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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 moste effective process for degradation of persistant 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 worke degradation of pentachlorophenol in aqueous solution with fenton reagent (H_2O_2 +Ferrous ion)was studied. The experiment was done in batch mode, and the initial concentration of PCP was 0.055mM, in pH=3, H_2O_2=0.6mM, Fe=0.2mM, more than 95% of PCP was degraded in first minute after the reaction was started.Therefor this reaction is very fast and in the initial phase degredation of PCP follows first order kinetics and kinetict constant (K) was 0.026 (S^{-1}). Chloride ion generatation as PCP degredation by product was investigated ,and it was found that the scavenging effect of chloride is negligible. pH and UV_{215} 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 UV_{215} absorbance decreasees from 0.48 to 0.1, therefor 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 intermadiate is important in highe doses of H_2O_2.

keywords: *Oxidation, Fenton reagent, Pentachlorophenol, AOP*

Introduction

Pentachlorophenol is a common water contaminant, released into environment as a results 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 interupt formation of ATP and lead to the death of all forms of life (4). Because of its highly chlorinated nature, PCP is a toxic [1]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 requring 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 persistant 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 improved the economy of single process. Fenton reagent is a mixture of H_2O_2 and ferrous iron, wich generates hydroxyl radical according to below reaction (9):

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^o + OH^-$

The ferrous iron initiates and catalizes the decomposition of H_2O_2, 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, H_2O_2/Fe, H_2O_2/PCP, oxidation time and determination of optimume 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 cylandrical 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 controled by orion pH meter 420 A modle. Each test began with 500 ml of PCP wastewater, that made of 2 times distillated 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 $FeSO_4.7H_2O$ added in solution and Fenton reaction started up adding H_2O_2. Effluent were colected at a predeterminated 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 80ºC at injection and immediate 8ºC /min to 150ºC. 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.

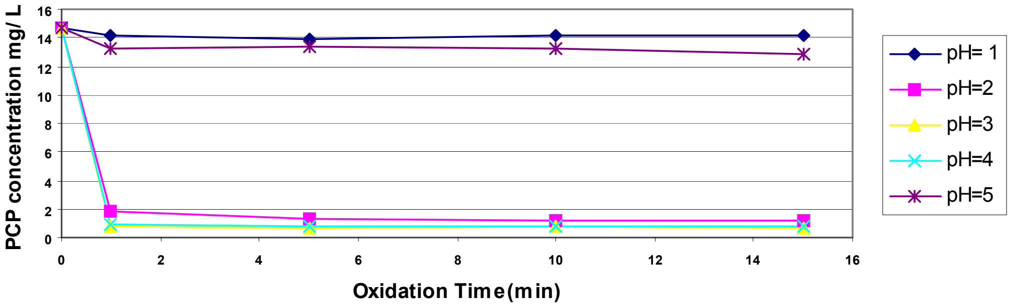

Fig. 1 - PCP Decrease by Fenton oxidation in different pH

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.

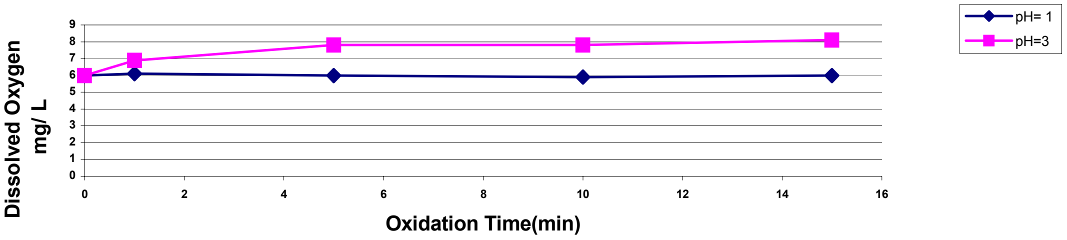

Fig. 2 - Dissolved oxygen changes after Fenton oxidation in different pH

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.

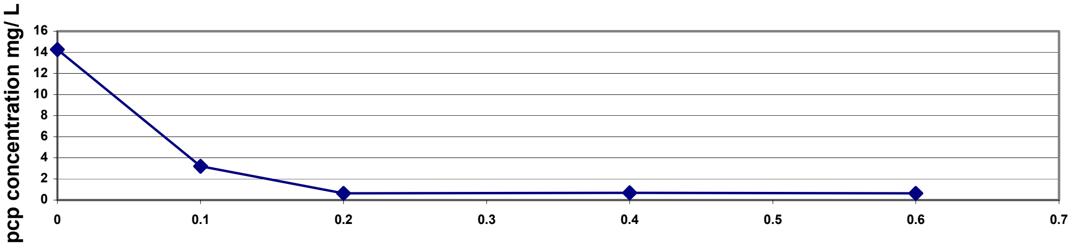

Fig.3 - PCP Concentration in different [Fe] & 15min oxidation Time , H_2O_2=0.6mM , PH=3

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.

