

2-chlorophenol oxidation kinetic by photo-assisted Fenton process

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Abstract: Experimental data are presented to test and validate a kinetic model for the oxidation of 2-chlorophenol wastewater by photo-assisted Fenton process. The data showed that this process had produced good effects under acidic condictions. Up to 90% 2-chlorophenol was removed after 90-minute reaction time with H_2O_2 of 25% COD_{Cr} , in, while in UV/ H_2O_2 system only 16.8% 2-chlorophenol was removed after one hour treatment. The optimal pH in this reaction occurred between pH 3.0 and pH 4.0. The reaction kinetics for photo-assisted Fenton process experimented in this research was investigated. Kinetic models were proposed for the treatment of 2-chlorophenol wastewater. The reaction was found to follow the 2nd order. The equations of reaction kinetics are as follows: $-\frac{d[RH]}{dt} = K_{RH} [RH] [H_2O_2]_0 \exp(-K_{H_2O_2} t)$; $-\frac{d[COD_{Cr}]}{dt} = K_{COD_{Cr}} [COD_{Cr}] [H_2O_2]_0 \exp(-K' t)$. The prediction of the models was found to be in a good agreement with experimental results, thus confirming the proposed reaction mechanism.

Keywords: 2-chlorophenol wastewater; photo-assisted; Fenton reagent; reaction kinetic

Introduction

The *o*-chlorophenol is a very toxic and poorly biodegradable pollutant, which is used as an intermediate in the manufacture of higher chlorophenol and phenol resins and for extracting sulphur and nitrogen compounds from coals. It is also used in organic synthesis(dyes and pesticide). Oxidation of *o*-chlorophenol wastewater in catalytic wet air oxidation is of practical interest since a wastewater containing *o*-chlorophenol over 200 ppm may not be treated effectively by direct biological methods.

Advanced oxidation processes(AOPs) have been successfully used in degrading many of the organic-compound-contaminated wastewaters. Among all of the chemical oxidation methods, the dark reaction of H_2O_2 with ferrous salts(known as Fenton's reagent) and the photo-assisted Fenton's reaction(photo-Fenton process) is a possible source of hydroxyl radicals in water and the oxidation of organic compounds by these AOPs have been the subject of numerous studies during the last decade.

Many hazardous organic-compound-pollutants can be mineralised by the hydroxyl radicals generated by Fenton's reagent or Fenton-like reactions. UV/ H_2O_2 / Fe^{2+} reaction can convert most of the organic or inorganic compounds into end products such as minerals, formic acid, carbon dioxide and water(Sadana, 1974; Huang, 1989; 1990; 1991; 1996). Practically, the hydroxyl radicals produced during the reaction can detoxify the contaminants. The hydroxyl radicals are generated by H_2O_2 reacted with a small amount of iron, concentration as low as 0.05 mmol/L, and also with other transition metals than iron. Numerous competing reactions, such as Fe^{2+} , Fe^{3+} , H_2O_2 , hydroxyl radicals, super-oxide radicals, and radicals derived from the substrate, may exist during Fenton's reagent treatment. This process has been successfully applied in the treatment of wastewater discharged from various sources such as medicament and chemical engineering industries. The photo-assisted Fenton process has become one of the most attractive destruction methods for hazardous wastewater treatment, which is too dilute to incinerate, or too concentrated or toxic for conventional biological treatment. In this paper, different oxidation processes employed in the oxidation of 2-chlorophenol in aqueous solutions were compared. The effect of different pH values and concentrations of H_2O_2 and iron compounds was evaluated. The reaction kinetics for photo-

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assisted Fenton processes experimented in this research was also investigated.

1 Experiments

1.1 Materials

All reagents used in this work were analytical reagent grade and used without further purification. Ferric sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99.5%), hydrogen peroxide (30%, w/w, unstabilized), 2-chlorophenol.

1.2 Experimental set up

All experiments were performed in a batch reactor, and the schematic diagram of the experimental set-up used in this study is shown in Fig. 1. The radiant power of the high-pressure mercury lamp (250 W) employed in the photochemical experiment is described there. The total volume of the photolysis solution was 1.0 L.

