Wilson Environmental
ENGINEERED WATER & WASTEWATER SYSTEMS

Chemical Oxidation of Organics Using Fenton's Reagent

Introduction:

The intent of this paper is to provide general information to assist in understanding chemical treatment systems and in determining the feasibility of using the chemical oxidation process known as Fenton's Reagent. Fenton's Reagent is also called Fenton's Reaction or Fenton Chemistry. It is used to treat industrial wastewater streams that contain difficult or toxic organic compounds that can interfere with other common treatment systems such as biological treatment systems.

This paper is intended to help you understand the chemical oxidation of organic compounds and to offer some guidance to determine if using the Fenton Regent is right for your industrial application.

Definitions

Equalization Tanks: Equalization tanks are required for most wastewater treatment systems to provide a consistent flow rate and consistent characteristics. Equalization tanks are used to collect wastewater over a period of time that is sufficient to "equalize" the flow so that the wastewater system receives a wastewater stream that is as consistent as possible.

As a rule of thumb. If the total flow occurs in less than 10 hours a day or if the characteristics of the wastewater varies from day to day an equalization tank is required. The actual size will of course be based on a case by case basis.

Fenton's Reagent: is a solution of Hydrogen Peroxide with dissolved ferrous iron as a catalyst. It is used to oxidize organic contaminates found in industrial wastewaters. Fenton's reagent is most commonly used to destroy organic compounds that are resistant to other wastewater treatment techniques such as biological treatment or carbon adsorption. Typical application is the destruction of organic solvents that are resistant to biological oxidation such as phenols, formaldehyde, methylene chloride and chlorinated solvents. It was developed in the 1890's by Henry Fenton.

Hydrogen peroxide: is a chemical compound with the formula H_2O_2. In its pure form, it is a colorless liquid, similar to water, (H_2O) only slightly more viscous. Hydrogen peroxide is the simplest peroxide (peroxides are compounds with an oxygen–oxygen single bond) the oxygen-oxygen bond is highly unstable making it a strong oxidizer, bleaching agent and disinfectant.

It is commonly available at 50 % strength. It is also available in higher strengths, but at strengths over 50 percent it can cause serious burns on skin, fire on contact and is a potential explosion hazard.

Industrial wastewater: Industrial wastewater may be composed of various chemicals, toxins, heavy metals, pharmaceuticals, petroleum based oils and greases. By weight industrial wastewater varies considerably and may have as much as 5 % solids.

Note: All industrial discharges to a public sewer system are subject to general and specific prohibitions identified in the Code of Federal Regulations identified in 40 (CFR) 403.6 which prohibits the discharge of any pollutant that may impair worker or public health and safety, or that might upset or pass through the wastewater treatment plant untreated. Always check with your local sewage treatment authority for permit requirements.

Ferrous (Fe^{2+}): Ferrous iron is a divalent iron compound (+2 oxidation state), as opposed to ferric, which is a trivalent iron compound (+3 oxidation state). In the Fenton Reagent, Ferrous Sulfate FeSO4 in granular form is most commonly used. It is inexpensive and readily available in 50 pound bags.

pH: pH is a measure of how acidic or basic a solution is, The pH scale runs from 0 to 14. From 0 to 7 is acidic and from 7 to 14 is basic also called alkaline. A pH of 7 is neutral.

ORP-Oxidation Reduction Potential: Is a common measurement for the oxidizing potential of a wastewater stream. It is a millivolt (MV) reading. A positive reading indicates the wastewater has a positive oxidizing strength. The higher the mv reading the more the oxidizing power. A reading of +500 mv is required in the Fenton’s process. A negative reading indicates the wastewater has a reducing potential.

Fenton Reagent Basic Chemistry

In the presence of iron, Hydrogen peroxide will undergo several reactions the most common of which is the following reaction:

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

The OH is known as a Hydroxyl Radical.

The chemical reactions of the hydroxyl radical in water are of four types:

Addition: $^{\cdot}OH + C_6H_6 \rightarrow (OH)C_6H_6{}^{\cdot}$
where the hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product.

Hydrogen Abstraction: $^{\cdot}OH + CH_3OH \rightarrow {}^{\cdot}CH_2OH + H_2O$
where an organic free radical and water are formed.

Electron Transfer: $^{\cdot}OH + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^{-}$
where ions of a higher valence state are formed, or an atom or free radical if a mononegative ion is oxidized.

Radical Interaction: $^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$
where the hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product.

In Fenton's Reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanisms (hydrogen abstraction and oxygen addition) predominate.

Relative Reactivity

The hydroxyl radical is one of the most reactive chemical species known, second only to elemental fluorine in its reactivity (see below).

Reactive Species	**Relative Oxidation Power** (Cl_2=1.0)
Flourine	2.23
Hydroxyl radical	2.06
Atomic oxygen (singlet)	1.78
Hydrogen peroxide	1.31
Perhydroxyl radical	1.25
Permanganate	1.24
Hypobromous acid	1.17
Chlorine dioxide	1.15
Hypochlorous acid (bleach)	1.1
Chlorine	1.0
Bromine	0.8
Iodine	0.5

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Jar Testing:

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) chelates such as phosphates, EDTA, and citric/oxalic acids.

