

Oxidation of Pentachlorophenol by Fenton's Reagent

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Abstract

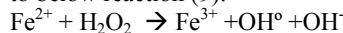
Several authors have indicated that PCP is a toxic chemical and recalcitrant to biodegradation. AOPs is one of the most effective process for degradation of persistent compound. Since the mineralization of recalcitrant compound by AOPs (Advanced Oxidation Processes) often requires long reaction time and strong doses of oxidant, the combination of this process with biological one, considered as an efficient and economic method. In this work degradation of pentachlorophenol in aqueous solution with fenton reagent (H₂O₂ + Ferrous ion) was studied. The experiment was done in batch mode, and the initial concentration of PCP was 0.055mM, in pH=3, H₂O₂=0.6mM, Fe=0.2mM, more than 95% of PCP was degraded in first minute after the reaction was started. Therefore this reaction is very fast and in the initial phase degradation of PCP follows first order kinetics and kinetic constant (K) was 0.026 (S⁻¹). Chloride ion generation as PCP degradation by product was investigated, and it was found that the scavenging effect of chloride is negligible. pH and UV₂₁₅ absorbance analysis, after reaction completion, indicated that generated intermediates have the less chlorinated nature, acidic properties and nonphenolic structure. Chloride ion increases from 0 mg/L to 6 mg/L, pH decreases from 3 to 2.82 and UV₂₁₅ absorbance decreases from 0.48 to 0.1, therefore it can be resulted that their biodegradability modified and their recalcitrance reduced. In the long time reaction (10hr) experiments, TOC and COD analysis indicated that PCP did not mineralize and TOC and COD reduction was only 20% and 30% respectively. Results from this study indicated that scavenging effects of generated intermediate is important in high doses of H₂O₂.

keywords: Oxidation, Fenton reagent, Pentachlorophenol, AOP

Introduction

Pentachlorophenol is a common water contaminant, released into environment as a result of wood preserving, wood treating, pulp and paper bleaching, pesticide manufacturing and leaching to groundwater from contaminated soil (1, 2). PCP has been designated as a priority pollutant and is a probable human carcinogen. The final NTP report may serve as a basis for a group B2 classification (2, 3). PCP is known as a fat-soluble chemical that can accumulate in animal tissue cells through their skins. When accumulated PCP reaches to a certain level, it can interrupt formation of ATP and lead to the death of all forms of life (4). Because of its highly chlorinated nature, PCP is a toxic and recalcitrant compound (5), although its aerobic and anaerobic biodegradation by bacteria and its aerobic degradation by fungi have been reported by many authors (1, 3, 5). But there is a limitation for biodegradation of PCP, biological process is often slow for example aerobic degradation of PCP requiring sometimes a treatment time of several weeks and anaerobic dechlorination and degradation of PCP requires treatment time of several months (6). For this reason, there has been increased interest in alternative treatment methods. AOPs can achieve complete

mineralization of different persistent compound (7). Although mineralization of contaminant by AOPs often requires long time of reaction and strong doses of oxidant, since less reactive intermediates are produced that inhibit the degradation of parent compound. Often, after chemical oxidation of recalcitrant compound and transformation of them, their biodegradability modified and their recalcitrance reduce (8). Since biological treatment is 10-20 times less expensive than chemical processes, integration of chemical oxidation and biological processes can improve the economy of single process. Fenton reagent is a mixture of H₂O₂ and ferrous iron, which generates hydroxyl radical according to below reaction (9):



The ferrous iron initiates and catalyzes the decomposition of H₂O₂, resulting in the generation of hydroxyl radical. The generation of hydroxyl radical involves a completely reaction sequence in an aqueous solution (9). The main goal of this research was examination of feasibility and efficiency of Fenton reagent for degradation of PCP wastewater, study on many important factors involving in this process, such as pH, H₂O₂/Fe, H₂O₂/PCP, oxidation time and determination of optimum condition of Fenton's oxidation for jointing to biological treatment.

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Materials and Methods

Experimental apparatus and methods. All reaction were performed in batch reactor. The reactor was 1L cylindrical glass, mixing was done by a plastic paddle jointed to an epoxy coated shaft, the shaft was connected to a variable speed electromotor, and agitation rate of 180-190 rpm was used in all testes. pH was controlled by orion pH meter 420 A modle. Each test began with 500 ml of PCP wastewater, that made of 2 times distilled and deionized water. The initial concentration of PCP wastewater was prepared as 14.6 mg/L (0.055)mM. Each initial pH was adjusted by using a sulfuric acid. Required $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ added in solution and Fenton reaction started up adding H_2O_2 . Effluent were collected at a predetermined reaction time. Potential reaction of hydroxyl radical in the collected effluent was quenched by using 6N NaOH and 10% Na_2SO_3 .

