FENTON PROCESS: A CASE STUDY FOR TREATMENT OF INDUSTRIAL WASTE WATER

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ABSTRACT:

This paper explains the Fenton process – Advanced Oxidation Process for treatment of industrial waste water and effect of various parameters on Fenton process. AOPs are the process that generates the hydroxyl radical that oxidizes the impurity compounds and purifies the waste water. For generation of hydroxyl radical there are many methods are available. Fenton process is an advanced oxidation process that uses the ferrous ion and hydrogen peroxide.

Many metals have special oxygen transfer properties which improve the utility of hydrogen peroxide. The most common of these is iron which, when used in the prescribed manner, results in the generation of highly reactive hydroxyl radicals ( OH ). The reactivity of this system was first observed in 1894 by its inventor H.J.H. Fenton. Fenton’s reagent is the result of reaction between hydrogen peroxide ( H 2 O 2 ) and ferrous iron ( Fe 2+ ), producing the hydroxyl radical ( OH ). The hydroxyl radical is a strong oxidant capable of oxidizing various organic compounds. Today, Fenton’s Reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals.

Keywords: Aop: Advanced oxidation process, COD chemical oxygen demand, Pentachlorophenol (PCP),COD Chemical oxygen Demand, BOD Biological oxygen demand

1. INTRODUCTION

A. Advanced Oxidation Processes (AOP)

In 1987, Glaze et al. defined AOPs as “Near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”. The AOPs have proceeded along one of the two routes:

- Oxidation with O 2 in temperature ranges intermediate between ambient conditions and those found in incinerators. Wet Air Oxidation (WAO) processes in the region of 1–20 MPa and 200–300 °C);
- The use of high-energy oxidants such as ozone and H 2 O 2 and/or photons those are able to generate highly reactive intermediates *OH radicals.

B. Mechanism of AOPs

It involves the generation and use of the hydroxyl free radical as a strong oxidant to destroy impurity compounds. The hydroxyl radical ( *OH ) is a powerful, non-selective chemical oxidant, which acts very rapidly with most organic compounds. Once generated, the hydroxyl radicals aggressively attack virtually all-organic compounds. As a rule of thumb, the rate of destruction of a contaminant is approximately proportional to the rate constant for the contaminant with *OH radical. The oxidation potential of various oxidants are shown in table 1.1 and the comparison of overall rate constants for the reactions of ozone and hydroxyl radical with various organic compounds in water is shown in table 1.2.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidation Potential (electron volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>2.80</td>
</tr>
<tr>
<td>O 3</td>
<td>2.07</td>
</tr>
<tr>
<td>H 2 O 2</td>
<td>1.77</td>
</tr>
<tr>
<td>Perhydroxy radical</td>
<td>1.70</td>
</tr>
</tbody>
</table>
Table 1.1 Oxidation Potential of Several Oxidants in Water

<table>
<thead>
<tr>
<th>Compound Type</th>
<th>Overall Rate Constant (liter per mole second)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>O₃</strong></td>
</tr>
<tr>
<td>Aromatics</td>
<td>1 to 10²</td>
</tr>
<tr>
<td>Ketones</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogen containing organics</td>
<td>10 to 10²</td>
</tr>
<tr>
<td>Phenols</td>
<td>10³</td>
</tr>
<tr>
<td>Sulfur containing organics</td>
<td>10 to 1.6 x 10³</td>
</tr>
</tbody>
</table>

Table 1.2 Overall Rate Constants for O₃, and *OH Reactions with Organic Compounds in Water

1.3 Methods to Produce Hydroxyl Radicals (*OH)

Several methods are available for generating *OH radicals. These are ozone based as well as non-ozone based processes. These include both non-photochemical and photochemical methods:

