ADVANCED CHEMICAL OXIDATION OF 2,4,6-TRICHLOROPHENOL
BY USING FENTON'S REAGENT
- DECHLORINATION AND TOXICITY REDUCTION

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ABSTRACT

Chlorinated phenols are priority pollutants, regulated by stringent discharge limits. The presence of chlorine increases the toxicity of these phenolic compounds and decreases their biodegradability. This study is to examine the removal of a priority chlorinated aromatic pollutant, 2,4,6-trichlorophenol (TCP), in aqueous solution by using Fenton’s Reagent (a mixture of hydrogen peroxide and ferrous iron catalyst), in terms of dechlorination and toxicity reduction.

Test results indicate that the higher the molar ratio of H₂O₂ to TCP, the faster the release of chloride from TCP. However, the chloride released in all runs eventually approach the
same level of theoretical chloride concentration, 26.62 mg/L. This process of dechlorination is essentially complete in two hours. TCP appears to be transformed to organic intermediates in the course of dechlorination and oxidation.

In terms of Microtox EC_{50}, significant toxicity reduction takes place as a result of the advanced oxidation by Fenton's Reagent; and amounts of oxidant and catalyst used appear to have some effects on the extent of toxicity reduction.

KEY WORDS - Fenton’s reagent; hydrogen peroxide; 2,4,6-trichlorophenol; dechlorination; advanced oxidation; toxicity reduction.

INTRODUCTION

Many industrial wastewaters contain chemical species that are very difficult to treat biologically. The microorganisms in a treatment plant may respond to these chemicals in one of the following ways:

- substantial reduction in biological activity, leading to very little treatment and degradation of the wastes containing the species;

- no biological activity, leading to no treatment and destruction of the waste; or

- decay and wash out due to toxicity of the particular chemical species.

Industrial wastes containing such chemicals need pretreatment prior to their discharge into the treatment plant. The purpose of the pretreatment is to degrade the 'difficult-to-treat' chemical species to some other form(s) that is (are) less toxic and also acceptable to the microorganisms for biotreatment. Advanced oxidation has been widely accepted by industries as an effective means of pretreatment of hazardous chemicals contained in aqueous phase. Two most commonly used methods of advanced oxidative treatment use UV-peroxide and ozone as the treatment agents. Application of Fenton's Reagent as the oxidant is relatively new, and is presently limited to laboratory scale studies only.

Fenton's Reagent is a dilute solution of ferrous ions and hydrogen peroxide in water. Originally reported by H. J. H. Fenton (1894), this reagent was very extensively studied by Merz and Waters (1947) for its oxidation kinetics with various organic substrates. The mechanism of reactions was originally proposed by Haber and Weiss (1934), as follows:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^+ + \text{OH}^- \]

The hydroxyl radical (OH^+) is a highly energized chemical species that attacks any organic substrate as an oxidant according to the following reaction steps, as proposed by Merz and Waters (1947):
OH' + H - R -------------> R' + H₂O

R' + H₂O₂ ----------------> R - OH + OH'

This suggests initiation of a set of chain reactions whereby the hydroxyl radicals, the active reactant, are regenerated to propagate further oxidation of an organic substrate. Since then there have been numerous studies on interpretation of mechanisms for oxidative degradation of various aliphatic and aromatic substrates by hydroxyl radicals. A few of the notable studies have been performed by the research group of Walling (1974) at the University of Utah. Walling and Kato (1971) proposed that the active organic radical R' regenerates ferrous from ferric ion as follows:

R' + Fe³⁺ -------------> R' + Fe²⁺

The interest in Fenton's Reagent has increased significantly in the recent past, because of its strong oxidizing ability, which has made it a candidate for application in the emerging field of industrial and hazardous wastes remediation. The first such investigation was undertaken by Eisenhaur (1964) who studied degradation of phenolic wastewaters - synthetic, as well as actual, from various sources. Phenol was totally removed from the synthetic wastewater within five minutes, using a molar ratio of H₂O₂ : Fe²⁺ : Phenol = 3:1:1. However, a significantly higher quantity of hydrogen peroxide had to be used to remove phenol from stripped refinery waste. Very little removal was observed from steel mill waste.

Bowers, et. al (1987) evaluated the effectiveness of pretreatment of synthetic wastewaters containing 2,4-Dichlorophenol (DCP) and Dinitro-ortho-cresol by Fenton's Reagent on toxicity removal and subsequent biotreatability of these wastewaters. They observed toxicity improvement of the parent substrates by at least one order of magnitude, as indicated by the EC₅₀ value from the Microtox test.

