

## Characteristics of Fenton's Oxidation of 2, 4, 6 Trichlorophenol

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### ABSTRACT

2, 4, 6 trichlorophenol (TCP) is one of the most toxic chlorophenols which is very difficult to biodegradation. Advanced Oxidation Processes (AOPs) is one of the most effective processes for degradation of persistent compounds. Since the mineralization of recalcitrant compound by AOPs often requires long reaction time and strong doses of oxidant, the combination of this process with biological one, is considered as an efficient and economic method. In this work degradation of 2, 4, 6 trichlorophenol 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 TCP was 0.60mM. In pH=3,  $H_2O_2$ =1.8mM, Fe=0.6mM, more than 99% of TCP was degraded in 10 minutes after the reaction was started. Chloride ion generation as TCP degradation 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 had the less chlorinated nature, acidic properties and nonphenolic structure. Chloride ion increases from 0 mg/L to 40 mg/L, pH decreased from 3 to 2.7 and  $UV_{215}$  absorbance decreased from 3.2 to 0.6, therefore it can be resulted that their biodegradability modified and their recalcitrance reduced. COD analysis indicated that TCP did not mineralize and in  $H_2O_2$ /TCP = 3 and oxidation time of 1 h, COD reduction was only 37%.

**Keywords:** *Oxidation, Fenton reagent, 2, 4, 6 trichlorophenol*

### INTRODUCTION

2,4,6 Trichlorophenol 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 (AWWA, 1990; Marie paul otte et al., 1999). TCP 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 (Pringer and Bhattacharya, 1999; Farrokhi et al., 2003). Because of its highly chlorinated nature, TCP 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 (Mueller et al., 1993; Marie paul otte et al., 1999; Pringer and Bhattacharya, 1999), but the biodegradation of TCP is often slow, for example aerobic degradation of TCP requiring sometimes a treatment time of several weeks and anaerobic dechlorination and degradation of TCP requires treatment time of several months (Hendriksen and Ahring, 1991). For this reason, there has been increased interest in alternative treatment methods. AOPs can achieve complete mineralization of different persistent compound (Binle and Yamaguchi, 1998). However mineralization of contaminant

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by AOPs often requires long time of reaction and strong doses of oxidant, often less reactive intermediates are produced that inhibit the degradation of parent compound. Once the recalcitrant compounds have been transformed by means of the chemical treatment, their properties including biodegradability are modified. Often the intermediates have reduced recalcitrance with respect to the parent compound (Marco et al., 1997). 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  $\text{H}_2\text{O}_2$  and ferrous iron, which generates hydroxyl radical according to the following reaction (Kitis et al., 1999):



The ferrous iron initiates and catalyzes the decomposition of  $\text{H}_2\text{O}_2$ , resulting in the generation of hydroxyl radical.

The generation of hydroxyl radical involves a complete reaction sequence in an aqueous solution (Kitis et al., 1999). The main goal of this research was examination of feasibility and efficiency of Fenton reagent for degradation of TCP wastewater and determination of optimum conditions of Fenton's oxidation for jointing with biological treatment.

## **MATERIALS AND METHODS**

All reactions 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 model.

Each test began with 500 ml of TCP wastewater with 2 times distilled and deionized water. The initial concentration of TCP wastewater was prepared as 120 mg/L (0.60mM.) Each initial pH was adjusted by using sulfuric acid.