Analytical methods. All chemicals were purchased from MERK and ALDRICH compony.

The concentration of PCP was determinated, by using a gas chromatograph(philips UP 4410) with FID and packed column 1% sp 1240 (10). Temperature program was 80°C at injection and immediate 8°C /min to 150°C. The sample was acidified by H_2SO_4 and extracted with methylen chloride. COD and chloride ion analyzed according to standard methods (10). Dissolved oxygen measured by orion 420A DO meter. The UV absorbance was measured at 215 nm. UV absorbance is reported as undiluted extract, thus it is indicative of the total phenolic compound concentration(11).TOC(Total Organic Carbon)was measured with a TOC analyser (shimatso TOC-VCPN).

Results

Figure 1 shows the PCP degradation by Fenton reagent in different pH. It could be observed that pH significantly influenced the degradation of PCP.

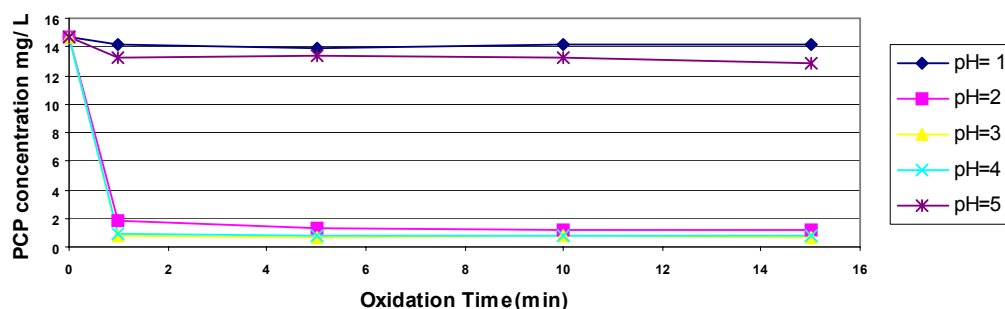


Fig. 1 - PCP Decrease by Fenton oxidation in different pH

Figure 2 shows the dissolved oxygen changes after Fenton oxidation, and it is showed that dissolved oxygen level is constant in pH=1, and DO increased in pH=3.

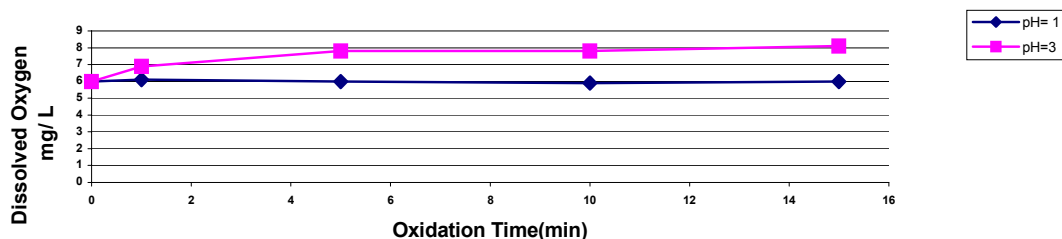


Fig. 2 - Dissolved oxygen changes after Fenton oxidation in different pH

Figure 3 shows the Fenton reagent efficiency for PCP degradation in different Fe^{2+} concentration. The degradation of PCP increased to increasing Fe^{2+} concentration.

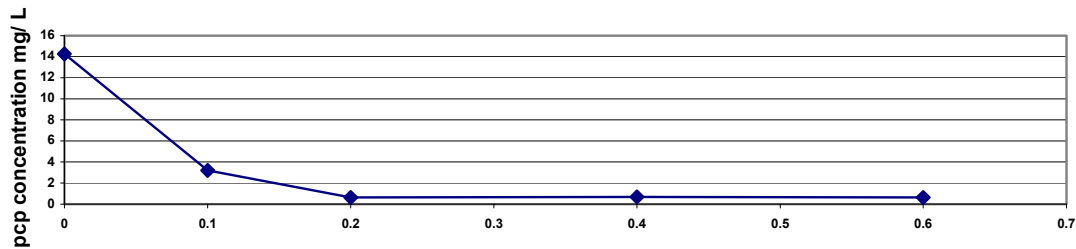


Fig.3 - PCP Concentration in different [Fe] & 15min oxidation Time , $H_2O_2=0.6mM$, $pH=3$

Figure 4 shows the PCP concentration in different H_2O_2 doses, and oxidation time. It is observed that H_2O_2 doses significantly influenced the degradation of PCP.