Potter and Roth (1993) investigated the kinetics of oxidation of several mono- and dichlorinated isomers of phenol. The reaction conditions were maintained as follows:

\[
[\text{Substrate}]_0 = 5 \text{ mM; } [\text{H}_2\text{O}_2]_0 = 60 \text{ mM} \\
[\text{Fe}^{2+}]_0 = 0.09 \text{ mM; } \text{Temperature} = 22 - 25 ^\circ \text{C} \\
\text{pH} = 3.5 \text{ (maintained constant throughout the reactions)}
\]

For the monochlorophenols, they observed that at least 90% disappearance of the original substrates was complete within an hour of the start of the reactions. They also observed simultaneous release of chlorine atoms attached to the aromatic rings of chlorophenols.

The present paper reports the effects of advanced oxidation of 2,4,6-Trichlorophenol (TCP), in aqueous phase, by Fenton's Reagent. TCP is a RCRA listed hazardous waste (CAS Registry # 88-06-2). It represents two groups of toxic priority pollutants - an
aromatic ring compound, and also a chlorinated organic compound. It is a very commonly used industrial chemical, principally used as a biocide. It may also be found in petroleum refinery wastewaters. From these points of view, it is a good candidate for a study of its reaction with Fenton's Reagent, and the resultant reduction of toxicity.

EXPERIMENTAL DESIGN

Experiments were conducted in one-liter stirred batch reactors in a constant temperature room at 20°C. Six experiments were run between solutions of TCP and H₂O₂ (3% by weight) with various molar ratios of H₂O₂ to TCP. The various molar ratios of H₂O₂ to TCP are 11 to 1 (Run #A and #A1), 5.5 to 1 (Run #B and #E), and 2.75 to 1 (Run #C and #D). The ferrous ions to hydrogen peroxide ratios were also varied. The reaction conditions for the six runs were shown in Table 1. The initial concentration of TCP for runs #A, #A1, #B, and #C were 0.25 mM, whereas, those for runs #D and #E were 1 mM. The initial pH of mixtures was about 4.8 and no buffer was used to maintain constant pH. The chloride concentration and pH in the reactor were monitored on line through the entire experiment.

Table 1. Starting Conditions for the Various Test Run and Analytical Methods Followed

<table>
<thead>
<tr>
<th>Run#</th>
<th>Molar Ratio</th>
<th>Condition</th>
<th>Type of Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O₂</td>
<td>TCP</td>
<td>Fe²⁺</td>
</tr>
<tr>
<td>A</td>
<td>11</td>
<td>1</td>
<td>1.33</td>
</tr>
<tr>
<td>A1</td>
<td>11</td>
<td>1</td>
<td>1.33</td>
</tr>
<tr>
<td>B</td>
<td>5.5</td>
<td>1</td>
<td>0.66</td>
</tr>
<tr>
<td>C</td>
<td>2.75</td>
<td>1</td>
<td>0.33</td>
</tr>
<tr>
<td>D</td>
<td>2.75</td>
<td>1</td>
<td>0.17</td>
</tr>
<tr>
<td>E</td>
<td>5.5</td>
<td>1</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Samples were collected at regular intervals of time and preserved at 4°C after quenching immediately with appropriate amount of sodium thiosulfate for later analyses.

Analytical methods

The chloride concentration and pH measurement

Fenton's Reactions are done under acidic conditions, typically pH 2-6, with a pH between 3-4 considered optimum. Both pH and chloride concentrations were monitored simultaneously by using pH/ISE ion analyzer (ORION Model 720A) with a pH probe (ORION pH combination electrode) and a chloride electrode (ORION Chloride combination electrode Model 9617BN).

HPLC and GC/MS Analyses

The principal means of organic compounds identification was High Performance Liquid
Chromatography (HPLC) analyses. Results from the HPLC analyses were used to evaluate the intermediate peaks that appeared in the course of reaction, as well as to monitor the disappearance of TCP. It was attempted to identify the intermediate peaks appearing in HPLC by Gas Chromatography / Mass Spectrometry (GC/MS) analyses.

