

Mechanism of the enhanced degradation of pentachlorophenol by ultrasound in the presence of elemental iron

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Abstract

Ultrasound combined with elemental iron (US/Fe⁰) is effective in oxidizing organic contaminants in water. The sonolysis degradation of pentachlorophenol (PCP) was significantly enhanced by a factor of 4.2 with the addition of elemental iron, mainly via reaction with hydroxyl radicals (\bullet OH radicals), and the synergistic mechanism of the enhancement in the combined system was investigated. Experiments were performed with (1) sole ultrasonic treatment; (2) ultrasound in presence of iron; (3) ultrasound combined with copper powder as the same particle size as iron powder; (4) ultrasound in presence of Fe(II). It was observed that PCP degradation and \bullet OH radicals production were both enhanced in these combined methods, and the pitting on the sonicated iron surface was apparent. These results indicated that the rate enhancements in US/Fe⁰ system were attributed to (1) the iron solid effect and the catalysis of Fe(II) produced from corroded-iron with promoting the production of \bullet OH radicals; (2) the increased surface area of iron particles by acoustic cavitation with promoting the adsorption process.

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1. Introduction

Sonolysis can convert ideally the organic pollutants to carbon dioxide and water, or convert them to compounds which are less harmful than the original pollutants. Since 1990s, there has been a resurging interest in application of ultrasound in waste water treatment. Studies on the sonolysis of a wide range of organic compounds demonstrated that ultrasonic irradiation has potential as treatment technique for hazardous wastewater [1–6], but the efficiency of the technique, especially in the case of hydrophilic compounds, should increase. It was reported that ultrasound in conjunction with other techniques such as photocatalytic, biological catalytic, inorganic catalytic and the other methods could increase the decomposition efficiency and reduce the time required for removing the pollutants [7–14].

The combination of ultrasound and elemental iron is a good alternative to increase the efficiency of degradation process. Since iron is relatively inexpensive and nontoxic, it was pro-

posed that it could be useful for the sonolysis degradation of hazardous compounds. Sonication in the presence of elemental iron has been explored for the reduction of hazardous compounds, such as carbon tetrachloride (CCl₄), nitrobenzene and C.I. Acid Orange 7. The kinetics and mechanism of CCl₄ degradation by Fe⁰ in the presence of ultrasound was studied, and it was noted that the rate of CCl₄ degradation was enhanced by a factor of 40 compared to the same reaction system in the absence of ultrasound [15]. Similar rate enhancement for the reduction of nitrobenzene was also observed by Hung et al. [16]. The first-order rate constant for nitrobenzene degradation by ultrasound was $1.8 \times 10^{-3} \text{ min}^{-1}$, while in the presence of Fe⁰, the rate was found to be substantially faster. The effects of pH, iron loading and initial dye concentration on the decolorization of C.I. Acid Orange 7 by elemental iron combined with ultrasound radiation were investigated by Zhang. It was shown that the reduction of C.I. Acid Orange 7 was enhanced by ultrasound and the decolorization appeared to be a first-order reaction [17]. In our previous study, sonolysis, reduction by elemental iron (Fe⁰) and the combination of the two process (US/Fe⁰) were used to facilitate the degradation of chlorinated organics compounds in water, such as chlorobenzene and chlorophenol. The sonolysis of those contaminants was found to be substantially

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faster in the presence of iron and the influence of parameters was also discussed [18,19]. These studies are focused on parametric and kinetic analyses of contaminant degradation, and comparison of reaction efficiencies with those conducted in the absence of ultrasound.

To the refractory organic compound, ultrasound combined with Fe^0 is an effective methods compared to sole ultrasound. In order to increase the degradation efficiency of the method, it is essential to investigate the enhancement mechanism of the process. However, for the reactions in the heterogeneous system are complicated, the deep study of synergistic mechanism of ultrasound and iron for contaminants removal is very limited.

In this study, pentachlorophenol (PCP), which is well-known as a hazardous toxic compound, was selected as the model organic compound. With our interests focus on the possible synergistic mechanism of ultrasound and iron, the synergistic effect in US/ Fe^0 system was studied by experiments performed with (1) sole ultrasonic treatment; (2) ultrasound in presence of iron; (3) ultrasound combined with copper powder as the same particle size as iron powder; (4) ultrasound in presence of $\text{Fe}(\text{II})$. The effects of *t*-butyl alcohol (*t*-BuOH), iron solids and $\text{Fe}(\text{II})$ on the degradation of PCP by ultrasound in presence of elemental iron were investigated.

