

Study on Ultrasonic Degradation of Pentachlorophenol Solution

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Pentachlorophenol (PCP) ion was degraded by ultrasound at 25 °C. Four aspects that could affect the degradation of PCP were investigated, i.e. initial pH of solution, initial concentration of pentachlorophenol ion, different sound intensity with catalyst and different frequencies of ultrasound. Results showed that PCP ion could be ultrasonic degraded totally after 3 hour treatment if CCl_4 , which can provide free radical, was added in solution. The mechanism of ultrasonic degradation was considered as free radical oxidation by adding n-butyl alcohol as free radical scavenger.

Key word:

Ultrasonic, degradation, pentachlorophenol, ion

Introduction

Pentachlorophenol sodium (PCPNa) is widely used as wood preservative and conservative containing protein (glue, leather, paper, etc),^{1,2} as well as pesticide, weedicide in agriculture.³ Zhang, et al indicate that PCPNa is of little poison to human being and livestock.¹ But it might be very harmful to fish and other creature.⁴ Thus, PCPNa has been listed among the 65 priority pollutants by the US EPA because they are refractory and hard to be removed (Bernard and Hoberman, 2001). Research on prevention of contamination of PCP is being carried out.³

In recent researches, PCP ion remained in water is always degraded by biotechnology and fenton agent methods. However, biotechnological degradation is time consuming, and Fe^{2+} or Fe^{3+} will be remained in water after degradation by fenton agent method. Some researchers have done experiments on ultrasound enhanced degradation of chlorinated aromatics with only one Cl.^{5–7} Ultrasonic degradation of Chlorinated aromatics with more Cl is seldom reported. Petrier researched low fraction ($1 \cdot 10^{-6}$) PCP solution degradation under ultrasound.⁸ However, in this work, high fraction (least $100 \cdot 10^{-6}$) is carried out. Ultrasonic degradation method with non-additive was studied in detail.

Experimental

Reagent

Different fraction (10^{-6} of 100, 1000, 3000, 5000, 7000) of PCP (99.9% purity, Qinqu chemical

reagent plant) solution were prepared in 1000 ml constant volume flask. Dilute hydrochloric acid and dilute sodium hydroxide solution were used to adjust pH of PCP ion solution.

Equipments

Ultrasonic horn used in the present work (Dejia Co., Ltd. Wuxi, China, maximum power rating of 1000 W driving frequency of 20, 40 kHz) has a tip diameter of 2 cm and was always dipped to 1 cm beneath the surface of solution. The experiments were done in a jacket beaker (outer diameter 6.4 cm, height 8 cm, inner diameter 5.5 cm, height 7.5 cm) filled with distilled water shown as Fig. 1(a). When high frequency ultrasound was used, only paster transducer can fit for experiment. Ultrasound was transmitted upward, and reflected when it reached water-gas boundary layer. Inductor can capture wave in solution and deliver signal to oscillograph, then oscillograph can transfer signal to level wave, from which we can monitor sound intensity. HPLC with electrocapillary (P/ACE 5000, Beckman, USA) was used to determine the content of sample. All-wave displayer (UV-VIS, Tianmei Science Apparatus Co., Ltd., Shanghai, China) was used to scan the characteristic spectrum of PCP ion solution. Ultraviolet-visible spectrophotometer (752, Precision Science Apparatus Co., Ltd., Shanghai, China) was utilized to detect the content of PCP ion. Ultrasonic reaction equipments were setup as Fig 1.

Method of detection

150 ml PCP ion solution was sonicated using different intensities and frequencies. The temperature of solution was maintained at 25 ± 2 °C by cy-

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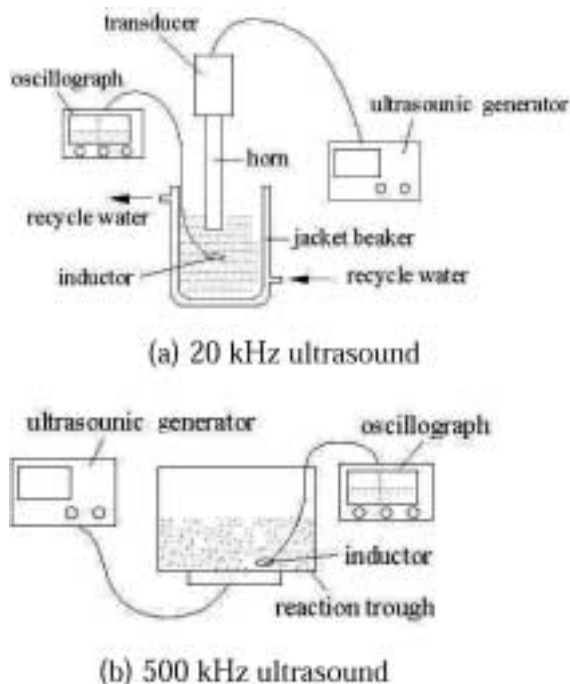


Fig. 1 – Equipment of ultrasonic irradiation for the waste water treatment

cleared water. Samples were taken every 30 min and diluted to $5\sim 20 \cdot 10^{-6}$ solution to detect. National Standards of P.R.China (GB8972-88, GB9803-88) were adopted in this detection. Characteristic spectrum of PCP ion solution ($10 \cdot 10^{-6}$) was 248 nm.