The HPLC conditions used to obtain the chromatograms in Figure 3 were as following:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPLC system</td>
<td>Hewlett-Packard HP 1050 Liquid Chromatography with ultraviolet absorbance detector</td>
</tr>
<tr>
<td>Column</td>
<td>Hypersil ODS, 5μm, 10 cm X 2.1 mm i.d. (HP 79916 OD Opt. 552)</td>
</tr>
<tr>
<td>Mobil Phase</td>
<td>Solvent A - 0.005 M KH₂SO₄ adjusted to pH 2.5 with H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Solvent B - Acetonitrile</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>0.5 mL / min.</td>
</tr>
<tr>
<td>Injection Volume</td>
<td>5 microL</td>
</tr>
<tr>
<td>Gradient</td>
<td>25 to 45% B in 3 mins., 45 to 65% B in 6 mins., 65 to 85% B in 9 mins. then to 100% B in 12 mins. and finally maintain 100% B in 15 mins.</td>
</tr>
<tr>
<td>Stop / Post time</td>
<td>15 mins. / 5 mins.</td>
</tr>
<tr>
<td>Detection</td>
<td>Wavelength / Bandwidth: 295 nm / 5 nm</td>
</tr>
</tbody>
</table>

The GC / MS conditions used to obtain the chromatograms and spectra were as following:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC / MS system</td>
<td>Hewlett-Packard 5996</td>
</tr>
<tr>
<td>Data system</td>
<td>RTE-6</td>
</tr>
<tr>
<td>Column</td>
<td>J &amp; W; DB-5MS, 30 meters, ID 0.32 mm; Film: 0.25 microns</td>
</tr>
<tr>
<td>Oven Temp.</td>
<td>Starting at 100°C for 1 min. and then heated at 10°C / min. up to 285°C, held at 285°C for 12 mins.</td>
</tr>
<tr>
<td>Injection Volume</td>
<td>2 microL</td>
</tr>
<tr>
<td>Method</td>
<td>EPA 625 for Acid, Base, Neutral extractable organics analysis for wastewaters</td>
</tr>
</tbody>
</table>

**Chemical Oxygen Demand (COD) analysis**

For each run, the COD values were measured at the beginning and the end of the run. These samples were first digested in Hach COD reactor at 150°C for two hours after adding 2 mL of the sample to Hach COD reagent vials and then placing the vials containing digested samples in a spectrophotometer (Milton Roy Spectronic 20D). The absorbivities were read at 440 nm for low range or 600 nm for high range and compared against that for a solution of potassium acid phthalate of known concentration. The removal of COD is a strong evidence that oxidation was taking place in the experiment.
**Total Organic Carbon (TOC) analysis**

The TOC concentration were determined by injecting samples directly into a Dohrmann DC-80 Total Organic Carbon Analyzer. The TOC values were measured at the beginning and the end of the run.

**Toxicity Assay (Microtox Test)**

The real value of the pretreatment of a hazardous waste lies in its toxicity reduction, resulting in greater acceptance by the biomass in a biological treatment plant. In other words, inclusion of a pretreatment step can be justified if the pretreatment process results in reduction of toxicity for a hazardous waste. In the present research, the Microtox Test, a proprietary toxicity assay of Microbics Corporation, Carlsbad, CA, was employed to test for the toxicity reduction.

Microtox Test involves exposing the proprietary microtox reagent to the toxic substance that is being tested. The test reagent consists of living luminescent microorganisms (marine bacteria) grown and harvested under optimal conditions, and preserved in freeze dried condition. Before the test, Reference Water (also supplied by Microbics Corporation) is added to the test reagent which brings the microorganisms back to the active state from dormant state. This renders the test reagent ready for use.

The test compares the light output from the microorganisms, when they are exposed to a sample of the toxic substance, to the light output from the blank reagent that is not exposed to the toxic substance. The presence of the toxic substance in the reagent reduces the activity of the microorganisms, resulting in reduced light output. The result of the Microtox test is reported as EC$_{50}$, which means the concentration of the toxic substance at which the light output has reduced by 50% with respect to that of the blank. The EC$_{50}$ value decreases as toxicity increases, and increases as toxicity decreases.

The test procedure consists of exposing the test reagent to various dilutions of the toxic substance. The ratio of light reduced with respect to that for the blank reagent and the remaining light output is called Gamma value. The Gamma values are recorded and plotted against the corresponding concentration on a log-log scale. The concentration at which the reduction of light output is 50%, which means the EC$_{50}$ value for the substance, is interpolated from the plot. The Gamma value equals one. The EC$_{50}$ value for the substance is obtained by determination of the concentration corresponding to the Gamma value of 1 from interpolation of the above plot.