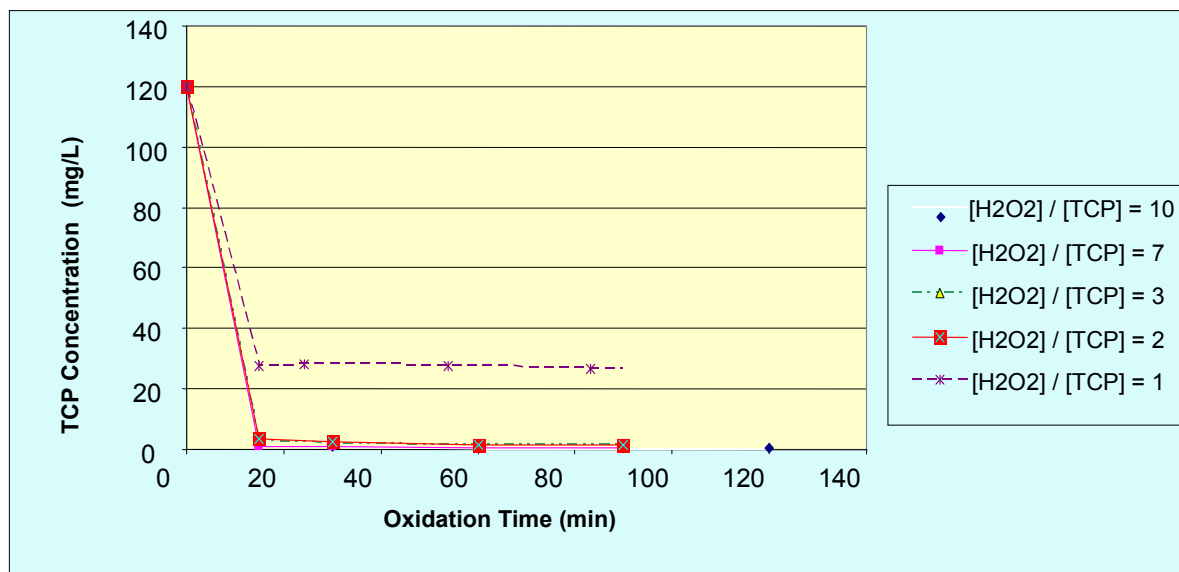
Required  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added in to the solution and Fenton reaction was started up adding  $\text{H}_2\text{O}_2$ . Effluent was collected at a predetermined reaction time. Potential reaction of hydroxyl radical in the collected effluent was quenched by using 6N NaOH and 10%  $\text{Na}_2\text{SO}_3$ . For the study on Fenton oxidation of TCP in different  $\text{H}_2\text{O}_2$  / TCP ratios, many parameters such as TCP concentration, COD, pH, chloride ion and UV215 absorbance in 72 runs were evaluated.

### **Analytical methods**

All chemicals were purchased from MERK and ALDRICH Company. The purity of chemicals were 98% and higher (except for  $\text{H}_2\text{O}_2$  which was 33%). The concentration of TCP was determined, using a gas chromatograph (Philips UP 4410) with FID and packed column 1% sp 1240. The initial temperature was 80°C at injection and immediately a rate of 8°C /min temperature increase was applied up to 150°C. The sample was acidified by  $\text{H}_2\text{SO}_4$  and extracted with methylen chloride. The chemical oxygen demand (COD) was measured to investigate the mineralization of TCP by Fenton reagent. Chloride ion and UV absorbance at 215 nm analyses were performed on some samples to characterize the reaction by products and study the scavenging effect of chloride ion. COD and chloride ion were analyzed according to standard, 5220-C and 4500-B methods, respectively (APHA, AWWA, WEF, 1995). 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 (Field and Lettina, 1991).

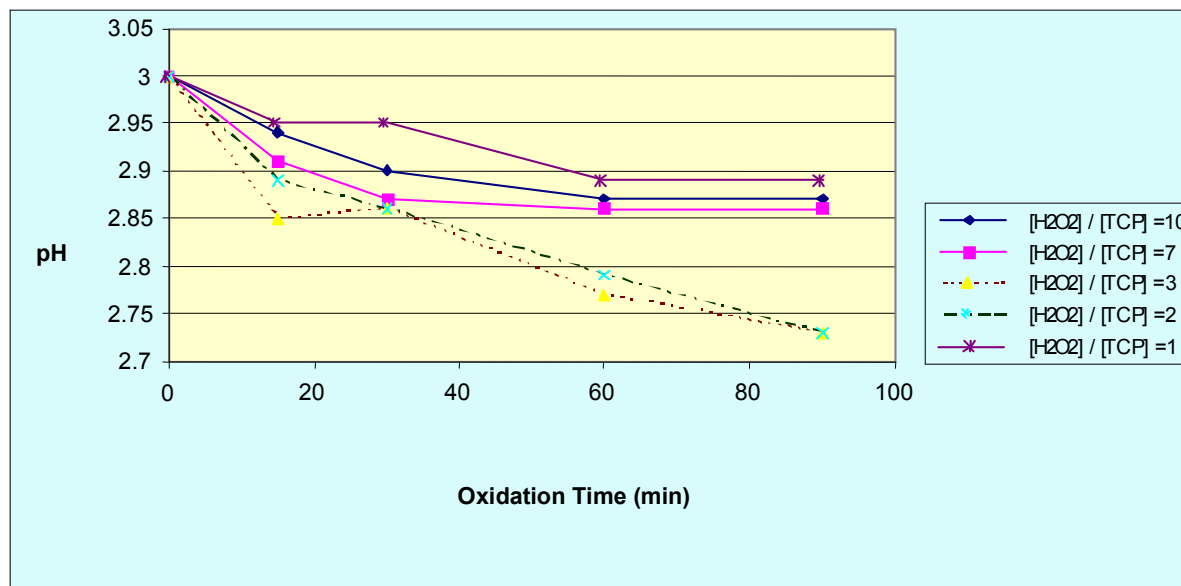
## **RESULTS**

The degradation of TCP by Fenton reagent in different  $\text{H}_2\text{O}_2$ /TCP ratios and oxidation time is presented in Fig.1. It may be observed that  $\text{H}_2\text{O}_2$  doses significantly influenced the degradation of TCP.