In infinite dilution solution, relation between absorbance response of PCPNa ion and its concentration can be described linearly ($Abs = 0.0272$ fraction (10^{-6}), $R^2 = 0.9979$). Sample should be diluted below $20 \cdot 10^{-6}$, then its fraction can be calculated by interpolation of absorbance fraction curve.

Results and discuss

Results and discussion

Initial pH of solution

PCP ion solution was sonicated when its pH value was adjusted to 6.0, 7.0 and 8.0, respectively, by adding hydrochloric acid and sodium hydroxide solution. In acid situation, after 2 h sonication, the colour of solution turned pink, that is, PCP ion was oxidized and was familiar to the phenol oxidation.

Degradation ratio $\zeta = \frac{\Delta \bar{m}}{m_0}$, in which m_0 means initial PCP ion mass, \bar{m} means PCP ion mass when reaction ends, $\Delta \bar{m} = \bar{m}_0 - \bar{m}_1$.

In alkaline situation, PCP ion was degraded more than 15 %, than it was in neutral or acid situation as shown in Fig. 2. Increment of degradation ratio in acid solution is greater than that in neutral solution. Furthermore, in acid solution, ultrasound

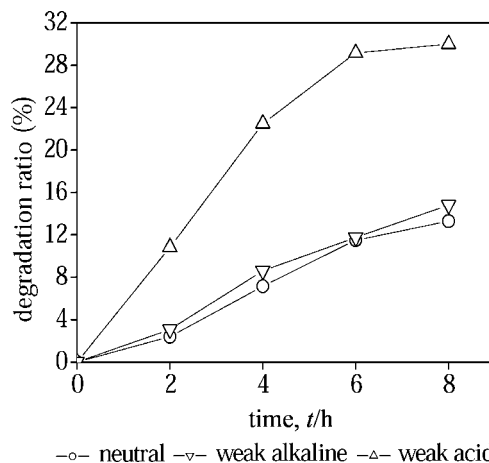
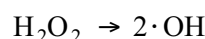
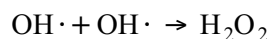


Fig. 2 – Influence of pH on ultrasonic degradation

horn slightly rusts although it is made of titanium alloy.



In alkaline circumstance, existence of soluble metal cation made it easy to cleave chlorine from main body of benzene ring. From (1) and (2).^{9,10} it is possible that H_2O_2 might be present because of OH^- existence, and then it generates free radical which oxides degrades chemicals aggressively.

Initial fraction of PCP ion

The influence of PCP ion initial mass fraction is to find out the limit concentration that experimental condition in this work could undertake. On the degradation high ultrasonic degradation ratio could be obtained, if initial fraction is low, however, the ratio would decrease when initial fraction increased. Another goal of this experiment is to find out the best condition, in which more PCP ion is degraded, then acceptable-degradation ratio could be gained.

From table 1, it is clear that after 3 h of ultrasonic degrading PCP ion solution, in which initial

Table 1 – Influence of initial PCP ion fraction on ultrasonic degradation ratio and mass

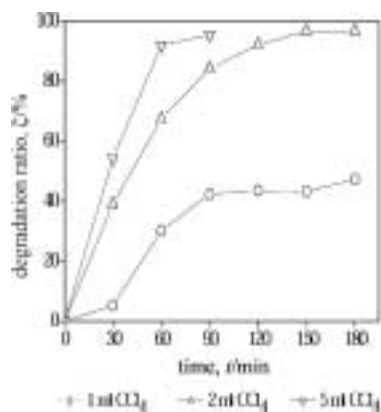
Initial PCP ion fraction $w / 10^{-6}$	Degradation ratio $\zeta / \%$	Degradation mass $m / 100$ mg
100	100	0.1
1000	70.588	0.70588
3000	38.971	1.16912
5000	32.721	1.63603
7000	10.662	0.74632

fraction was $5000 \cdot 10^{-6}$, degraded quantity was the highest, however the degradation ratio was only 33 %, that would increase more if treatment time can be prolonged.