The pH was adjusted using H_2SO_4 to the initial value of 6.0. Because the products of oxidation were carbon dioxide, oxalic and other carbonic acids, the pH value would drop from 6.0 to 3.0–4.0 during the reaction. No significant dependence of the reaction rates of 2-chlorophenol-degradation was observed between pH 2.0 and 4.0. The analysis was performed immediately after the samples were taken from the reactor and filtered using nylon luer-lock-membrane filters.

As pre-treatment of the sample prior to the analysis of 2-chlorophenol, 2.0 ml "reduction and precipitation agent", which was composed of 0.10 mol/L Na_3PO_4 , 0.10 mol/L KI and 0.10 mol/L Na_2SO_3 , was added to the 5.0 ml samples taken from the batch reactor at various photolysis intervals. This procedure led to complete decomposing of the residual H_2O_2 as well as the removal of most of the iron(II/III) by precipitation. The precipitates were removed by the nylon filters (Roth).

The detection of possible low molecular weight intermediates produced during photochemical enhanced Fenton reaction, such as oxalic acid, acetic acid, acetaldehyde and ethanol, was performed using an HPLC.

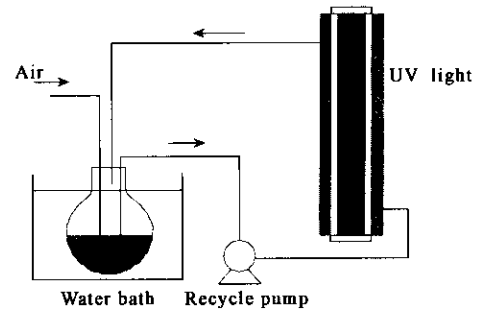


Fig. 1 Schematic diagram of photo-assisted reaction facility

2 Results and discussion

2.1 Comparison of different oxidation processes

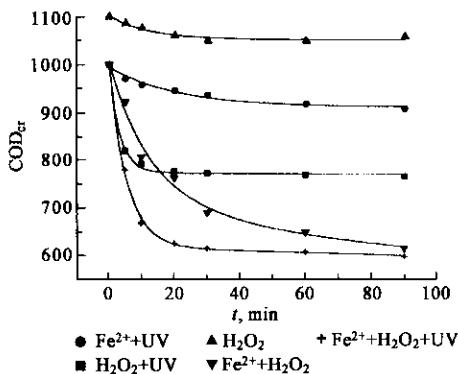


Fig. 2 Comparison of UV/ H_2O_2 / Fe^{2+} with other oxidation processes (1/4Qth, 25°C)

A series of experiments with different oxidation processes were carried out in the reactor. The results are compared in Fig. 2. As expected, among all the systems the COD_{Cr} of 2-chlorophenol wastewater removal was highest in UV/ H_2O_2 / Fe^{2+} system, in which about 40% COD_{Cr} was removed after 60 min of reaction. Within 5 min a nearly complete destruction of 2-chlorophenol could be observed using photo-Fenton processes. But in H_2O_2 system only 3.6% COD_{Cr} was removed after 60 min.

2.2 Effect of H_2O_2 concentration

Fig. 3 presents the effect of the initial hydrogen peroxide level on the removal of COD_{Cr} and 2-chlorophenol with the use of photo-assisted Fenton reaction process. As

expected, degradation of 2-chlorophenol and COD_{Cr} was expedited by elevating the initial H_2O_2 concentration. Reaction with H_2O_2 at 25% of its required stoichiometric amount to mineralise organic carbons in 2-chlorophenol wastewater ($COD_{Cr,in}$) gave a 2-chlorophenol removal of 90% after 90 min in this reaction. Reaction with H_2O_2 of 6.25% $COD_{Cr,in}$ also had 45% 2-chlorophenol removed after 90 min reaction. This can be explained by the effect of the presence of extra amount of OH radicals. Therefore, H_2O_2 should be added at an optimal concentration to achieve the best degradation.

