz and their combination.

1 Experimental

1.1 Materials

PCP and copper sulphate(from the first mill of chemical reagent, Tianjin) are A. R. grade (99%). Hydrogen peroxide (30% wt.) (from the second mill of chemical reagent, Shanghai), and other chemicals are used as received. Aqueous solution of PCP is prepared by stirring the neat liquid with deionized water in a closed flask. Extreme care is taken to prevent the contamination of solutions. The solutions are left overnight with slow stirring to equilibrate. The concentration of the PCP is 66.5 mg/L.

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1.2 Analytical method

Process of the reactions is monitored by HPLC (high-performance liquid chromatography) with Waters Model 999 Photodiode Array detector and Waters Lambda-Max model 481 LC spectrophotometer. Separations are achieved on a spherisorb column (C18, 150 mm × 3 mm, 5 μm) for solution quantification. The detection wavelength is 254 nm. The mobile phase is a methanol/H_2O (75:25). The flow rate is 1 ml/min. Using a glass syringe, 1 ml samples are taken from sampling port at 15 min intervals during sonication, and then filtered for HPLC analysis through Nylon 66 filters (0.2 μm prose size) to remove aluminum metallic particles produced during sonication by corrosion of the aluminum tip of the sonication. After this, 20 μl of the samples filtered are at once injected into the chromatograph for solution quantification.

1.3 Apparatus

Schematic description of the ultrasonic setup is shown in Fig. 1. The 800 kHz ultrasonic waves are emitted from a ceramic transducer, diameter 38 mm, fixed on a stainless steel plate having a thickness of half a wavelength (6.3 mm). The 16 kHz irradiation is made by ourselves with aluminum probe having tip diameter 38 mm. The horn tip is immersed ≈1.5 cm into the solution. The system is driven by signal generator (made by ourselves) and power amplifier (model 2100 L, USA). A rated output electric power of 30 W is used as a source of ultrasonic energy. When the combination of two frequencies, each output electric power of 15 W is used, i.e. total output electric power is 30 W.

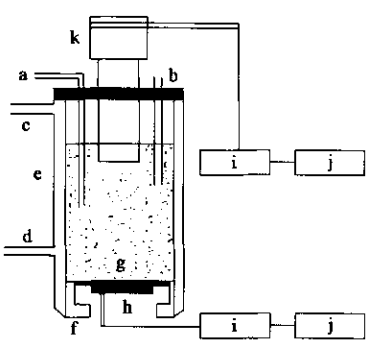

Fig. 1 Experimental apparatus

a: O_2 inlet; b: sampling port; c and d: cooling fluid; e: glass reactor; f: teflon holder; g: stainless steel plate (diameter 40 mm); h: ceramic transducer; i: power amplifier; j: signal generator; k: aluminum probe. The reactor has an inner diameter of 42 mm

1.4 Procedure

In all cases, 100 ml of solution are treated. In experiment, aqueous solution is saturated with O_2. All experiments are carried out in the same manner. Hydrogen peroxide is added to solution by changing its concentration. The combination of copper sulphate and hydrogen peroxide (i.e. Fenton type reagent) are considered. Copper sulphate is first dissolved in the solution and then hydrogen peroxide is added to PCP aqueous solution, their concentrations in 100 ml of PCP aqueous solution are 2.25 mmol/L and 48.2 mmol/L, respectively. Reactions are performed at 30 ± 2℃ in a cylindrical jacketed glass cell equipped with a Teflon holder. The solution is sonicated under their natural pH, without adding buffer solution.