2. Materials and methods

2.1. Materials

PCP (purity > 99%) was purchased from Alfa Aesar Chemical company (USA). Iron powder and copper powder were obtained from Tianjin Kernel Chemical Reagent Development Center (China). All other chemicals (analytical grade) were purchased from Hunan Normal University Chemical Plant (China).

2.2. Ultrasonic irradiation

The experimental set-up for ultrasonic irradiation is shown in Fig. 1, it consisted of a KQ-600B ultrasound generator (600 W, 40 kHz, Kunshan Ultrasound Generator Instrument Co., China)

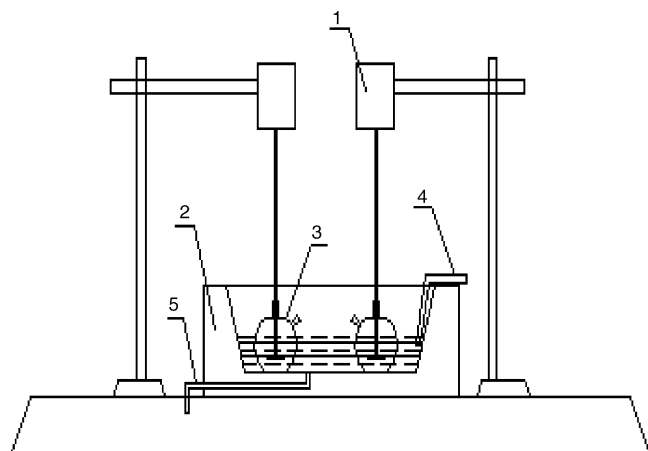


Fig. 1. The experimental set-up: 1, stirrer; 2, ultrasound generator; 3, glass vessel; 4, waterpipe; 5, drainpipe.

equipped with two glass vessels. Iron powder with the concentration of 2 g/l was added in one glass vessel for the combined process of ultrasound and iron and the other glass vessel was used for US system in absence of Fe^0 . A stirrer was equipped in the two vessels to make powder suspending and cooling water was used to keep the temperature of the reactor at $20 \pm 2^\circ\text{C}$.

All experiments were performed at initial PCP concentration of $37.5 \mu\text{M}$ and initial pH of 3.0. Experiments for investigating the productive principle of $\bullet\text{OH}$ radicals were performed under the above condition except the absence of PCP.

2.3. Analytical methods

Samples were taken out prior to irradiation and at various reaction times. A 5 ml aliquot sample of was removed from the reaction solution using a glass syringe, and then was filtered with $0.45 \mu\text{m}$ PTFE filters before analysis.

The concentration of PCP was determined using a P680 HPLC system (Dionex, USA) equipped with a Lichrospher C18 inverse phase column. A diode array detector (DAD) was used for the analysis and the detection wavelength was 280 nm. The HPLC mobile phase was the mixture of water (15%) and methanol (85%) at flow rate of 1 ml/min, and the injection volume was $20 \mu\text{l}$.

Ferrous iron was determined by a 722S spectrophotometer (Shanghai Precision & Scientific Instrument Co. Ltd., China). Copper iron was determined using a WYX-9003A atomic absorption spectrometry (Shenyang Yitong Analytical Instrument Co. Ltd., China). The morphology of the iron surface with/without sonication was analyzed with a S-570 Scanning Electron Microscope (Hitachi, Japan).

The productive principle of $\bullet\text{OH}$ radicals in the systems was studied by $\text{Fe}(\text{phen})_3^{2+}$ spectrophotometry. The $\bullet\text{OH}$ radicals could oxidate $\text{Fe}(\text{phen})_3^{2+}$ to $\text{Fe}(\text{phen})_3^{3+}$ and thus $\bullet\text{OH}$ radical was determined indirectly by $\text{Fe}(\text{phen})_3^{2+}$ spectrophotometry at 510 nm with a 722S spectrophotometer (Shanghai Precision & Scientific Instrument Co. Ltd.).