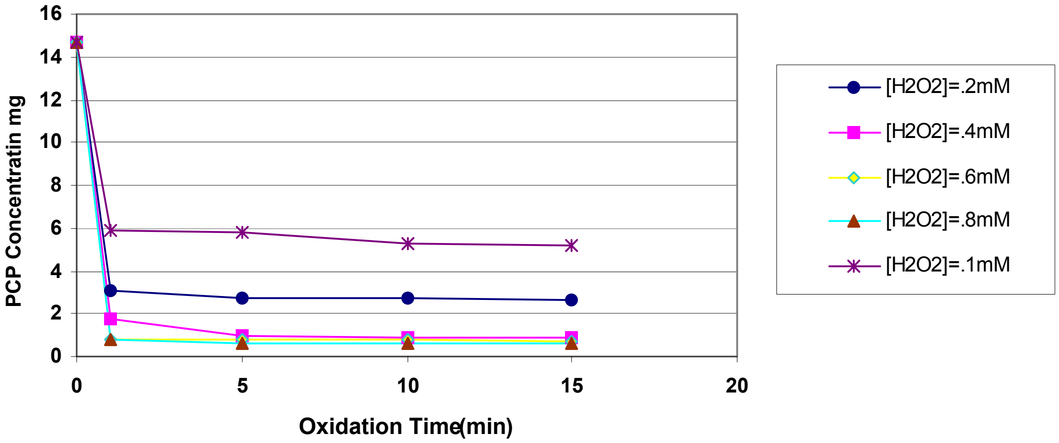

Fig. 4 - PCP Concentration in different [H2O2]&Oxidation Time
pH=3, [Fe^{++}]=0.2mM

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 theUV215 absorbance changes after Fenton reaction, as total phenolic compound. It is observed that UV215 absorbance decreases by increesing of oxidation time.

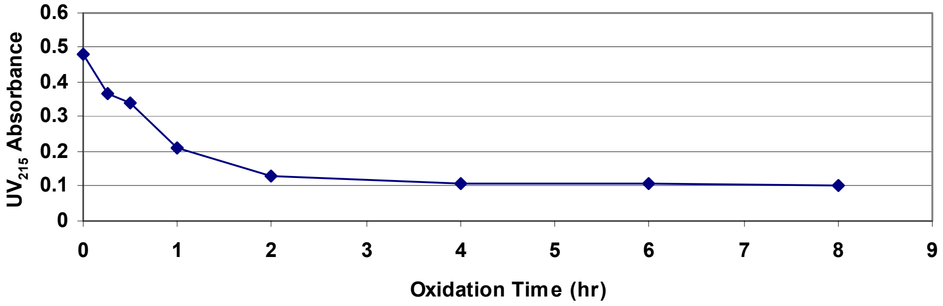

Fig. 5 - UV_{215} absorbance as total phenolic compound at the varoius reaction times pH = 3, [H2O2]=0.6mM,[Fe2+]=0.2mM,[pcp]0=0.055mM

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 degredaded 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 hyrogen peroxide decomposes by Fe^{2+} at pH=3, the dissolved oxygen level would increas. Thus there would be no H_2O_2 decomposition, no hydroxyl radical generation and no PCP degredation. When the pH reaches to 4 and above, the degredation 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 Fe^{2+} concentration, (Fig.3). But increasing of ferrous ion above 0.2mM does not have significantly effects on PCP degradation, however this result is valid only for this concentration of H_2O_2, because the oxidation of ferrous iron is dependet on the hydrogen peroxid dose and at higher hydrogen peroxid dose, the more ferrous iron oxidized, and hydroxyl radical generation will be improved. As shown in Fig.4, H_2O_2 doses significantly influenced the degradation of PCP, It was observed that at the H_2O_2 doses 0.2mM, 79% of PCP was degraded in the first two minutes after the hydrogen peroxide was dosed. With increasing the H_2O_2 dose to 0.4-0.8mM, it could be observed that PCP concentration reduced more than 95% within the first minute after H_2O_2 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 peroxid dose below o.2 mM, partial oxidation of ferrous ion was occurred and in the hydrogen peroxid dose above 0.4 mM ferrous ion completely oxidized and the maximume 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 degredation was according to first order kinetics and the kinetics constant for pH = 3, $[H_2O_2]$=0.6mM, $[Fe^{2+}]$=0.2mM and $[PCP]_0$ =0.055 was 0.0268 (S^{-1}). To study scavenging effects of PCP by product, long term PCP degredation (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 chlorid ion concentration increasing after H_2O_2 was dosed into reactor, however the observed dechlorination never reach the theoretical maximume yield of 5 moles of chloride per mol of PCP degraded, may be that the chlorid generation might also depend on the strength of oxidation, althoug only one chloride is necessary to convert PCP to a 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 H_2O_2 doses scavenging effects were important. This is due to the fact that the concentration of the PCP by products (that are not mineralized to CO_2, as indicated by TOC and COD analysis even in highe dose of H_2O_2) effectively create major factor for the scavenging effects, the less PCP degredation, 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 H_2O_2 doses after a reactin time of 10 h. It showed that pH decreasing is about 0.18 in H_2O_2 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, therefor 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 dose not occure 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 highe 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 optimume 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 occure. In the initial phase degredation of PCP follows first order kinetics Chloride ion, pH and uv_{215} 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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