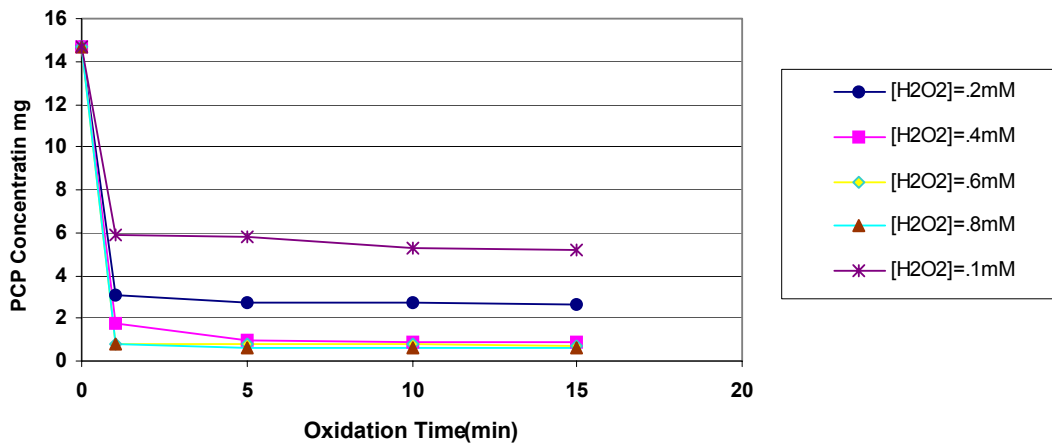


Fig. 4 - PCP Concentration in different [H2O2]&Oxidation Time
 $pH=3$, $[Fe^{2+}]=0.2mM$

To study scavenging effects of PCP by product, long term PCP degradation (10hr) performed. Results from long term PCP degradation are given in table 1.

Table 1: Results from long term degradation of PCP by Fenton reaction

No	[H2O2] mM	[PCP] mg/L	[Cl ⁻] mg/L	COD mg/L	TOC mg/L	pH
1	0	14.6	0	11.5	4.2	3
2	0.05	8.2	1.7	10.7	4.3	2.95
3	0.1	4.7	2.3	10.5	4	2.91
4	0.2	2.1	4	11	3.8	2.85
5	0.4	1.1	5.7	9.4	3.5	2.84
6	0.6	0.9	6.1	9	3.4	2.82

Figure 5 shows the UV₂₁₅ absorbance changes after Fenton reaction, as total phenolic compound. It is observed that UV₂₁₅ absorbance decreases by increasing of oxidation time.

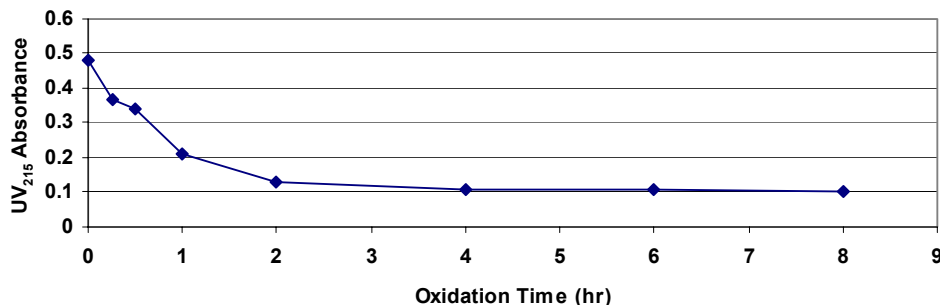


Fig. 5 - UV₂₁₅ absorbance as total phenolic compound at the various reaction times
pH = 3, [H₂O₂]=0.6mM, [Fe²⁺]=0.2mM, [PCP]₀=0.055mM