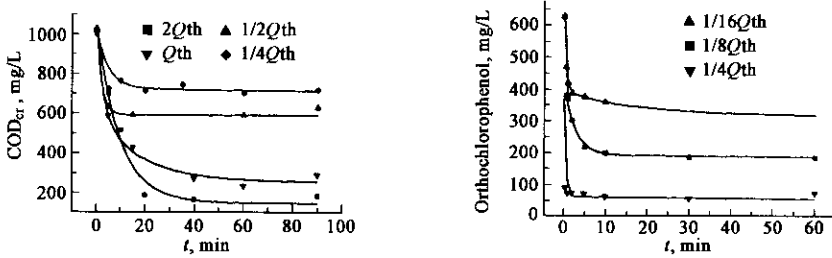


Fig.3 Effect of H_2O_2 addition in UV/Fenton's reaction system ($Fe^{2+} : H_2O_2 = 1:20$, $25^\circ C$)

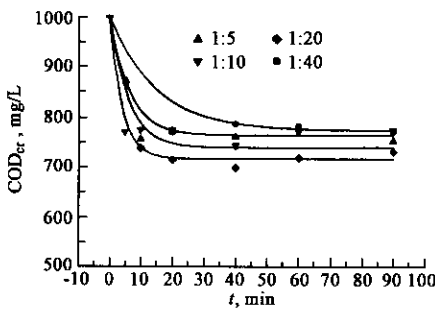


Fig.4 Effect of Fe^{2+} addition in UV/Fenton's reaction system ($1/4Q_{th}$, $25^\circ C$)

2.3 Effect of Fe^{2+} concentration

Iron in its ferrous and ferric forms acts as a photo-catalyst and requires a working pH below 4.0. To obtain the optimal Fe (II) concentration, experiments were done with various amount of the iron salt. Fig.4 shows that COD_{Cr} changes as a function of the added Fe (II). Apparently, the degradation rate of 2-chlorophenol and COD_{Cr} went up with increasing amount of iron salt when Fe^{2+} to H_2O_2 ratio was below 1:20. But adding more iron salt resulted in higher brownish turbidity that hindered adsorption of the UV light required for photolysis and caused recombination of OH radicals. In this case, Fe^{2+} reacted with

OH radicals as a scavenger. It is desirable to have the Fe(II) to H_2O_2 ratio as small as possible, so the recombination can be avoided and the sludge production from iron complex is also reduced. The optimal Fe (II) to H_2O_2 ratio should be less than 1:20.

2.4 Effect of pH

pH value affects the oxidation of organic substances both directly and indirectly. Photo-assisted Fenton process is strongly affected by the pH of wastewater. The pH value influences the generation of OH radicals and the oxidation efficiency. Fig.5 shows the effect by the pH value during photo-assisted Fenton process. As expected, pH value will decline during the reaction process. When the initial pH is greater than 6.5, the pH of wastewater does not decrease significantly. But when the initial pH is less than 6.5, the pH will go down to 3.0—4.0, and also give the best performance. More than 45% of the 2-chlorophenol is removed after 90 min reaction with H_2O_2 at 12.5% $COD_{Cr,in}$. The optimal pH in the reaction course occurs between pH 3.0 and pH 4.0.

The second aspect of pH deals with its shift as the reaction

Photo-assisted

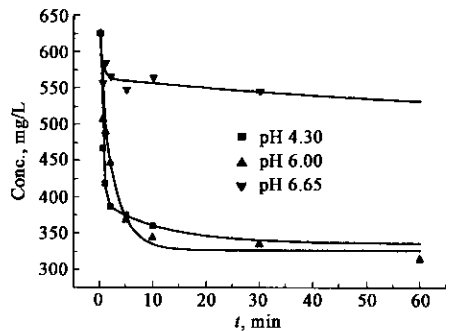


Fig.5 Effect of pH in UV/Fenton's reaction system ($1/8Q_{th}$, $25^\circ C$)

progresses. Providing an initial wastewater pH of 6.0, the following profile is typical to Fenton reactions. The first inflection is caused by adding FeSO_4 catalyst, which usually contains residual H_2SO_4 . The second and more pronounced drop in pH starts as H_2O_2 is added, and continues at the rate that is largely dependent on the catalyst concentration. This drop in pH is attributed to the fragmentation of organic materials into organic acids. The pH change is often monitored to ensure that the reaction is progressing as planned because dropping in pH value may indicate an inhibition on reaction and a potentially hazardous build-up of H_2O_2 in the reaction mixture.