Pilot Testing:

Pilot testing is sometimes recommended if favorable results are obtained from the bench scale testing.

Pilot testing can be described as on site testing at the actual location under actual conditions. This is accomplished by taking a real time side stream of the wastewater and testing the actual process that is being considered before going to full-scale construction. Pilot testing is optional.

Effect of Iron Concentration

In the absence of iron, there is no hydroxyl radical formation. If H_2O_2 is added to a phenolic wastewater no reduction in the level of phenol occurs. As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes inefficient. An optimal dose range for iron catalyst is determined by jar testing.

A minimal threshold concentration of 15 – 30 mg/L Fe which allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material. Again Jar Testing is required.

Iron dose may also be expressed as a ratio to H_2O_2 dose. Typical ranges are 1 part Fe per 5-25 parts H_2O_2 (wt/wt).

Effect of Iron Type (Ferrous or Ferric)

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction -- the catalytic cycle begins quickly if H_2O_2 and organic material are in abundance. However, if low doses of Fenton's Reagent are being used (e.g., < 10-25 mg/L H_2O_2), some research suggests ferrous iron may be preferred.

Iron Recycle:

It is also possible to recycle the iron following the reaction. This can be done by raising the pH, separating the iron floc, and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

Effect of H_2O_2 Concentration

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory using Jar Testing for each waste to be treated.

As the H_2O_2 dose is increased, a steady reduction in COD will occur with little or no change in toxicity until a threshold is attained, whereupon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity.

H_2O_2 dosage in an automated process is determined by ORP. +500 mv is typical.

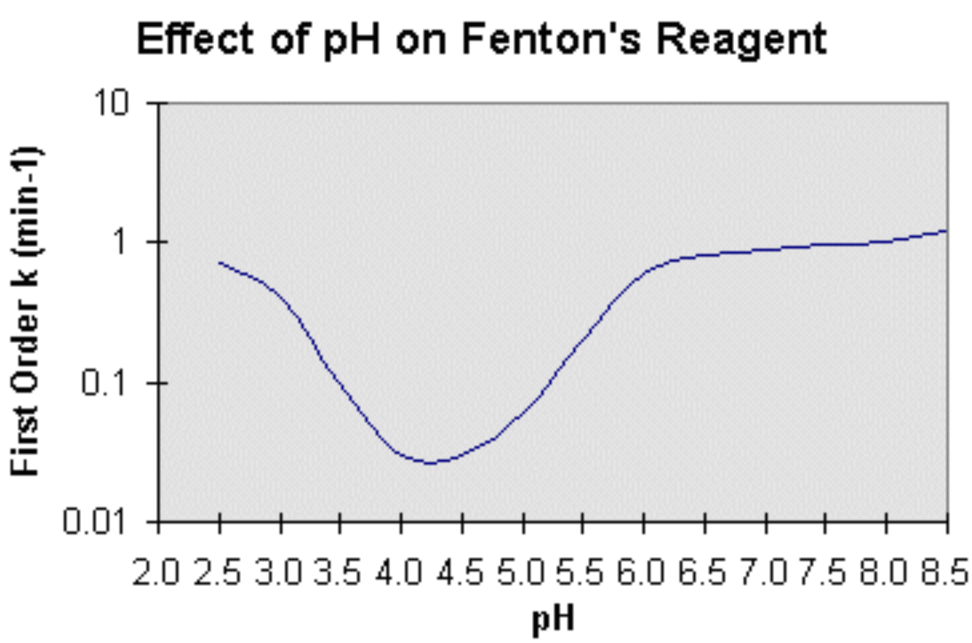
Effect of Temperature

The Fenton Reagent is an Exothermic reaction. The rate of reaction with Fenton's Reagent increases with increasing temperature, with the effect more pronounced at temperatures < 20 deg-C. However, as temperatures increase above 40-50 deg-C, the efficiency of H_2O_2 utilization declines. Most commercial applications of Fenton's Reagent occur at temperatures between 20-40 deg-C.

Applications of Fenton's Reagent for treating high strength wastewaters will require controlled or sequential addition of H_2O_2 to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when dose H_2O_2 exceeds 10-20 g/L (10 gallons per 1,000 gallons of waste water). Monitoring the temperature and controlling the rise in temperature is important to control the reaction and for safety reasons. This easily accomplished in an automated system.

Effect of pH

The effect of pH on reaction efficiency is illustrated below:



The optimal pH occurs between pH 3.5 and pH 4.5. Typical set points are 3.5 to insure that the Iron is dissolved.

In highly concentrated waste streams (>10 g/L COD), it may be necessary to perform the oxidation in steps, readjusting the pH after each step so as to prevent pH from inhibiting the reaction.