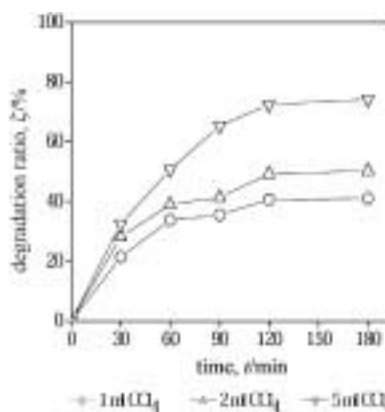
Sound Intensity

150 ml PCP ion solution ($100 \cdot 10^{-6}$) can be totally degraded after 2 h catalytic ultrasonic degradation as shown in Fig. 3. When sound intensity was

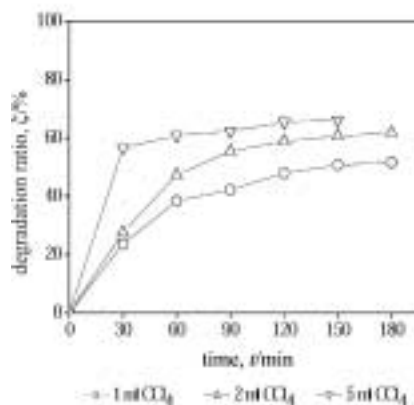
larger than 15 W cm^{-2} , the less catalyst CCl_4 added, the degradation ratio of PCP ion was greater. When sound intensity was lower than 12.18 W cm^{-2} , the more catalyst was added, the high degradation ratio of PCP ion was. More PCP ion can be degraded if input power increased. And PCP ion fraction would not change after 3 h of ultrasonic degradation. So 3 h should be considered as the maximum reaction time.



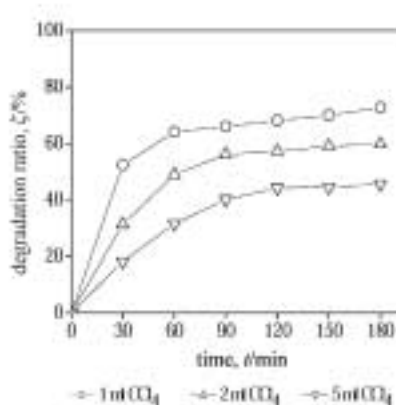
(a) Ultrasonic degradation under 4.14 W cm^{-2} sound intensity



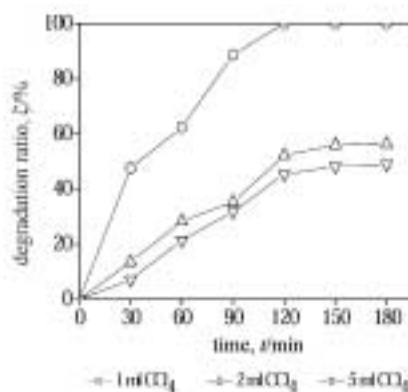
(b) Ultrasonic degradation under 8.07 W cm^{-2} sound intensity



(c) Ultrasonic degradation under 12.18 W cm^{-2} sound intensity



(d) Ultrasonic degradation under 15.12 W cm^{-2} sound intensity

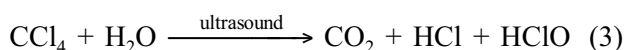


(e) Ultrasonic degradation under 19.11 W cm^{-2} sound intensity

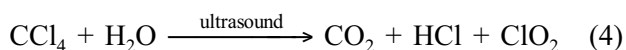
Fig. 3 – Catalytic ultrasonic degradation of PCP ion under different electric power

As PCP ion quantity to be treated is constant, as concerned, to decrease input electric power and to increase relatively the amount of catalyst can greatly increase the ultrasonic degradation ratio, and augment the totally degradation quantity as well. Its reason is catalyst added may generate more ClO_2 or HClO under sonication, however, if more input power is added, ClO_2 or HClO would quickly make HCl prior react on PCP ion.

According to the published article,¹¹ CCl_4 was decomposed to HClO , which can oxidize other material, shown as (1)



But in this article, HClO was added in PCPNa degradation, the result showed that neither ultrasound was involved nor ultrasound was not involved, decomposition ratio was very small. It means HClO can not degrade PCPNa to the degree that CCl_4 can. So under ultrasound, CCl_4 was composed to other material which has much more oxidation power than HClO has. ClO_2 has power oxidation, which is stable, easily turned to other material. ClO_2 can treat waste water of printing and dyeing works. Its treatment effect was better than O_3 's.¹² And *Puplampu*¹³ found that ClO_2 had good results in treating o-nitrophenol. So it was thought that CCl_4 may turn to ClO_2 under ultrasound, shown as (2).