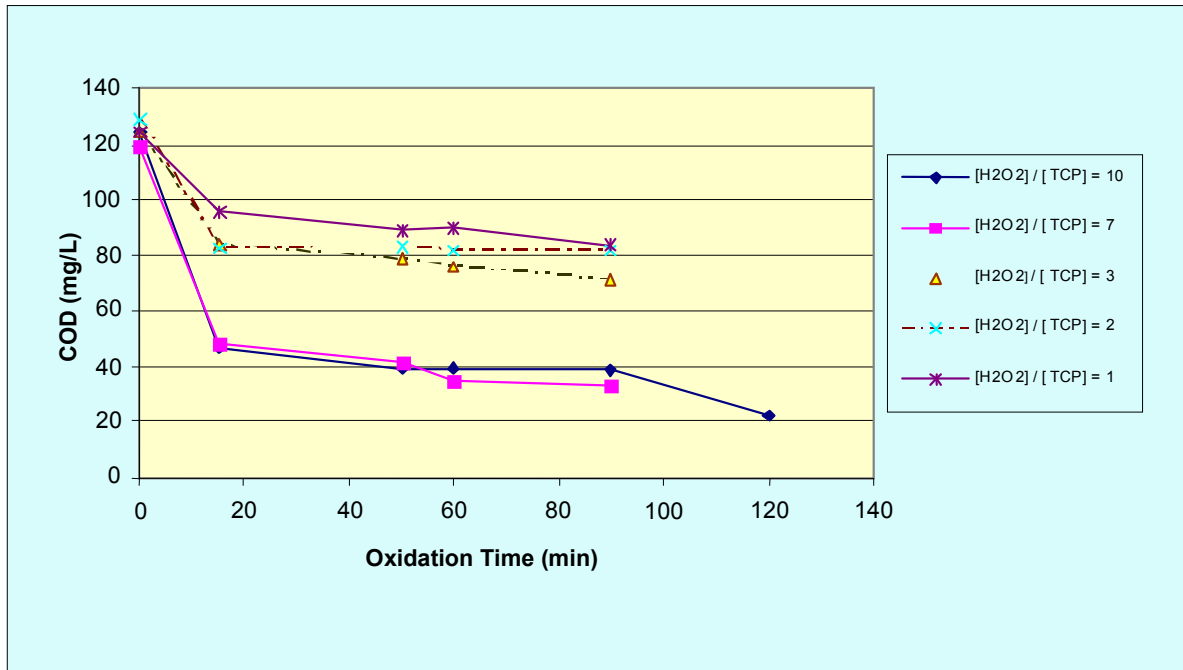
**Fig. 1:** TCP concentration in different  $H_2O_2$ /TCP and oxidation time

pH was measured along the experiment, the TCP wastewater was adjusted to pH= 3 at the beginning of the experiment. After the completion of reaction a pH reduction was observed (Fig.2).



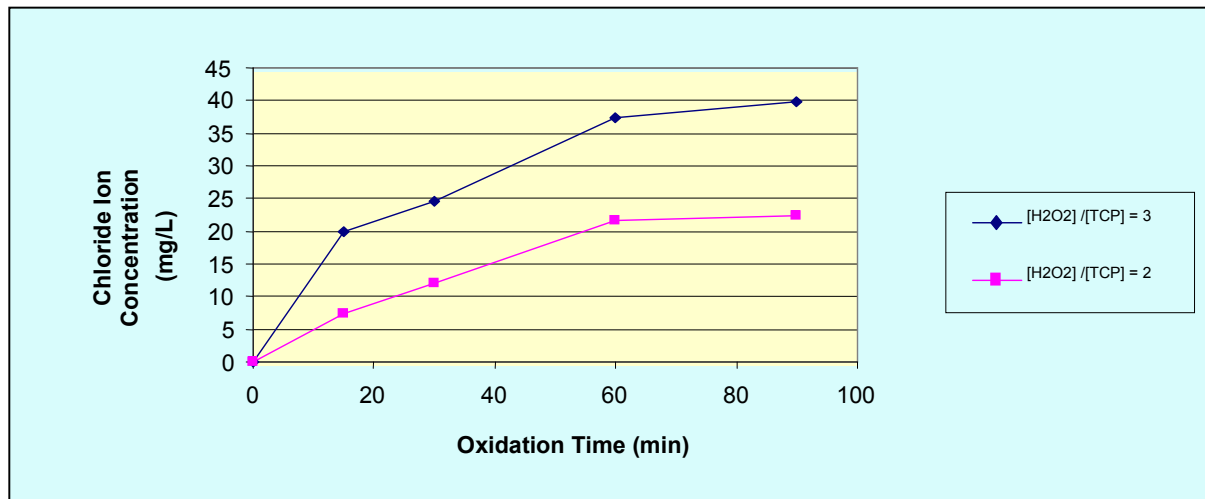
**Fig. 2:** pH changes after Fenton oxidation in different  $H_2O_2$ /TCP and oxidation time