2.5 Effect of carry gas

A series of experiments with different carry gases were done in lab scale reactors. The experimental results are compared in Fig.6. As expected, the largest COD_{Cr} removal was observed with pure oxygen in which more than 41% of COD_{Cr} was removed after 90 min reaction with H_2O_2 of 25% COD_{Cr} , in, while the COD_{Cr} removal with pure nitrogen was only 26% after the same reaction time.

2.6 Effect of temperature

Fig. 7 shows the degradation effect by changing temperature during photo-assisted Fenton process. As expected, the degradation rate of COD_{Cr} increased with rising temperature if it is not too high, which conforms to the Arrhenius equation. Since the activation energy is not too high, the effect of the temperature does not play a major role in this process. On the contrary, with a higher temperature, such as more than 60°C , the total degradation of COD_{Cr} will decrease because too high temperature causes decomposition of H_2O_2 . The appropriate reacting temperature is $20\text{--}40^\circ\text{C}$.

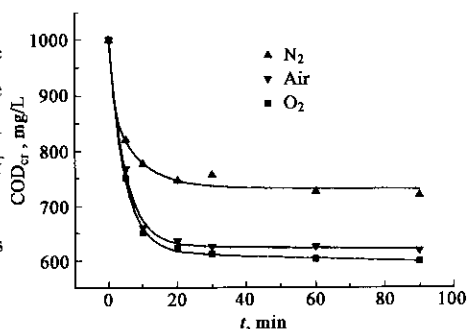


Fig.6 Effect of carry gas in UV/Fenton's reaction system(1/4Qth, 25°C)

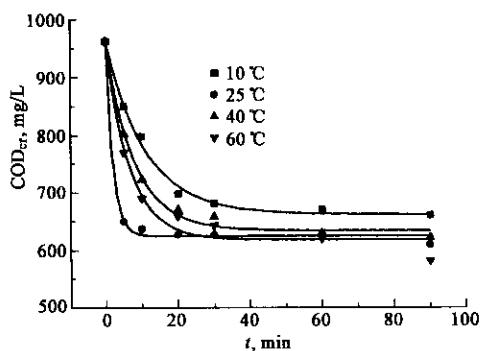
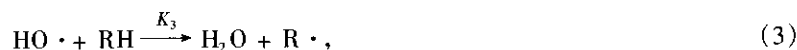
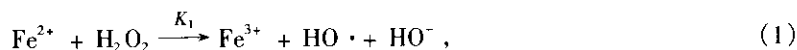


Fig.7 Effect of reacting temperature in UV/Fenton's reaction system(1/2Qth, $\text{Fe}^{2+} : \text{H}_2\text{O}_2 = 1:20$)

2.7 Kinetics of photo-assisted Fenton oxidation in 2-chlorophenol wastewater

The kinetic model for the oxidation rate of 2-chlorophenol by $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$ involves the single-step dissociation of H_2O_2 into two hydroxyl radicals($\text{OH}\cdot$). These hydroxyl radicals can oxidise organic compounds (RH) through proton extraction and thus generate organic radicals ($\text{R}\cdot$), which are highly reactive and can be further oxidised. This multiple step reaction, which occurs during $\text{UV}/\text{H}_2\text{O}_2$ oxidation, can be written as follows (Marechal, 1997; Blough, 1988; Venkatadri, 1993; Bigda, 1995):





Based on the above equations, RH reaction equation can be written as follows (Yang, 2001):

$$-\frac{d[\text{RH}]}{dt} = K_{\text{RH}}[\text{RH}][\text{H}_2\text{O}_2]_0 e^{-K_{\text{H}_2\text{O}_2} t}, \quad (9)$$

$$\ln[\text{RH}] = K_{\text{RH}} \frac{[\text{H}_2\text{O}_2]_0 \exp(-K_{\text{H}_2\text{O}_2} t)}{-K_{\text{H}_2\text{O}_2}} + C. \quad (10)$$

According to the above equation in this study we can calculate K_{RH} , $K_{\text{H}_2\text{O}_2}$, and C (integration constant) using the resourceful exploring model. Fig. 8 shows the plot of second-order kinetics for 2-chlorophenol, in which all the experimental data fit well with the second order kinetic model.