2 Results and discussion

2.1 The effect of frequency on the degradation of PCP

2.1.1 The effect of frequency on hydroxyl radical concentration

Cavitation during ultrasonic treatment of aqueous solutions results in three reactive zones, which exist in the region of cavitation: the gas phase, the gas-liquid interface, and the liquid directly surrounding the cavitation bubble (i.e. bulk solution). Numerous reports indicated the formation of hydroxyl radical and hydrogen atom in the vicinity of the cavitation site. In the general theory, volatile organic compounds participate in the pyrolysis reactions inside collapsing bubbles, while nonvolatile solutes mainly react with hydroxyl radical in bulk solution and the gas-liquid interface. PCP is hydrophobic, nonvolatile organic compound. So it is mainly degraded by hydroxyl radical. Hence, it is necessary to detect concentration of hydroxyl radicals with different frequency. According to Fricke dosimetry (Jana, 1995), concentrations of hydroxyl radicals are detected in Fig. 2. From Fig. 2, it can be seen that concentration of hydroxyl radical is higher at 800 kHz than at 16 kHz. This phenomenon had been explained by Petrier (Peterier, 1992b). The concentration is the highest at bi-frequency. This can be explained by production of hydroxyl radical through two pathways, first by the respective cavitation process, second by collapse of each cavitation bubbles, and then many new cavitation nuclei are produced. These new nuclei not only provide re-cavitation for each frequency, but also provide more cavitation nuclei for other frequency. The interaction of them means that more hydroxyl radicals are formed. Their ratio is $k_{16+800} : k_{800} = 2.5$, $k_{800} : k_{16} = 7.5$.

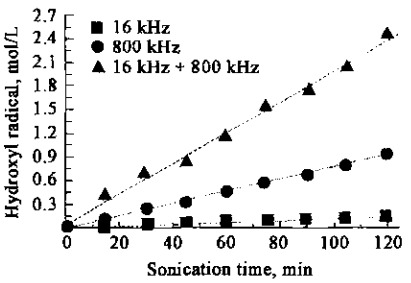

Fig. 2 Concentration of hydroxyl radical vs sonication time

2.1.2 The effect of 16 kHz on PCP degradation

Sonication at 16 kHz of the solution leads to little decomposition. This low efficiency is mainly due to the low concentrations of hydroxyl radicals that escape from the

cavitation bubble at this frequency (Petrier, 1992b). A change in the reaction rate can be obtained by addition of hydrogen peroxide. Fig. 3 shows the efficiency of the degradation is increased with addition to the concentration of hydrogen peroxide. This can be explained by the injection of hydrogen peroxide into the cavity and its cleavage into hydroxyl radical during the collapse of the cavitation bubble. The results revealed that there are more OH radicals generated on addition of H_2O_2. The formation of additional hydroxyl radicals is contributed to PCP disappearance. The combination of copper sulphate and hydroxyl peroxide is also tested in ultrasonic conditions. The result showed the efficiency of sonochemical degradation is enhanced markedly. But, the results at Table 1 show that comparison of the degradation rate in the presence and absence of ultrasound does not affect the kinetics noticeably. This means that synergistic effects have not been taken place.

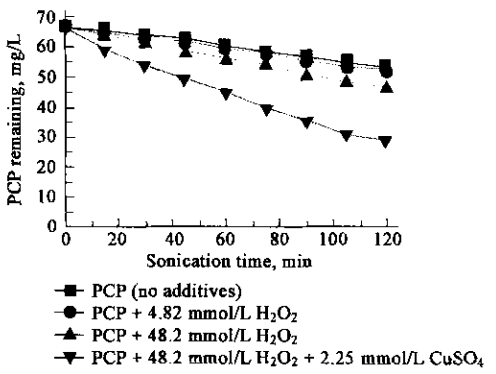

Fig.3 Effect of 16 kHz ultrasound on PCP decomposition

2.1.3 The effect of 800 kHz on PCP degradation

In Fig. 4, at this frequency, the sonochemical degradation of PCP is faster than at 16 kHz. Petrier(Petrier, 1994) have clearly shown this effect, and interpreted it. Addition of hydrogen peroxide to the PCP solution increases the sonodegradation rate, and the same explanation can be given in 2.1.2 section.

Contrary to the observation at 16 kHz with the $CuSO_4$-H_2O_2 (Fenton type) reagent, the ultrasound activation for PCP degradation is increased markedly at 800 kHz. This is because the production of hydroxyl radical is enhanced by two pathways, first by the cavitation process(in Fig.2), second by the decomposition of hydrogen peroxide by the copper sulphate.