Fig .3 shows the COD reduction in different  $H_2O_2$ /TCP ratios, and oxidation time. It could be observed that maximum COD reduction occurred in  $H_2O_2$ /TCP =10 and oxidation time = 2 h.



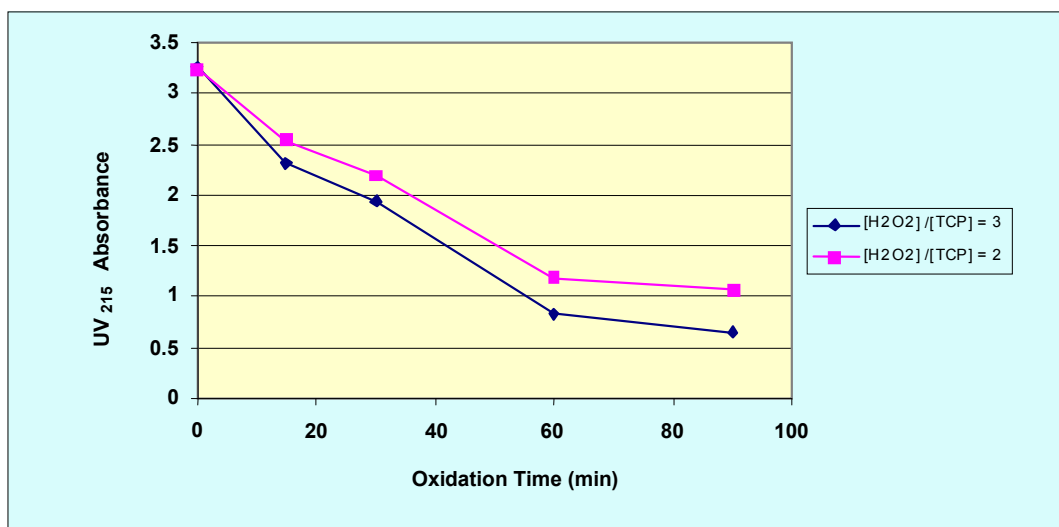
**Fig. 3:** COD reduction after Fenton oxidation in different  $\text{H}_2\text{O}_2/\text{TCP}$  and oxidation time

The production of chloride ion as a function of oxidation achieved by different  $\text{H}_2\text{O}_2/\text{TCP}$  ratios is shown in Fig.4. It is observed that maximum chloride ion generation occurred in  $\text{H}_2\text{O}_2/\text{TCP} = 3$  and oxidation time = 1 h.



**Fig. 4:** Chloride ion production in Fenton oxidation in different  $\text{H}_2\text{O}_2/\text{TCP}$  and oxidation time

Fig.5 shows the  $\text{UV}_{215}$  absorbance changes after Fenton reaction, as total phenolic compound. It is observed that  $\text{UV}_{215}$  absorbance decreased by increasing of oxidation time and the maximum decrease occurred in  $\text{H}_2\text{O}_2/\text{TCP}=3$  and oxidation time = 1 h.



**Fig. 5:** UV<sub>215</sub> absorbance as total phenolic compound in Fenton oxidation in different H<sub>2</sub>O<sub>2</sub>/TCP and oxidation time

## DISCUSSION

The results from a previous study (Farrokhi et al., 2003) showed that the optimum pH and H<sub>2</sub>O<sub>2</sub> / Fe<sup>2+</sup> for degradation of chlorophenols by Fenton reagent are 2.5-3 and 3, respectively, because the oxidation of ferrous iron is dependent on the hydrogen peroxide dose and at higher hydrogen peroxide doses, the more ferrous iron was oxidized, and hydroxyl radical generation would be improved. As shown in Fig.1, H<sub>2</sub>O<sub>2</sub> doses significantly influenced the degradation of TCP. It is observed that at H<sub>2</sub>O<sub>2</sub> / TCP =1, 70% of TCP was degraded in the first ten minutes after the hydrogen peroxide was dosed. With increasing the H<sub>2</sub>O<sub>2</sub> / TCP to 3-10, it could be observed that TCP concentration was reduced more than 99% within ten minutes after H<sub>2</sub>O<sub>2</sub> was dosed into the reactor. There was no significant difference between 2, 3, 7 and 10 (ANOVA test,  $P=0.005$ ).