For the present research the products of Run #D, Run #E, and the original substrate (1 mM TCP solution), after adjusting the pH to 7, were tested for toxicity. In each case the solution was diluted to 5.63, 11.25, 22.50, and 45% strengths of the original solution. The diluent used was a solution of 2% sodium chloride in water, as required by the marine bacteria for osmotic pressure adjustment. Each of these samples was first equilibrated to a temperature of 15°C, and then exposed to the test reagent that contains the microorganisms.
Light output from each sample and the reagent blank were measured by the Microtox instrument, after 5 minutes of incubation. The built-in software automatically compared the outputs and printed out the Gamma versus concentration plots, and the 95% probable EC50 values for the products of Runs #D and #E, and also for 1 mM TCP solution. EC50 is normally determined after a 5 minutes contact between the sample and test reagent.

RESULTS AND DISCUSSION

The principal runs investigated were #A, #B, and #C. They differ from each other in terms of the molar ratios of hydrogen peroxide to TCP. The molar ratio of ferrous ions to hydrogen peroxide for these three runs was maintained constant at 0.12 to 1.

The following results were obtained.

(i) Release of Chloride Ions:

In every case the progress of reaction is accompanied by a release of organically bound chlorine atoms as free chloride ions in solution. The chloride ion concentrations, monitored with time by using a Chloride Ion Selective Electrode (ISE), as shown in Fig. 1. In each run, the concentration of free chloride ions asymptotically approaches the ultimate stoichiometric concentration of chlorine atoms in the 0.25 mM TCP solution, 26.62 mg/L. This suggests that regardless of the amount of peroxide used in relation to TCP, in two hours more than 99% of the organically bound chlorine atoms are released as inorganic chloride ions. The rate of dechlorination depends greatly upon the amount of hydrogen peroxide used. As in the case of pH change, the free chloride ion concentration for Run #A stabilizes fastest - within about 10 minutes of the start of the reaction. In case of Run #C, this happens after about 90 minutes of the start of the run.
(ii) pH:

The starting pH in every run was the pH of TCP solution itself. The reaction starts immediately with the addition of the required amounts of hydrogen peroxide and ferrous sulfate solutions. The start of reaction is indicated by a sharp drop of pH, which levels off as time progresses. As shown in Fig. 2, the rate of the drop of pH increases with increase in the molar ratio of hydrogen peroxide to TCP. At the maximum ratio (11:1 - Run #A) the pH drops down and stabilizes at 2.75 within the first five minutes of the reaction. For each of the runs #B and #C, within the first five minutes the pH drops sharply to an intermediate value, followed by a change at a slower rate over the course of about two hours. In all cases the pH ultimately stabilizes between 2.7 and 2.9. A possible explanation of the drop of pH is the formation of organic acids as a result of partial oxidation of the TCP.

![Figure 2. pH vs. Reaction Time in the Course of Fenton's Reaction](image)

(iii) TCP Disappearance:

As a result of oxidation and dechlorination, the TCP concentration gradually decreased with time. The TCP concentrations were monitored by analyzing samples withdrawn at regular intervals of time, and quenched by addition of sodium thiosulfate. As described in the 'Analytical Methods' section, the TCP analyses were done by HPLC technique. Figure 3 (a) shows the HPLC peak for pure TCP in 0.25 mM solution. Figure 3 (b), (c) and (d) show diminishing of TCP peak in Run #C after 10, 30 and 60 minutes. Figure 3 (e) and (f) show a total disappearance of TCP in Run #C after 90 minutes. It was also observed that for Run #A TCP totally disappears in 2 minutes, and for Run #B it takes about 10 minutes. Here also the speed of reaction follows the same trend as in the cases of pH and chloride ion concentration.
Figure 3. HPLC Chromatograms for Run#C Depicting Disappearance of 2,4,6-TCP with Time

(a) $T = 0$ mins.

(b) $T = 10$ mins.

(c) $T = 30$ mins.

(d) $T = 60$ mins.

(e) $T = 90$ mins.

(f) $T = 120$ mins.
(iv) **Product Identification:**

Some unknown peaks appeared in HPLC analyses, suggesting formation of organic byproducts. It was attempted to identify these products by using GC/MS technique after extraction into an organic phase following EPA Method 625 for semivolatiles. This attempt was not successful, probably because of the loss of active species from the sample during handling and extraction procedure. Some reaction products have not been identified conclusively by GC/MS at this time.