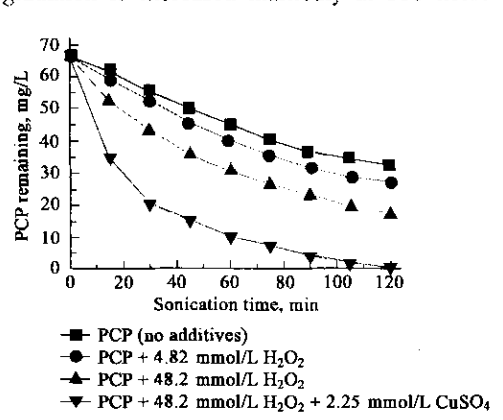

Fig.4 Effect of 800 kHz ultrasound on PCP decomposition

2.1.4 The effect of the combination of two frequencies on PCP degradation

The sonochemical degradation of PCP at bi-frequency under different conditions is shown in Fig.5. The degradation results showed the effect of the bi-frequency treatment on PCP is the best. This is because that the concentrations of the hydroxyl radicals are highest at bi-frequency. The data in Fig.2 have demonstrated this phenomenon, and explained it. In the presence of the Fenton type reagent, the degradation rate of PCP is the fastest at bi-frequency. After 60 min, about 99.8% PCP is degraded, and treatment time also reduces one hour as compared to 800 kHz.

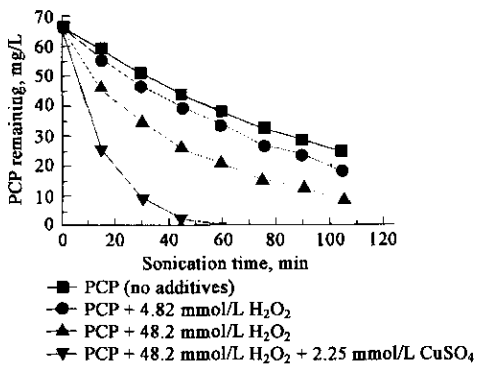

Fig.5 Effect of bifrequency ultrasound on PCP decomposition

2.2 Study of parameters on decomposition and mineralization of PCP at 800 kHz

2.2.1 Effect of pH

The effect of pH on the decomposition of PCP vs. time is shown in Fig.6a.

The results indicated that a smaller pH value is more effective. After reaction for 120 min, the degradation of PCP attains 85.4% at pH 2, 77.8% at pH 3, 73.78% at pH 6, and 42.67% at pH 13. The obvious variation among these values arises because the pKa(Brzezinshi, 1996) value of PCP is 4.74 at 25℃. The molecular species of PCP predominates when pH is less than pKa(4.74), but PCP is in the ionic form when the pH exceeds 4.74. The fraction in the molecular state of PCP is larger when the pH is smaller. The molecular PCP species in the bulk solution region diffuse into the film region, and part of the molecular species may evaporate into the gaseous(bubble) region from film region. Thus, the overall decomposition of PCP is attributed to the pyrolysis and free radical attack occurred in both the gaseous and film regions. On the other hand, the PCP ions do not vaporize into the cavitation bubbles; they can react only outside of the bubble film with the OH radicals cleaved from water. Hence a smaller pH(especially less than pKa) is effective for degradation. The removal rate of TOC is

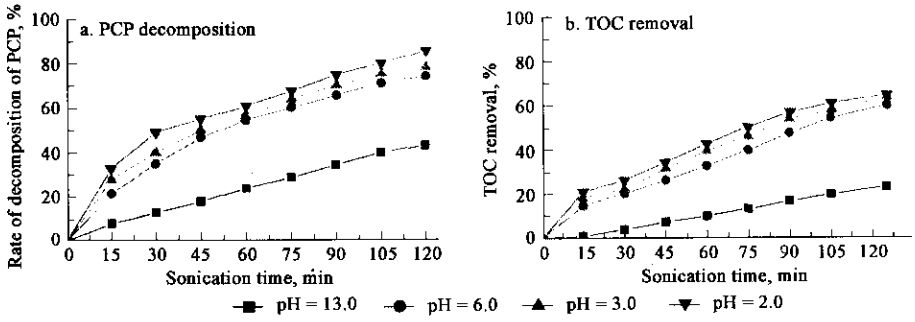

Fig.6 Effect of pH on PCP decomposition and TOC removal with ultrasound(800 kHz)/H_2O_2 (H_2O_2 in 100 ml of PCP solution is 48.2 mmol/L)

determined. From data in Fig.6b, TOC removal lags behind degradation of PCP relative to Fig. 6a. At pH 2, the efficiency of decomposition of PCP is 85.4% but the removal of TOC is only 64.9%; a similar situation applied at pH 3, 6, and 13. But, the rate of mineralization has not marked difference at pH 2, 3, and 6. Hence, these data indicate intermediate compounds are produced and PCP is not completely mineralized.