It was resulted that in low hydrogen peroxide doses, partial oxidation of ferrous ion was occurred and in high hydrogen peroxide doses ferrous ion was completely oxidized and the

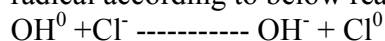
maximum hydroxyl radical was generated. The more hydroxyl radical generation, the more oxidation efficiency. The pH reduction in all experiments was observed, as shown in Fig. 2. After the reaction, a pH reduction of about 0.3 units in H<sub>2</sub>O<sub>2</sub> / TCP=3 after 1hr reaction time was observed. This change in pH could have been caused by more acidic organic intermediates resulting from the degradation of TCP, probably such as oxalic, acetic and maleic acid. Additionally, the effect on the acid-base equilibrium due to reactions in which inorganic compounds producing weak acids (such as H<sub>2</sub>O<sub>2</sub>) can be expected.

In this study the wastewater was prepared by adding only TCP, therefore the determination of removal of (COD) indicated the mineralization of TCP. Fig.3 shows the COD reduction during Fenton's oxidation of TCP. In the H<sub>2</sub>O<sub>2</sub>/TCP less than 3 and after 1hr oxidation time, the COD reduction was only <37% and with increasing H<sub>2</sub>O<sub>2</sub>/TCP ratio above 7, the COD removal efficiency improved and increased to more than 70%. This indicated that mineralization (conversion of organic carbon to CO<sub>2</sub>) did not occur at H<sub>2</sub>O<sub>2</sub>/TCP ratio below 3.

Despite the almost complete degradation of TCP and it is concluded that organic intermediates generated. In contrast, previous reports indicated that strong AOP oxidation of many organic substrates lead to CO<sub>2</sub> production (Seldak, 1991; Farrokhi et al., 2003).

For study on biodegradability enhancement of TCP by Fenton's reagent, the H<sub>2</sub>O<sub>2</sub> / TCP = 1 was rejected because in this case, the residual TCP in wastewater after Fenton oxidation was more than 30 mg/L that is toxic for biological processes. H<sub>2</sub>O<sub>2</sub> / TCP ratio above 3, 7 and 10 were rejected too because the COD reduction in these ratios was more than 70%, thus organic availability for microbial growth is not enough, therefore the next experiment was performed H<sub>2</sub>O<sub>2</sub> / TCP = 3 and 2.

Chloride ions are reactive with hydroxyl free radicals; the reaction generates the chloride free radical according to below reaction.



The Chloride free radical is a very reactive species that can chlorinate organic compounds. Chloride ions can exert other effects by forming complexes with ferric ions, and these can significantly reduce the effectiveness in Fenton system. Because chloride is itself a production of TCP degradation due to Fenton reagent, its effect on the TCP degradation was investigated. As shown in Fig.4, the chloride ion concentration increased after H<sub>2</sub>O<sub>2</sub> was dosed into the reactor, however the observed dechlorination never reached to the theoretical maximum yield of 3 moles of chloride per mol of TCP degraded.

Chloride ion effects were reported to become a concern normally at concentration greater than 28mM or 1000mg/L (Kitis et al., 1999). In our work the chloride ion effect was negligible, because the maximum chloride production was 40mg/L. The production of chloride ions in H<sub>2</sub>O<sub>2</sub> / TCP=3 was more than H<sub>2</sub>O<sub>2</sub> / TCP=2 (t-test  $P=0.005$ ).

The maximum chloride ion was produced in H<sub>2</sub>O<sub>2</sub> / TCP=3 after 1h oxidation time and it was concluded that generated intermediate in

this condition had less chlorinated nature and the less chlorinated nature the less toxicity and the more biodegradability.

As shown in Fig.5, UV<sub>215</sub> absorbance decreased with increasing of oxidation time and the decreasing of UV<sub>215</sub> absorbance in H<sub>2</sub>O<sub>2</sub> / TCP=3 was more than with H<sub>2</sub>O<sub>2</sub> / TCP=2 (t-test  $P=0.01$ ). It could be concluded that total phenolic compound was reduced and nonphenolic intermediate may be generated (Field and Lettina, 1991).

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