<table>
<thead>
<tr>
<th>Method Type</th>
<th>Ozone based processes</th>
<th>Non Ozone based processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Photochemical processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozone at elevated pH (&gt; 8.5)</td>
<td></td>
<td>Fenton system (H₂O₂/Fe²⁺)</td>
</tr>
<tr>
<td>Ozone + hydrogen peroxide (O₂/H₂O₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozone + catalyst (O₂/CAT)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photochemical processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₃/UV</td>
<td></td>
<td>H₂O₂/UV</td>
</tr>
<tr>
<td>O₃/H₂O₂/UV</td>
<td></td>
<td>Photo-Fenton (H₂O₂/Fe²⁺/UV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fenton-like systems (H₂O₂/Fe³⁺/UV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.3 Methods to Produce Hydroxyl Radicals

II. FENTON PROCESS (H₂O₂/Fe²⁺)

A. Fenton’s reagent

Many metals have special oxygen transfer properties which improve the utility of hydrogen peroxide. The most common of these is iron which, when used in the prescribed manner, results in the generation of highly reactive hydroxyl radicals (*OH). The reactivity of this system was first observed in 1894 by its inventor H.J.H. Fenton, but its utility was not recognized until the 1930’s once the mechanisms were identified.

Fenton’s reagent is the result of reaction between hydrogen peroxide (H₂O₂) and ferrous iron (Fe²⁺), producing the hydroxyl radical (*OH). The hydroxyl radical is a strong oxidant capable of oxidizing various organic compounds.

Today, Fenton’s Reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (phenols, formaldehyde, BTEX, and complex wastes derived from dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals).
B. Chemistry of Fenton Process

The rate constant for the reaction of ferrous ion with hydrogen peroxide is high and Fe^{2+} oxidizes to Fe^{3+} in a few seconds to minute in the presence of excess amounts of hydrogen peroxide.

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

Hydrogen peroxide decomposes catalytically by Fe^{3+} and generates again hydroxyl radicals according to the following reactions:

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{H}^+ + \text{Fe} + \cdot\text{OOH}^2+ \\
\text{Fe} - \text{OOH}^2+ & \rightarrow \text{HO}_2^- + \text{Fe}^{2+} \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}
\end{align*}
\]

For this reason, it is believed that most waste destruction catalyzed by Fenton’s reagent is simply a Fe^{3+}–H\text{H}_2\text{O}_2 system catalyzed destruction process, and Fenton’s reagent with an excess of hydrogen peroxide is essentially a Fe^{3+}–H\text{H}_2\text{O}_2 process (known as a Fenton-like reagent). Thus, the ferrous ion in Fenton’s reagent can be replaced with the ferric ion. Iron salts act as a catalyst for hydrogen peroxide decomposition, further reactions regenerate iron Fe^{2+}. It has been demonstrated by various researchers that:

- Fenton’s reagent is able to destroy different phenols, nitrobenzene, and herbicides in water media as well as to reduce COD in municipal wastewater.
- The Fe^{2+}/H\text{H}_2\text{O}_2 system acts as a potential oxidant for soil contaminants can also been investigated.
- Pentachlorophenol (PCP) and trifluralin are extensively degraded while hexadecane and dieldrin can partially transformed in a soil suspension at acidic pH.
- The use of Fe^{2+}/H\text{H}_2\text{O}_2 as an oxidant for wastewater treatment is attractive due to:
  1. Iron is a highly abundant and non-toxic element,
  2. \text{H}_2\text{O}_2 is easy to handle and environmental friendly substance.

Thus, the Fenton process is very effective for °OH Hydroxyl radicals generation; however, it involves consumption of one molecule of Fe^{2+} for each °OH radical produced, demanding a high concentration of Fe^{2+}.