3. Results and discussion

3.1. Synergistic effect

The degradation of PCP in various systems is shown in Fig. 2. It could be seen that the hyperbolic logarithm value of C/C_0 has a linear relationship with reacting time, and thus the degradation of PCP would be described by a first-order kinetic model:

$$-\frac{dC}{dt} = kC \quad (1)$$

Its integrated form can be obtained as follows:

$$C_t = C_0 e^{-kt} \quad (2)$$

where C_t is the PCP concentration at different reaction time, C_0 the initial PCP concentration and k is the apparent first-order rate constant.

Table 1 illustrates the kinetics of PCP degradation in the three systems. The rate constant in the US/ Fe^0 system was a factor

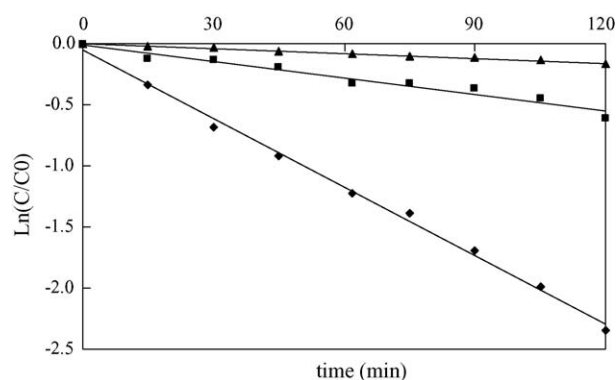


Fig. 2. The degradation rates of PCP in (■) US, (▲) Fe^0 and (◆) US/ Fe^0 systems.

of 4.2 greater than that in the US system, and a factor of 14.8 greater than that in the Fe^0 system. Furthermore, the degradation rate constant of PCP by US/ Fe^0 was greater than the sum of those in US system and Fe^0 system. The results indicated that the synergistic effects between ultrasound and iron existed in US/ Fe^0 system for enhancing PCP degradation significantly.

3.2. Effect of hydroxyl scavenger

When a liquid is irradiated by intense ultrasound, many cavitation bubbles form and collapse violently, leading to hot spot of local extreme condition with high temperature and high pressure. Under this condition, water is easily dissociated to produce hydroxyl radical which is responsible for many kinds of chemical reactions. In general, it has been recognized that the sonochemical decomposition of organic compounds proceeds in the three different regions in an aqueous solution system: (I) the inside of the collapsing cavitation bubbles at high temperature and high pressure [20], (II) the interface region between the cavitation bubbles and the bulk solution and (III) the bulk solution at ambient temperature. It is suggested that in regions (I) and (II), pyrolysis and radical reactions mainly occur, and in region (III), reactions with OH radicals chiefly occur. Since PCP used in the present study are non-volatile compounds, the solutes do not pyrolyze in the cavitation bubbles. To confirm the reaction pathway, the effect of the radical scavenger, *t*-butyl alcohol, on the rate of PCP decomposition was investigated in the US/ Fe^0 system. *t*-Butyl alcohol (*t*-BuOH) is known as an effective $\bullet\text{OH}$ radical scavenger in water sonolysis [21–23].

Fig. 3 shows the scavenging effect of *t*-BuOH on the degradation of PCP. It was clear that the degradation was effectively inhibited after the addition of *t*-BuOH. The degradation efficiency of PCP decreased with the increase of concentration of

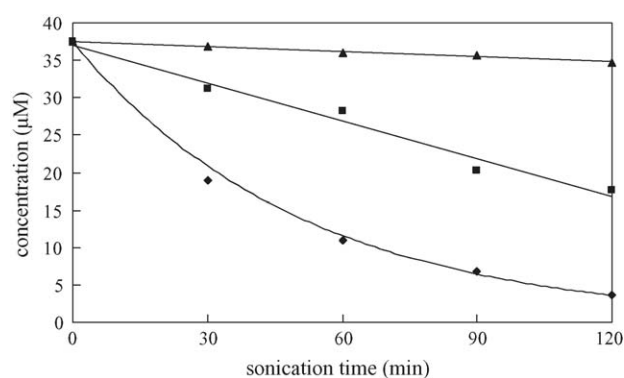


Fig. 3. The scavenging effect of *t*-butyl alcohol on the degradation of PCP in US/ Fe^0 system ((◆) without *t*-BuOH; (■) *t*-BuOH 5 mM; (▲) *t*-BuOH 50 mM).