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 (Phenol conc. less than 250 mg/L), typical reaction times are 30 - 60 minutes. Actual reaction time will vary with the organic loading and type of organic chemicals that are present. 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_2O_2) may be more effective (and safer) than increasing the initial charges.

Determining the completion of the reaction is typically done by bench testing of the wastewater. Bench testing is readily available from several suppliers of scientific equipment.

Observing color changes can also be used to assess the reaction progression. Wastewaters will typically darken upon H_2O_2 addition and clear up as the reaction reaches completion.

General Steps to Treat Wastewater:

The procedure requires the following steps:

1. **pH adjustment:** Wastewater is first drawn from an Equalization tank to the reactor tank where the pH is adjusted to 3.0 to 4.0. This is done by the addition of Sulfuric Acid (H_2SO_4). The lower pH will cause the iron to dissolve into the wastewater. At neutral or higher pH levels (>7 pH units) the iron granules of Ferrous Sulfate will not dissolve. Lowering the pH also brings the oxidation strength of the Fenton Reagent into the optimum range. Dosage is typically less than 5 gallons for 1,000 gallons of wastewater. Note: Sulfuric Acid can be purchased at 93% but it can dangerous at that concentration. A lower concentration is recommended. Commercially available concentrations vary. May be purchased in 55

gallon drums or in 290 gallon totes.

2. **Iron Catalyst:** Adding the iron catalyst, Ferrous Sulfate, as dry granules or as a premixed solution in water and mixing for 2 to 4 hours. The amount required is determined by jar testing. Typical iron requirement is 8 to 10 pounds per 1,000 gallons of wastewater. Ferrous Sul;fate is purchased in 50 pound bags.

3. **Hydrogen Peroxide H2O2 addition:** The H_2O_2 is added slowly. The pH is monitored continuously to maintain a pH of 3 to 5 during the oxidation step. H2O2 is added until an ORP reading of +500 is maintained. The temperature is also monitored to prevent overheating. 10 gallons per 1,000 gallons of wastewater is typical usage for wastewater. H2O2 is the cost driver for operational costs. Current cost is around $3.00/gallon. Purchased in 55 gallon drums or 290 gallon totes.

4. **Lime Flocculation and pH adjustment:** The pH is now adjusted back to neutral (7 pH) using lime. If metals are present and metals removal is being conducted the pH will be adjusted in this step to optimal pH for the removal of the metal. The presence of iron in the reaction mixture makes it particularly suited to lime flocculation. 8 pounds is typical for 1,000 gallons. Purchased in 50 pound bags.

   Note: Metals removal is a separate subject but can be accomplished at this time in the process. Further pH adjustment is accomplished by using lime.

5. **Polymer Addition:** A small amount of polymer is added to create a floc (flakes of precipitate material visible to the eye). Typical dosage of Polymer is 2 oz. per 1,000 gallons. Purchased in 5 gallon containers.

6. **Settling**: The reactor tank is allowed to settle for 4 hours or more, no mixing.

7. **Decant:** The clear water is now removed by decanting from the reactor vessel.

8. **Solids Removal:** The settled solids are removed and sent to a filter press to remove excess water. The filter press will produce what is called filter cake. The solid residues, like a cake, can usually be sent to a landfill for disposal.

Note: Jar testing should be conducted to determine dosage rates. Estimated dosage rates are based on wastewater produced at an aircraft paint striping and painting operation where the wastewater contains Phenols, and Methylene Chloride.

Process Equipment

Fenton's Reagent is typically applied in a batch process. However, it is being used in both continuous and batch processes. A typical batch operation would consist of an equalization tank, chemical storage and chemical metering pumps for H_2O_2, $FeSO_4$, H_2SO_4 acid, and lime, a primary reactor, with low speed mixer, sludge holding tank, solids dewatering device (Filter Press or De-watering box), control panel with monitoring and controls for temperature, pH and ORP. The materials of construction for the reactor are typically Fiberglass or stainless steel, while those for the chemical storage systems are High Density Poly Ethylene (HDPE). Packaged Fenton's systems are available but are costly. Wilson Environmental can provide you with engineering guidance on custom designs and retrofits.

Equipment Automation

A batch system can be fully automated to control the entire process. Only the amount of Iron addition must be calculated from jar testing or past experience with the same wastewater. The predetermined amount of Iron is then mixed in a slurry to be added in its entirety, and automatically, to the process.

Summary

- Wastewater containing recalcitrant organic compounds can be treated using Fenton's Reagent.
- Fenton's reagent is an iron catalyzed oxidation process.
- Fenton's reagent has been used in industrial applications for decades.
- Continuous systems are also available but considerably more expensive.
- Jar Testing is recommended prior to purchasing this or any other wastewater system.
- Industrial sewer permits are required for sewer discharge.
- Batch systems can be fully automated.

References

Bishop, D.F. et.al. "Hydrogen Peroxide Catalytic Oxidation of Refractory Organics in Municipal Waste Waters", in Ind. Eng. Chem., Process Design & Development, vol.7, pp. 1110-117 (1968).

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