C. Oxidation of impurity molecules by Hydroxyl radical (°OH)

Depending upon the nature of the organic impurity, following types of reactions are possible:

1. **By radical addition:** The addition of the hydroxyl radical to an unsaturated aliphatic or aromatic organic compound \(\text{(e.g.,C}_6\text{H}_6\text{)}\) results in the production of a radical organic compound that can be oxidized further. It can add itself to the contaminant, as in the case of olefins or aromatic compounds.

\[
\text{R} + °\text{OH} \rightarrow \text{ROH}
\]

2. **By hydrogen abstraction:** The hydroxyl radical can abstract a hydrogen atom from water, as with alkanes or alcohols. The removal of a hydrogen atom results in the formation of a radical organic compound, initiating a chain reaction where the radical organic compound reacts with oxygen, producing a peroxyl radical, which can react with another compound and so on.

\[
\text{R} + °\text{OH} \rightarrow \text{R}^* + \text{H}_2\text{O}
\]

3. **By electron transfer:** Electron transfer results in the formation of ions of a higher valence. Oxidation of a monovalent negative ion will result in the formation of an atom or a free radical.

\[
\text{R}^n + °\text{OH} \rightarrow \text{R}^{n-1} + \text{OH}
\]

4. **By radical combination:** Two radicals can combine to form a stable product. See reaction.

\[
°\text{OH} + °\text{OH} \rightarrow \text{H}_2\text{O}_2
\]
III PARAMETERS THAT AFFECTS THE FENTON OXIDATION PROCESS

Because of the sensitivity of Fenton’s Reagent to different wastewaters, it is recommended that the reaction always be characterized through laboratory treatability tests before proceeding to plant scale. The following parameters can influence the Fenton Process.

- Mass Ratio & Dosage of \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \)
- Iron type (Ferrous \( \text{Fe}^{2+} \) – Ferric \( \text{Fe}^{3+} \)), (Sulfate –Chloride).
- Temperature.
- \( \text{pH} \)
- Reaction Time.
- Adding chemicals in steps.
- The Reaction is followed by neutralization.
- Characteristic of Wastewater treated.

A. **Effect of Iron Concentration**: In the absence of iron, there is no evidence of hydroxyl radical formation when \( \text{H}_2\text{O}_2 \) is added to wastewater. As the concentration of iron is increased, impurity removal accelerates until a point is reached where further addition of iron becomes inefficient. The optimal dose range for iron catalyst is characteristic of Fenton’s Reagent and its range varies with the type of contaminants in wastewater. Three factors, typically influence the optimal dose are:
   1. A minimal threshold concentration of \( \text{Fe} \) which allows the reaction to proceed within a reasonable period of time regardless of the concentration of impurity material;
   2. A constant ratio of \( \text{Fe}:\text{substance} \) above the minimal threshold, which produces the desired end products. Note that the ratio of \( \text{Fe}:\text{substance} \) may affect the distribution of reaction products. Iron dose may also be expressed as a ratio to \( \text{H}_2\text{O}_2 \) dose
   3. A supplemental quantity of \( \text{Fe} \) which saturates the chelating properties in the wastewater, thereby availing unsequestered iron to catalyze the formation of hydroxyl radicals.

B. **Effect of Iron Type (Ferrous or Ferric)**: For most applications, it does not matter whether \( \text{Fe}^{2+} \) or \( \text{Fe}^{3+} \) salts are used to catalyze the reaction -- the catalytic cycle begins quickly if \( \text{H}_2\text{O}_2 \) and organic material are in sufficient amount. However, if low doses of Fenton’s Reagent are being used, some researchers suggest ferrous iron may be preferred. Neither does it matter whether a chloride or sulfate salt of the iron is used, although with the former, chlorine may be generated at high rates.

C. **Effect of \( \text{H}_2\text{O}_2 \) Concentration**: Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory for each waste to be treated. Each transformation in this series has its own reaction rate. In case of phenolic contaminants, there may generate undesirable intermediate (quinones), if insufficient amount of \( \text{H}_2\text{O}_2 \) is added. In pretreatment of a complex organic wastewater for toxicity reduction, as the \( \text{H}_2\text{O}_2 \) dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, whereupon further addition of \( \text{H}_2\text{O}_2 \) results in a rapid decrease in wastewater toxicity.