Discussion

As shown in Fig.1 pH significantly influenced the degradation of PCP. The degradation progressed at higher rate at pH 2-4. This supports the results reported in previous studies (9, 11). At the pH below 2 (pH=1) PCP was not degraded by fenton reagent. It is showed in Fig.2, that hydrogen peroxide at this pH was not decomposed by ferrous ion, as proved by constant oxygen level. If hydrogen peroxide decomposes by Fe²⁺ at pH=3, the dissolved oxygen level would increase. Thus there would be no H₂O₂ decomposition, no hydroxyl radical generation and no PCP degradation. When the pH reaches to 4 and above, the degradation rate significantly decreases. In this pH, the dissolved fraction of iron decreases, also the oxidation potential of OH radical decreases with increasing pH (12). The degradation of PCP increased to increasing Fe²⁺ concentration, (Fig.3). But increasing of ferrous ion above 0.2mM does not have significant effects on PCP degradation, however this result is valid only for this concentration of H₂O₂, because the oxidation of ferrous iron is dependent on the hydrogen peroxide dose and at higher hydrogen peroxide dose, the more ferrous iron oxidized, and hydroxyl radical generation will be improved. As shown in Fig.4, H₂O₂ doses significantly influenced the degradation of PCP, It was observed that at the H₂O₂ doses 0.2mM, 79% of PCP was degraded in the first two minutes after the hydrogen peroxide was dosed. With increasing the H₂O₂ dose to 0.4-0.8mM, it could be observed that PCP concentration reduced more than 95% within the first minute after H₂O₂ was dosed into reactor. And there was no significant difference between 0.4, 0.6 and 0.8mM. It was resulted that in the hydrogen peroxide dose below 0.2 mM, partial oxidation of ferrous ion was occurred and in the hydrogen peroxide dose above 0.4 mM ferrous ion completely oxidized and the maximum hydroxyl radical generated. Very high initial reaction rate was observed and reaction achieved completion in first few

minutes (i.e. maximum PCP reduction achieved in first minutes of reaction). In the initial phase of reaction (first two minutes) the rate of PCP degradation was according to first order kinetics and the kinetics constant for pH = 3, [H₂O₂]=0.6mM, [Fe²⁺]=0.2mM and [PCP]₀ =0.055 was 0.0268 (S⁻¹). To study scavenging effects of PCP by product, long term PCP degradation (10 hr) performed and many important parameter investigated (table 1). Since chloride ion was produced as PCP degradation by product, and it was OH^o radical scavenger, its effect on the PCP degradation was investigated. The chloride ion concentration increasing after H₂O₂ was dosed into reactor, however the observed dechlorination never reach the theoretical maximum yield of 5 moles of chloride per mol of PCP degraded, may be that the chloride generation might also depend on the strength of oxidation, although only one chloride is necessary to convert PCP to an intermediate one, and dechlorination of this intermediate can be same as PCP. Chloride ion effects were reported to become a concern normally at concentration greater than 28mM or (1000mg/L)(10), in our work the chloride ion effect was negligible. Scavenging effects of PCP by products on the degradation of PCP were not very important at low oxidant doses, but in high H₂O₂ doses scavenging effects were important. This is due to the fact that the concentration of the PCP by products (that are not mineralized to CO₂, as indicated by TOC and COD analysis even in high dose of H₂O₂) effectively create major factor for the scavenging effects, the less PCP degradation, the less PCP by product and the less scavenging effects and higher PCP degradation, the more PCP by products and the stronger scavenging effects. The changes in pH achieved due to different H₂O₂ doses after a reaction time of 10 h. It showed that pH decreasing is about 0.18 in H₂O₂ doses 0.6mM, this change in pH could have been caused by acidic organic

intermediate, probably such as oxalic, acetic and maleic acid. We prepared wastewater by adding only PCP, therefore the determination of removal of (TOC) or (COD) indicated the mineralization of PCP. Table 1 shows the concentration of TOC and COD during Fenton's oxidation of PCP. It is found that TOC and COD reduction is negligible even at highest H_2O_2 dose (only 20% and 30% respectively), that indicates mineralization of PCP does not occur in this condition of reaction. As shown in Fig.5, UV₂₁₅ absorbance decreased with increasing of oxidation time and it could be concluded that total phenolic compound reduced and nonphenolic intermediate may be generated (11). Final results from this study showed that Fenton's oxidation is a successful mean to degradation of PCP in aqueous solution, but mineralization of PCP by Fenton reagent requires to high dose of oxidant and long time of oxidation. pH, H_2O_2/Fe , H_2O_2/PCP , are the most important factor for PCP degradation with Fenton reagent and optimum pH=3, $H_2O_2/Fe^{2+}=3$, $H_2O_2/PCP=8$ were resulted. Fenton's oxidation of PCP is a fast reaction as reaction completed in the first few minutes after the reaction started, and PCP reduction about 95% achieved but mineralization did not occur. In the initial phase degradation of PCP follows first order kinetics. Chloride ion, pH and UV₂₁₅ absorbance analysis showed that generated intermediate have less chlorinated natures, acidic properties and nonphenolic structure, and it is concluded that these by products can become more biodegradable and less toxic.

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