(v) **Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) Removal:**

The TOC and COD of the initial substrate, 0.25 mM solution of TCP, were measured to be 14.4 and 40 mg/L, respectively, while the corresponding theoretical values are 18 and 44 mg/L, respectively. For run #C, the TOC and COD were determined to be 14 and 20.3 mg/L respectively, after 150 minutes of reaction. This indicates that very little of the organic substrate is totally oxidized to carbon dioxide in two and a half hours, although close to 50% of it is partially oxidized to other organic compound(s).

All three reaction mixtures from runs #A, #B and #C, were left in the reactors, and after three months they were tested for TOC and COD again. The final TOC and COD results and percent reduction are reported in Table 2, which indicate that during this period of time at least about 85% of COD and 80% of TOC of the original substrate got totally oxidized.

**Table 2. Results of COD and TOC**

<table>
<thead>
<tr>
<th></th>
<th>COD (mg/L)</th>
<th>COD Removal (%)</th>
<th>TOC (mg/L)</th>
<th>TOC Removal (%)</th>
<th>COD / TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Value</td>
<td>44</td>
<td>n/a</td>
<td>18</td>
<td>n/a</td>
<td>2.4</td>
</tr>
<tr>
<td>Initial Value</td>
<td>40</td>
<td>n/a</td>
<td>14.4</td>
<td>n/a</td>
<td>2.8</td>
</tr>
<tr>
<td><strong>After Reaction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#C (after 150 mins.)</td>
<td>20.3</td>
<td>49.3</td>
<td>14.0</td>
<td>2.8</td>
<td>1.5</td>
</tr>
<tr>
<td>#A (after 3 months)</td>
<td>6.2</td>
<td>84.5</td>
<td>1.5</td>
<td>89.6</td>
<td>4.1</td>
</tr>
<tr>
<td>#B (after 3 months)</td>
<td>4.8</td>
<td>88.0</td>
<td>2.2</td>
<td>84.7</td>
<td>2.2</td>
</tr>
<tr>
<td>#C (after 3 months)</td>
<td>4.8</td>
<td>88.0</td>
<td>3.0</td>
<td>79.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>

(vi) **Toxicity Reduction:**

The Microtox test results indicate that 5 minute EC50 value of the original substrate (1 mM TCP solution) is 5.72%, which corresponds to about 11 mg/L of TCP. For the oxidation products of Runs #D and #E, the 5 minute EC50 values were obtained respectively as
12.01% and 43.9% of the reaction products, after three hours of reaction.

These results, as shown in Table 3, indicate that significant toxicity reduction compared with the original substrate was achieved after chemical oxidation for three hours, by Fenton's reagent. Interestingly, the amounts of oxidant (hydrogen peroxide) and catalyst (ferrous ions) did make some difference in terms of the extent of toxicity reduction which can be achieved.

Table 3. Toxicity Reduction of 2,4,6-TCP by Fenton's Reagent

<table>
<thead>
<tr>
<th>RUN #</th>
<th>Initial Molar Ratio</th>
<th>Toxicity (EC-50)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H2O2</td>
<td>TCP</td>
</tr>
<tr>
<td>D</td>
<td>2.75</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>5.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Summary and Conclusions

The results above can be summarized as follows:

1. The reaction between TCP and Fenton's Reagent is spontaneous and occurs under ambient conditions (at 20°C).

2. The reaction results in simultaneous dechlorination of organically bound chlorine to free chloride ions, as well as oxidation of the organic molecule.

3. Almost complete dechlorination of the substrate occurs after about 1.5 hours, while complete oxidation requires much more time.

4. The original substrate, TCP, completely disappears in the course of reaction.

5. The rate of reaction increases with an increase in the oxidant amount.

6. The pH drops continuously with the progress of reaction, probably because of the formation of organic acids.

7. Significant toxicity reduction takes place as a result of the advanced oxidation by Fenton's Reagent.

8. The amounts of oxidant and catalyst appear to have some effects on the extent of toxicity reduction.
9. Fenton's Reagent is an effective oxidant that can be used to degrade a highly chlorinated aromatic priority pollutant, 2,4,6-Trichlorophenol.

REFERENCES


Eisenhaur, H. R., J. WPCF, 36 (9), 1116-1128 (1964)


Haber, F., and Weiss, J., Proc. Royal Soc. (Lond.), A147, 332-351 (1934)