D. **Effect of Temperature**: The Rate of Reaction with Fenton’s Reagent Increases With Increasing Temperature, With The Effect More Pronounced At Temperatures Less Than 20 Deg-C. However, As Temperatures Increase Above 40-50 Deg-C, The Efficiency Of \( \text{H}_2\text{O}_2 \) Utilization Declines. This Is Due To The Accelerated Decomposition Of \( \text{H}_2\text{O}_2 \) Into Oxygen And Water. As A Practical Matter, Most Commercial Applications Of Fenton’s Reagent Occur At Temperatures Between 20-40 Deg-C. Moderating The Temperature Is Important Not Only For Economic Reasons, But For Safety Reasons As Well.

E. **Effect of \( \text{pH} \)**: The effect of \( \text{pH} \) on reaction efficiency is shown in figure. The optimal \( \text{pH} \) occurs between 3 and 6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the \( \text{H}_2\text{O}_2 \) into oxygen and water, without forming hydroxyl radicals.
A second aspect of pH deals with its shift as the reaction progresses. Provided an initial wastewater pH of 6.0, the following profile is typical of Fenton reactions. The first inflection is caused by the addition of Fe salt catalyst having acidic pH. A second, more pronounced drop in pH occurs when the H$_2$O$_2$ is added, and continues gradually at a rate which is attributed to the fragmenting of organic material into organic acids. The absence of such a pH decrease may mean that the reaction is inhibited and that a potentially hazardous build-up of H$_2$O$_2$ is occurring within the reaction mixture.

F. Effect of Reaction Time: The time needed to complete a Fenton reaction will depend on the many variables discussed above, most notably catalyst dose and wastewater strength. For simple phenol oxidation (less than ca. 250 mg/L), typical reaction times are 30 - 60 minutes. For more complex or more concentrated wastes, the reaction may take several hours. In such cases, performing the reaction in steps (adding both iron and H$_2$O$_2$) may be more effective than increasing the initial charges. Determining the completion of the reaction may prove troublesome. The presence of residual H$_2$O$_2$ will interfere with many wastewater analyses. Residual H$_2$O$_2$ may be removed by raising the pH to 7 - 10, or by neutralizing with bisulfite solution. Often, observing color changes can used to assess the reaction progression. Wastewaters will typically darken upon H$_2$O$_2$ addition and clear up as the reaction reaches completion.

IV APPLICATIONS, ADVANTAGES AND LIMITATIONS

a. Applications
Fenton’s Reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (phenols, formaldehyde, BTEX, and complex wastes derived from dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals). The process may be applied as pre-treatment to wastewater, sludge, or contaminated soil, with the effects being:
- Organic pollutant destruction
- Toxicity reduction
- Biodegradability improvement
- BOD / COD removal
- Odor and color removal

b. Advantages over conventional treatment processes
- Very effective at removing resistant organic compounds
- Capable of complete mineralization of organic contaminant into carbon dioxide if desired
- Less susceptible to the presence of toxic chemicals
- Produce less harmful by-products
Less maintenance required
Rapid
Low production of residual sludge
Un-Reacted H$_2$O$_2$ degrades to Oxygen

c. Points to be considered for efficient application:
- A better understanding of the mechanisms;
- Large amount of reagents needed;
- Measurements of the efficiency of candidate processes under controlled experimental conditions;
- Realistic evaluations of the relative costs of processes for selected treatment objectives versus other treatment processes;
- Evaluation of by-products and their toxicity;
- Reliability factors for processes.
- Because of the sensitivity of Fenton’s Reagent to different wastewaters, it is recommended that the reaction always be characterized through laboratory treatability tests before proceeding to plant scale.
- In addition to free radical scavengers, the process is inhibited by (iron) chelants such as phosphates, EDTA, formaldehyde, and citric/oxalic acids.