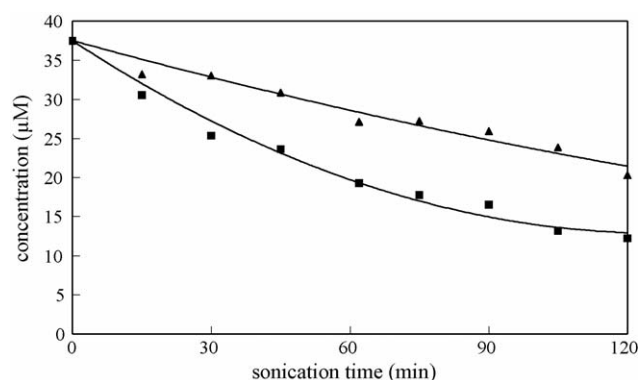


Fig. 4. Plot of degradation efficiency on time in (■) US/ Cu^0 and (▲) US systems.

t-BuOH in solution, and the degradation was nearly quenched in the presence of 50 mM *t*-BuOH. The results showed that most of the degradation proceeds via $\bullet\text{OH}$ radicals reaction in the combined system (US/ Fe^0).

3.3. Effects of iron

3.3.1. Effect of iron as solid particles

To clarify the effect of particle addition, experiments were performed with (1) sole ultrasonic treatment and (2) ultrasonic treatment in the presence of copper powder with the same particle size as iron powder (US/ Cu^0). As shown in Figs. 4 and 5, the

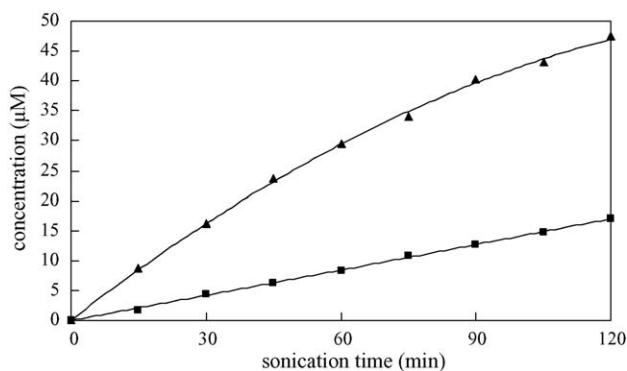


Fig. 5. Plot of $\bullet\text{OH}$ radicals concentration on time in (◆) US/ Cu^0 and (■) US systems.

Table 1

Kinetics models of PCP degraded in US, Fe^0 and US/ Fe^0 systems ($k_{\text{US}/\text{Fe}^0}$, k_{US} and k_{Fe^0} were the rate constant in US/ Fe^0 , US and Fe^0 system, respectively)

Systems	Kinetics models (C_t)	Rate constants	Correlation coefficients (R^2)
US/ Fe^0	$10e^{-0.0193t}$	$k_{\text{US}/\text{Fe}^0} = 0.0193$	0.9948
US	$10e^{-0.0046t}$	$k_{\text{US}} = 0.0046$	0.9585
Fe^0	$10e^{-0.0013t}$	$k_{\text{Fe}^0} = 0.0013$	0.9941

degradation of PCP and the production of $\bullet\text{OH}$ radicals by ultrasound were both enhanced by the addition of copper powder. No copper ion was detected in the sonication solution, showing that there was no chemical reaction at the copper surface under such conditions. These results indicated that the enhancement of PCP removal was not probably attributed to the chemical reaction of added copper particles. The effect of particle is based on the increase of the cavitation bubbles due to the supply of crevices as well as the wall of particle that plays a role in producing tiny-bubbles with a promotion of jet toward the wall. The existence of wall can easily break the spherical symmetry of the large-size cavitation bubble into many tiny cavitation bubbles. The increase of the cavitation bubbles accelerates production of $\bullet\text{OH}$ radicals and other oxidants during their collapse. It was reported that such addition of inert particle can promote the reaction rate by twice compared with that in the absence of particle [24]. The iron particles might have the similar effect in the US/ Fe^0 system with enhancing the degradation of PCP.

Another explanation for rate enhancements might be attributed to the fragmentation of iron particles by the cavitation process which produces higher surface area. There are two modes of cavitation bubbles collapse that can affect the surface of solids [15]. First, cavitation bubbles collapsing directly on a surface may cause direct damage by shock waves produced upon implosion. These bubbles are formed on nuclei such as surface defects, entrapped gases or impurities on the surface of the material. Second, cavitation collapse near the solid surface in the liquid phase would cause microjets to hit the surface and produce a nonsymmetrical shock wave. This phenomenon results in the well-known cleaning action of ultrasound. The morphology of the iron surface with/without sonication was analyzed via Scanning Electron Microscope (Fig. 6). It could be seen that the sonicated samples were visibly cleaned due to the continuous ultrasonic cleaning. In addition, the pitting on the surface caused by shock waves produced upon implosion was apparent.