2.2.2 Effect of catalyst

De Visscher (De Visscher, 1998) investigated the effects of $CuSO_4$ on 2-chlorophenol(2-CP) degradation rate. They discovered that the rates of degradation were increased on addition of Cu^{2+}. We call Cu^{2+} a catalyst. Sonication of water generates radicals: the water molecule is cleaved to OH and H radicals(Eq.(1)). Hydrogen peroxide is one product resulting from recombination of hydroxyl radicals(Eq.(2)). The Fenton type oxidation reaction (Entezari, 2003; Eq.(3)-(4)), requiring addition of both Cu^{2+} and H_2O_2 to aqueous solution, is also efficient to destruct organic pollutants. To distinguish from the Fenton type oxidation reaction, we examine the effect of catalyst ($CuSO_4$) on decomposition of PCP with ultrasound, in the presence/absence of H_2O_2(under natural pH).

$$H_2O +))) \rightarrow OH\cdot + H\cdot, \quad (1)$$

$$OH\cdot + OH\cdot \rightarrow H_2O_2, \quad (2)$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^{+} + OOH\cdot + H^{+}, \quad (3)$$

$$H_2O_2 + Cu^{+} \rightarrow OH^{-} + OH\cdot + Cu^{2+}. \quad (4)$$

The effect of catalyst on PCP decomposition with ultrasound irradiation is shown in Fig. 7. With $CuSO_4$ as catalyst, the PCP decomposition is 61.23% at 120 min of reaction. With the blank(with ultrasound only) is 50.98% (Fig. 4). The data indicated the degradation rate is not markedly increased in the only presence of $CuSO_4$. A similar result is found for TOC removal. These results revealed that the production of OH radical by ultrasound irradiation is inadequate(only 0.92 mmol/L OH radical produced in Fig.2 at 120 min). The small concentration of H_2O_2 limited the reaction of Equation (3) and (4). However, in the presence of H_2O_2, the degradation rate is 99.32%(copper sulphate is the first dissolved in the solution and then hydrogen peroxide is added to PCP aqueous solution, i.e. Fenton type reagent). This is because that the production of hydroxyl radical is enhanced through two pathways, first by the cavitation process, second by the decomposition of hydrogen peroxide by the copper sulphate. Thus, the ultrasound is somewhat enhanced for degradation of PCP and mineralization with only addition of $CuSO_4$. So, the combination of ultrasound and Fenton type reagent is effective method for PCP decomposition TOC removal.

2.2.3 Kinetics reaction rate constant

In order to test with/without synergistic effects of the Fenton type reagent and the ultrasound, degradation of 100 ml PCP in presence of $CuSO_4$-H_2O_2(without ultrasound, but with stirring system, i.e. in silent) must be considered. The temperature of the experiment is controlled at 30℃, other steps are the same. The result showed its kinetics reaction rate constant is 6.64×10^{-3} min^{-1}. Table 1 shows kinetics

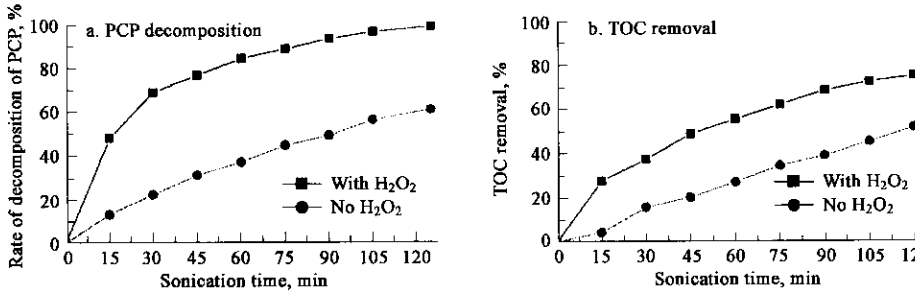

Fig.7 Effect of catalyst on PCP decomposition and TOC removal with ultrasound with ultrasound at 800 kHz($CuSO_4$ and H_2O_2 is 2.25 mmol/L and 48.2 mmol/L in solution)

reaction rate coefficients of PCP decomposition under different sonication conditions. In three cases, degradation follows a pseudo-first-order kinetic law.