Frequency

Higher frequency ultrasound may have more capability to degrade chemical agent.^{14,15} PCP ion degradation experiment with 20 and 500 kHz ultrasound condition was carried out without any catalyst (Fig. 4).

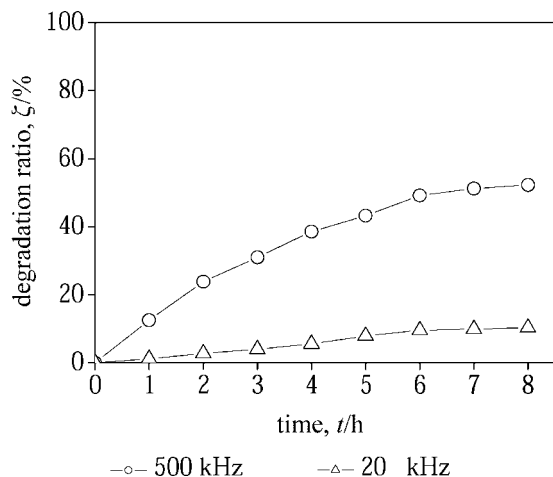


Fig. 4 – Influence of frequency on ultrasonic degrading PCP ion

It is clear that degradation rate of PCP ion under high frequency ultrasound is greatly larger than that under low frequency. During the experiment, degradation ratio under 20 kHz ultrasound was not more than 15 % in 8 h without any catalyst.

The mechanism of ultrasound degrading pentachlorophenol

There were two theories of ultrasonic degradation.¹⁶ The one was pyrolysis, the other was free radical oxidation. This part of experiment was to discuss the influence of n-butyl alcohol played as a free radical scavenger on PCP ion ultrasonic degradation.

If this mechanism is free radical oxidation, the more n-butyl alcohol was added, the more generated free radical was eliminated, and the less ultrasonic degradation ratio was gained. Otherwise, the mechanism might be pyrolysis, if degradation ratio did not change upon the quantity of n-butyl alcohol.

Three sets of n-butyl alcohol fractions ($0 \cdot 10^{-6}$, $5 \cdot 10^{-6}$, $10 \cdot 10^{-6}$) were added in PCP ion solution. Each reaction proceeded under 4.1 W cm^{-2} catalytic CCl_4 ultrasonic degradation, 2 ml CCl_4 was added. Ultrasonic generator with horn (Fig. 1 (a)) was adopted in this experiment. The effects of them were shown in Fig. 5.

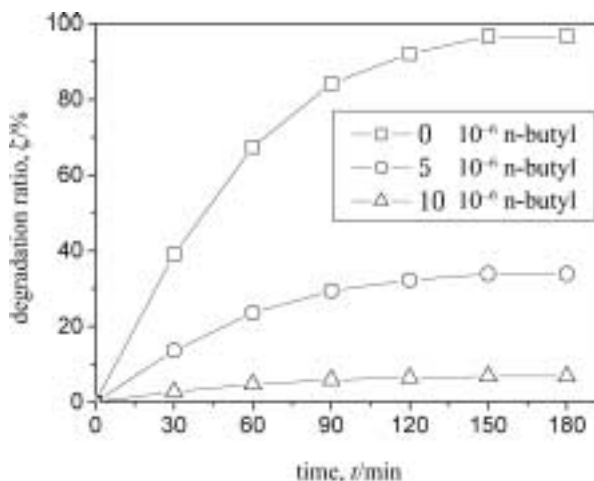


Fig. 5 – Influences of the n-butyl alcohol on PCP ion ultrasonic degradation

It is obviously that the more n-butyl alcohol was added, the less PCP ion degradation ratio was. So this ultrasonic degradation principle is free radical degradation.

Conclusion

Application of ultrasound to degradation PCP ion was a good way to treat chemicals that are diffi-

cult to biodegrade. Ultrasound method could totally degrade PCP ion in average for about 3 h. Relation of sound intensity and catalyst quantity should be considered. Generally, to increase input power can speed up the degradation rate. High frequency had more advantages than that of low frequency in degrading chemicals. In order to get satisfied degradation ratio, initial PCP ion fraction shouldn't be more than $1000 \cdot 10^{-6}$. The mechanism of ultrasonic degradation of PCP ion is believed as free radical oxidation.

Sonication can provide powerful sound energy. However, to achieve the most degradation rate using only ultrasound, it is necessary to use high sound intensity.¹⁷ So based on saving more energy and gaining better experimental result, it is important to combine ultrasonic method with other degradation method.

ACKNOWLEDGEMENT

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