The influence of ultrasonic waves on the desorption of pollutant from the surface of iron particles was negligible here [17]. In the coupled US/ Fe^0 method, ultrasonic waves not only destroys the pollutant through $\bullet\text{OH}$ radicals oxidation process but also increases the adsorption process by increasing the surface area of iron particles.

3.3.2. Effect of Fe(II) as a catalyst

Under our experiment condition, Fe^0 was corroded and thus Fe(II) was obtained in US/ Fe^0 system. As shown in Fig. 7, the concentration of Fe(II) increased with the time, and reached $1.6\ \mu\text{M}$ after 120 min of ultrasonic irradiation. To investigate the effect of Fe(II) , experiments were performed with (1) sole ultrasonic treatment and (2) ultrasonic treatment in the presence of $1.6\ \mu\text{M}$ ferrous sulfate. The sonolysis degradation of PCP increased significantly by the addition of Fe(II) (Fig. 8). It was showed that Fe(II) produced in US/ Fe^0 system also can enhance the degradation of PCP. These results were in line with those obtained by Nagata et al. [22], who reported that the sonolysis degradation of 3-chlorophenol was enhanced in the presence of Fe(II) .

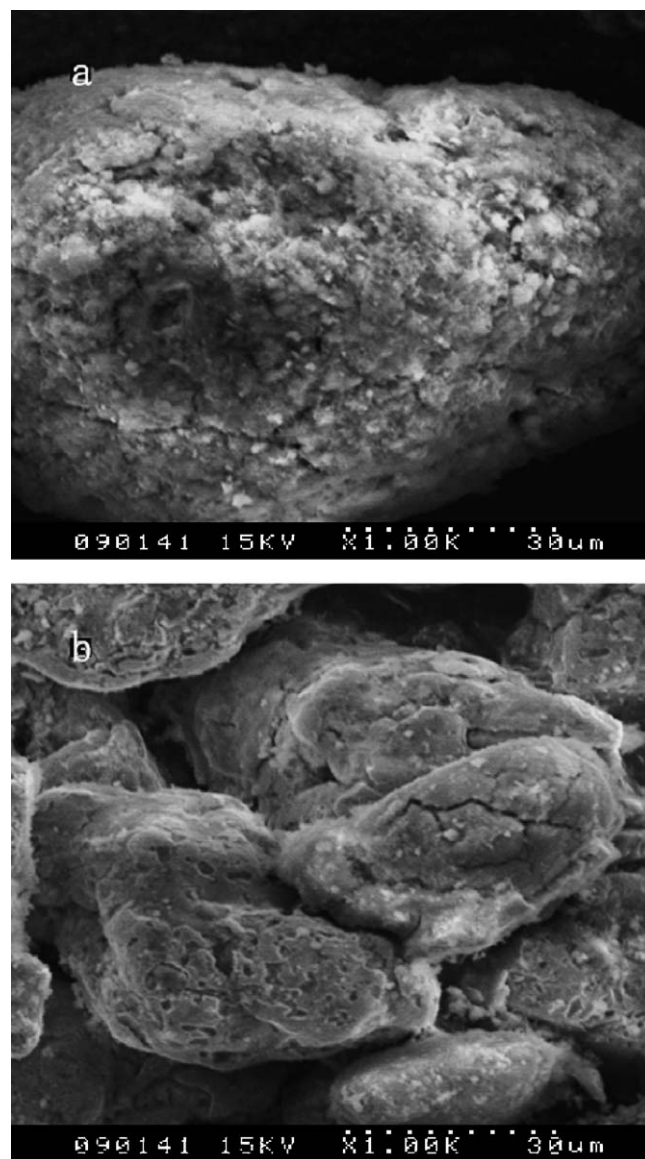


Fig. 6. SEM photographs of the iron surface after 60 min of reaction in the: (a) Fe^0 system; (b) combined US/ Fe^0 system.