Table 1 Pseudo-first-order kinetics reaction rate coefficients of PCP decomposition under different sonication conditions

Sonication	k^a, min	k^b, min	k^c, min	k^b/k^a	k^c/k^a	k^c/k^d
16 kHz	2.03×10^{-3}	2.98×10^{-3}	7.06×10^{-3}	1.47	3.48	1.06
800 kHz	6.32×10^{-3}	1.22×10^{-2}	3.26×10^{-2}	1.93	5.16	4.91
Bifr	9.76×10^{-3}	2.01×10^{-2}	1.39×10^{-1}	2.06	14.24	20.93
Bifr/16 kHz	4.81	6.74	19.7			
Bifr/800 kHz	1.54	1.65	4.26			

Notes: Bifr: the combination of 16 and 800 kHz; k: the kinetics reaction rate constant; k^a: the kinetics reaction rate constant of PCP in ultrasound; k^b: the kinetics reaction rate constant of PCP in presence of hydrogen peroxide (48.2 mmol/L) in ultrasound; k^c: the kinetics reaction rate constant of PCP in presence of Fenton type reagent in ultrasound; k^d: the kinetics reaction rate constant of PCP in presence of Fenton type reagent in silent (with stirring system), $k^d = 6.64\times10^{-3}$ min^{-1}

The rate of PCP degradation in the presence of Fenton type reagent is the highest at bi-frequency (20.93 times) as compared to the stirring system. This ratio is 4.91 and 1.06 at 800 kHz and 16 kHz, respectively. This demonstrated that the combination of Fenton type reagent and bi-frequency has synergistic action. The same conclusion is given for 800 kHz. But, for 16 kHz, ultrasound and Fenton type reagent has not synergistic action. This need make further study.

As far as 800 kHz, values of k for pH and catalyst are listed in Table 2. The squared correlation coefficient of the determination, R^2, generally is nearly unity, greater than 0.9 for varied values of each parameter. Thus, the kinetics of PCP decomposition and TOC removal are satisfactorily accord with pseudo-first-order reaction kinetic law.

Table 2 Values of k in the proposed pseudo first-order model

pH	PCP decomposition		TOC removal	
	k, min^{-1}	R^2	k, min^{-1}	R^2
2	1.43×10^{-2}	0.992	0.83×10^{-2}	0.987
3	1.17×10^{-2}	0.988	0.81×10^{-2}	0.994
6	1.22×10^{-2}	0.991	0.77×10^{-2}	0.984
13	0.44×10^{-2}	0.996	0.2×10^{-2}	0.982
Catalyst				
$CuSO_4$ (no H_2O_2)	7.66×10^{-3}	0.997	6.15×10^{-3}	0.993
$CuSO_4$ (with H_2O_2)	3.26×10^{-2}	0.938	1.072×10^{-2}	0.966

3 Conclusions

The sonochemical degradation of PCP follows pseudo-first-order kinetic law in three cases (16, 800 kHz, and bi-frequency). The order of reactivity deduced from degradation rate of PCP is as follows:

bi-frequency > 800 kHz > 16 kHz.

This means that the degradation rate is most by bi-frequency. The same orders are given in the presence of oxidant (hydrogen peroxide or Fenton type reagent). The combined method of ultrasound and oxidant for the PCP decomposition at bi-frequency is a more promising and effective method than the ultrasound or the Fenton type method taken individually. In presence of Fenton reagent, ultrasound at 800 kHz or bi-frequency has synergistic effects on PCP degradation. But, at 16 kHz, the result is contrary. This need make further study.

The degradation rate of PCP under their natural pH is higher at 800 kHz than 16 kHz. At 120 min of reaction, the decomposition of attains 50.98% at 800 kHz, and 20.45% at 16 kHz. This is because hydrogen peroxide is formed in larger amounts at 800 kHz than 16 kHz. Under ultrasound (800 kHz) /H_2O_2, when the pH of the solution is controlled at 2, the efficiency of degradation of PCP is 85.4% but the removal of TOC is only 64.9%; a similar situation applied at pH 3, 6, and 13. Hence intermediate compounds are produced and PCP is not completely mineralized. The experimental data demonstrate that a smaller pH value is more effective. With $CuSO_4$ as catalyst, in the absence of H_2O_2, the PCP decomposition is 61.23% at 120 min of reaction. The rate of degradation is only enhanced about 10% compared to the blank (with ultrasound only). A similar result is found for TOC removal. The kinetic data demonstrate the PCP decomposition and TOC removal follow pseudo-first-order reaction kinetic law.

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