VI CASE STUDY: DYE REMOVAL FROM WASTE WATER

Textile industries consume the large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products. The presence of very low concentrations of dyes in effluent is highly visible and undesirable. Many dyes are difficult to decolorize due to their complex structure and synthetic origin. There are many structural varieties of dyes that fall into either the cationic, nonionic or anionic type. The effluents thus generated contain a wide range of contaminants, such as salts, dyes, enzymes, surfactants, scouring agents, oil, oxidizing and reducing agents.

Djurdjica Parac-Osterman, Ana Marija Grancaric, and Ana Sutlovic have studied Influence of chemical structure of dyes on decolourisation effects. They used Fentons reagent (with and without ultrasound) and coagulation/flocculation method to treat the effluent with two reactive and two acid dyes C.I. Acid Blue 158 (azo), C.I.Reactive Blue 19 (anthraquinon), C.I. Acid Red 52 (xanthen) and C.I. Reactive Blue116 (phthalocyanin). The degree of decolourisation was determined spectrophotometrically.

![Figure 5.1 the Structure of Dyes](image_url)

The discoloration of dyed water was carried out using Fenton’s reagent (with and without ultrasound) and coagulation/flocculation method.

**Fenton treatment (H$_2$O$_2$ – FeSO$_4$)**

Process was carried out with and without ultrasound at 25 °C and 60 °C: In 1 g/l dye solution were added 0.5 ml/l H$_2$SO$_4$ p.a.(pH=3), 50 ml/l H$_2$O$_2$ 36% and 5 g/l FeSO$_4$. Coloured wastewater was mixed 15 minutes with magnetic mixer (700 rpm). pH 8 was set with NaOH 32%. Changing of concentration of dyes in wastewater was measured spectrophotometrically. Degree of decolourisation is shown on Figure 5.2.
Coagulation/flocculation method:
The wastewater was treated with the coagulant 0.1% Beifloc ACI (CHT) (modified polycrylamide, anionactive,) and in jar tests were carried out at a particular coagulant dosage, pH 7, was mixed 30 minutes (100 rpm). After the addition of the coagulant was added 7.5 ml/l flocculant Beifloc CV (CHT) (condensation nitrogen compounds, cationactive) was mixed 10 minutes (50 rpm). After 24 h samples were filtered through cotton fabric. Concentration of dyes in effluent was measured spectrophotometricaly. Degree of removed dyes is shown on Figure 5.3.

Wastewater biological control:
Before and after decolouration treatments the COD and BOD5 were measured (according ISO 5000) and determined the biodegradability of dye as BOD5/COD value in Figure 5.4.

From their studies Parac-Osterman et. al. have concluded that
- Fenton reagent has multifunctional activity having the oxidative and flocculation action. The lack of this method is the low oxidative degradability of some dyes, as the consequences of molecule stability.
- The lowest decolouration degree are shown in the case of acid dye C.I. Acid Red 52 with xanthen chromophore (80%) and for C. I. Reactive Blue 116 with phthalocyanine copper complexon.
The dyeing temperature above 25 °C decreases the activity of Fanton’s reagent because the catalytic degradation of H2O2 is happened.

With exception of azo dyes, by using the combination of Fanton’s reagent and ultrasound, there is no considerable decolouration effect of other dyes. It is confirmed, that chemical effect of water decolouration depends on molecular stability.

Coloured waters, with exception of phtalocyanine dye, treated with Fanton’s reagent are more biologically accepted, having the BOD5/COD values less than 0.2.

Applied coagulation/flocculation methods are shown very high decolouration degree of more than 95%.

VII CONCLUSION

Fenton Process is a very useful process to treat the waste water containing variety of compounds such as phenols, formaldehyde, BTEX, and complex wastes derived from dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals. The process can be applicable for treatment of wastewater, sludge, or contaminated soil with high organic contents, toxic compounds. It also improves biodegradability of the industrial wastewater and reduces the biological and chemical oxygen demand of the effluent. The Fenton process is very effective for the treatment of wastes from textile industry containing variety of dyes and pigments and other toxic and organic compounds.

REFERENCES