Fe(II) is an effective oxidation catalyst for producing the organic radicals with reaction of free radicals and the organic substrate. Furthermore, Fe(II) can catalyze the production hydroxyl radicals with a Fenton reaction (Fig. 9). During aque-

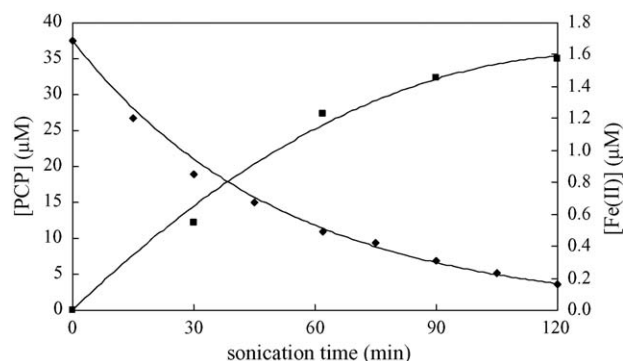


Fig. 7. Plot of concentration of (♦) PCP and (■) Fe(II) on time in US/ Fe system.

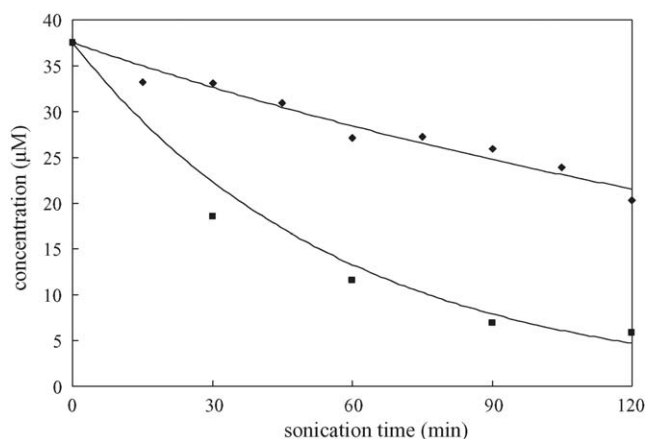


Fig. 8. Plot of PCP concentration on time in (◆) US and (■) US/Fe(II) systems.

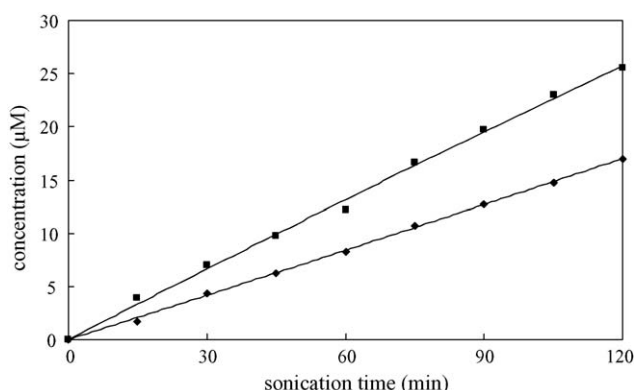
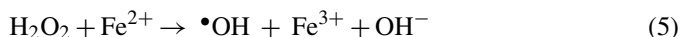


Fig. 9. Production of •OH radicals in (◆) US and (■) US/Fe(II) systems.

ous ultrasonic irradiation, water can be subjected to pyrolysis and generates hydroxyl radicals. The catalysis of Fe(II) in ultrasound system was confirmed by Abderrazik et al. [25] and Nam et al. [26]. It was reported that the partial recombination of hydroxyl radicals would result in the formation of hydrogen peroxide (H_2O_2) in ultrasound system, and the H_2O_2 production decreased by the addition of Fe(II), due to the reaction of Fe(II) with H_2O_2 (Fenton's reaction). The catalytic mechanism can be described as follows:



where ultrasound refers to the ultrasound irradiation.

4. Conclusions

The combination of ultrasound and iron is high effective in organic pollutants removal due to its several promoting effects, and thus provide a valuable strategy for the treatment of organic pollutants. In this study, it was demonstrated that the rate of sonolysis degradation of PCP could be enhanced by the presence of Fe^0 , and the main degradation proceeds via reactions with

•OH radicals. The rate enhancements in the US/ Fe^0 system could be attributed to the iron solid effect and Fe(II)-catalytic effect with promoting the production of •OH radicals. Furthermore, ultrasound increased the adsorption process by increasing the surface area of iron particles. This study provides some theoretic references for further studying the complicated reactions in such heterogeneous system.

Acknowledgement

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