COD_{Cr} removals can also be described by the following equations:

$$-\frac{d[\text{COD}_{\text{Cr}}]}{dt} = K_{\text{COD}_{\text{Cr}}}[\text{COD}_{\text{Cr}}][\text{H}_2\text{O}_2]_0 \exp(-K' t), \quad (11)$$

$$\ln[\text{COD}_{\text{Cr}}] = K_{\text{COD}_{\text{Cr}}} \frac{[\text{H}_2\text{O}_2]_0 \exp(-K' t)}{-K'} + C. \quad (12)$$

Interestingly, note that the order of COD_{Cr} removal can also be simplified as second order. Fig. 9 displays the plots of the experimental data and model-calculated data. The prediction of the models agrees well with the experimental results, thus confirming the proposed reaction mechanisms.

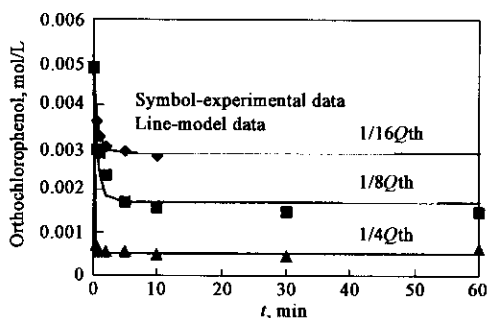


Fig. 8 The model fit of photo-assisted fenton oxidation

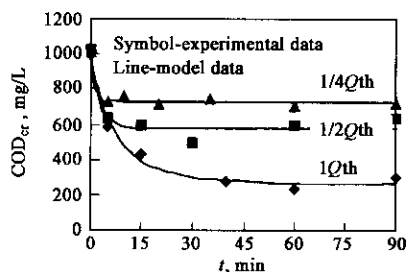
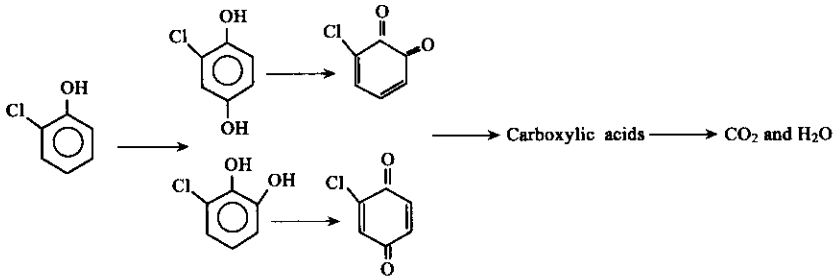


Fig. 9 The model fit of photo-assisted Fenton oxidation

2.8 Mechanism of photo-assisted Fenton oxidation in 2-chlorophenol wastewater

According to the observed intermediates, the dechlorination process seems much slower than the breaking down of orthochlorophenol because the amount of chloride ion measured is only a fraction of the theoretical value calculated by assuming 100% release of chloride ion by orthochlorophenol. Chlorinated intermediates are formed which are sequentially oxidised by hydroxyl radicals. In other words, chlorine atoms will not be released directly from the aromatic ring after hydroxylation. In terms of oxidation kinetics, the rate constants between hydroxyl radicals and chlorinated aliphatic compounds are several magnitudes smaller than that between hydroxyl radicals and aromatic compounds. In addition, hydroxyl radicals usually attack the aromatic ring preferably at the sites that are not occupied by chlorine atoms. Thermodynamically, the dissociation energy of a Cl-C benzene bond is 95 kcal/mol, whereas the highest bond dissociation energies of Cl-C in an aliphatic molecule are about 81 to 84 kcal/mol. Therefore, it is thermodynamically more difficult for chlorine atoms to dissociate directly from the aromatic ring than from

the chlorinated aliphatic intermediates. The pathways of Fenton oxidation are as follows:



3 Conclusions

Experimental results showed that the UV/H₂O₂/Fe²⁺ process is effective for the treatment of 2-chlorophenol wastewater. Up to 90% of 2-chlorophenol is removed after 90-minute reaction time with the H₂O₂ level of 25% COD_{Cr} and the optimal Fe²⁺ to H₂O₂ ratio as 1:20. While in the UV/H₂O₂ system (without adding ferrous ion), only 16.8% of 2-chlorophenol is removed in one-hour reaction. As expected, the COD_{Cr} and 2-chlorophenol removals increase with higher initial H₂O₂ dosage. Reaction with H₂O₂ of 100% COD_{Cr} gives the best performance in which more than 75% COD_{Cr} is removed after 90 min reaction; while reaction with H₂O₂ of 25% COD_{Cr} only 18% COD_{Cr} is removed after 90 min reaction. 2-chlorophenol removal yields the same result as COD_{Cr} does. It is interesting to note that the COD_{Cr} and 2-chlorophenol removals give the best performance when the Fe²⁺ to H₂O₂ ratio is about 1:20. Higher reaction temperature can accelerate the degradation rate of 2-chlorophenol, but at too high temperature, the treatment effect will be because of the decomposition of H₂O₂. The optimal pH in reaction process occurs between pH 3.0 and pH 4.0, whereas, with the degradation of 2-chlorophenol, organic acids will be produced simultaneously, then the pH of solution will drop. Therefore, the optimal initial pH would be chosen as 6.0.

The reaction kinetics for photo-assisted fenton processes experimented in this research was investigated. Kinetic models are proposed for the treatment of 2-chlorophenol wastewater and textile industry wastewater. The equations of reaction kinetics are as follows:

$$-\frac{d[\text{RH}]}{dt} = K_{\text{RH}}[\text{RH}][\text{H}_2\text{O}_2]_0 \exp(-K_{\text{H}_2\text{O}_2} t); \quad -\frac{d[\text{COD}_{\text{Cr}}]}{dt} = K_{\text{COD}_{\text{Cr}}}[\text{COD}_{\text{Cr}}][\text{H}_2\text{O}_2]_0 \exp(-K' t).$$

The prediction of the models agrees well with the experimental results, thus confirming the proposed reaction mechanisms.

References:

- Bigda R J, 1995. Consider Fenton's chemistry for waste water treatment[J]. *Chemical Engineering Progress*, 91(12): 62—66.
- Blough N, 1988. Electron paramagnetic resonance measurements of photochemical radical production in humic substances. Effects of O₂ and charge on radical scavenging by nitroxides[J]. *Environmental Science Technology*, 22: 77—82.
- Huang C P, Davis A P, 1989. Removal of phenols from water by a photocatalytic oxidation process[J]. *Water Science Technology*, 21(6/7): 455—464.
- Huang C P, Davis A P, 1990. The removal of substituted phenols by a photocatalytic oxidation process with cadmium sulfide[J]. *Water Research*, 24(5): 543—550.
- Huang C P, Tseng J M, 1991. Removal of chlorophenols from water by photocatalytic oxidation[J]. *Water Science Technology*, 23(1/3): 377—387.
- Huang C P, Tang W Z, 1996. 2,4-dichlorophenol oxidation by Fenton's reagent[J]. *Environmental Technology*, 17(12): 1373—1378.
- Marechal M, Slokar Y M, Taufer T, 1997. Decoloration of chlorotriazine reactive azo dyes with H₂O₂/UV[J]. *Dyes and Pigments*, (33):

281—298.

- Sadana A, James R K, 1974. Catalytic oxidation of phenol in aqueous solution over copper oxide[J]. *Ind Eng Chem Fundam*, 23(2):127—133.
- Venkatadri R, Peters R W, 1993. Chemical oxidation technologies: ultraviolet light hydrogen peroxide, Fenton reagent, and titanium dioxide assisted photocatalysis[J]. *Hazardous Waste & Hazardous Materials*, 10(2): 107—149.
- Yang Y P, Wu X Y, Xu X H, 2001. Treatment of dyeing wastewater by photoassisted Fenton system[J]. *Journal of University of Chemical Engineering*, 15(3): 242—247.

(Received for review May 20, 2002. Accepted October 24, 2002)