

Fenton Treatment: A Review on Treatment of Waste Water

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Abstract - Using the concept of bacterial growth in wastewater treatment has always remained the epicentre of treatment scheme. Although the process is largely accepted in almost all type of Effluent treatment plants, there always remains some scope of further treatment when there is presence of refractory compounds. Advance Oxidation Process (AOP'S) since late 1980's have become one important area for research and application in area of wastewater treatment dealing with the disposal of refractory compounds. AOP's are the process in which the impurities of effluent are removed by generating hydroxyl radical. There are different methods to generate hydroxyl radical. The present review paper explains the concept of Advanced Oxidation Process through most common AOP- Fenton process.

Keywords: Advanced Oxidation Process, Chemical Oxygen Demand, Fenton Treatment

I. INTRODUCTION

Advanced Oxidation process is an effective method of treatment to remove organic impurities immune to biological treatment processes. The main working principle

of treatment is the generation of highly reactive oxygen species having potential to degrade a wide range of organic compounds. On the basis of treatment route, the AOP can be bifurcated into two different routes.

- Oxidation with O₂ in temperature range from ambient to temperature of incinerators.
- The use of oxidants like Hydrogen peroxide and Ozone, which have the potential to generate highly reactive Hydroxyl radicals *OH.

Mechanism

The hydroxyl radical *OH is a non selective oxidant which reacts very rapidly with the organic refractory compounds. The rate of destruction of a contaminant is approximately proportional to the rate constant for the contaminant with *OH radical. There are many oxidants, which can initiate the degradation of impurities in Wastewater. The oxidation potential of these oxidants varies and is mentioned in the table 1.1.

Oxidant	Oxidation Potential (Electron Volt)
OH	2.80
O ₃	2.07
H ₂ O ₂	1.77
Perhydroxy radical	1.70
Permanganate ion	1.67
Chlorine Dioxide	1.50
Chlorine	1.36
Oxygen (O ₂)	1.23

Table 1.1 Oxidation potential of oxidants

II. FENTON PROCESS

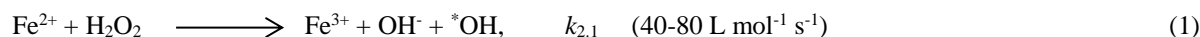
A. INTRODUCTION

Fenton process was discovered by H.J.H Fenton in 1894. He observed that Hydrogen peroxide can be activated by ferrous salts. Fenton process is a reaction between peroxides and iron ions which generates active oxygen species that oxidises organic or inorganic compounds. Though the Fenton reaction is more than 120 years old, its potential for wastewater treatment was recognized in the decade of 1930's after the identification of reaction mechanism.

Hydrogen peroxide and Ferrous ion combined together is popularly known as Fenton's Reagent. This reagent is capable of treating a whole wide range of Wastewater including phenols, Formaldehyde, BTEX and complex waste of pesticide, speciality chemicals, dyes etc.

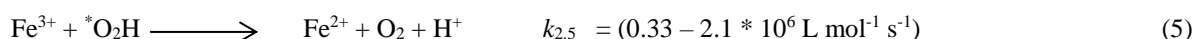
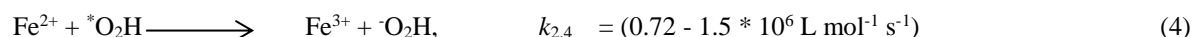
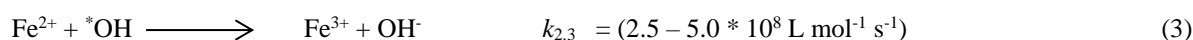
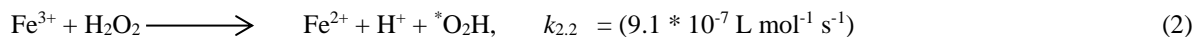
B. CHEMISTRY OF FENTON PROCESS

The reaction rate of Hydrogen peroxide with ferrous ion is very high. In presence of excess Hydrogen Peroxide, Fe²⁺ oxidises to Fe³⁺ in just few seconds to minute decomposing hydrogen peroxide into Hydroxyl radicals. This is the reaction mechanism of Fenton process.



The generated Ferric ions can be reduced to form ferrous again by reaction with excess hydrogen peroxide and more radicals as shown in eq.(2). This reaction is termed as "Fenton-like" reaction. The reaction rate of this reaction is particularly slower than Fenton reaction allowing regeneration of Fe^{2+} . Along with regeneration of ferrous ions

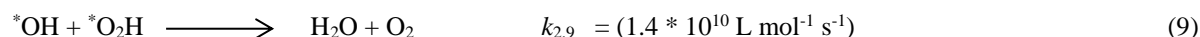
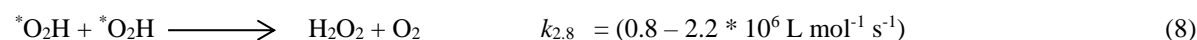
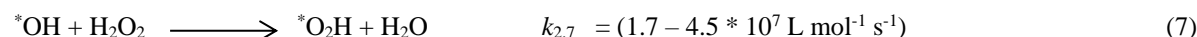
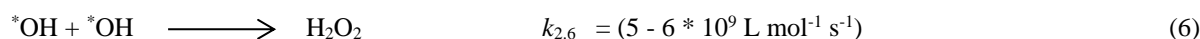
in Fenton like reaction, hydro-per-oxyl radicals are also generated. Hydro-per-oxyl also carries out the degradation of the organic compounds but they are less sensitive than Hydroxyl radicals. While the iron added in the reaction acts as a catalyst, H_2O_2 is consumed throughout the reaction to generate hydroxyl radicals.



The equations mentioned above Eq. (2) to (5) are the reactions where hydrogen peroxide is consumed and ferrous ions are regenerated from ferric ions. Hence they represent the rate limiting step.

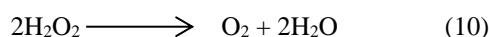
The dissolved solids in the effluent are precipitated. Continuous small flocs are observed during the process and the Flocs generally take a lot of time to settle down. Hence during the actual treatment application of this process, it is required to provide chemical coagulation to reduce the settling time of the flocs.

The ferrous ions generated reacts with hydroxide ions to produce Ferric Hydroxo complexes. The coagulation capability of the Fenton's reagent depends on this conversion.



Equation (6) to (9) also occurs during the Fenton process. They are either radical – peroxide reaction or radical – radical reaction. Unnecessary increase in treatment cost occurs when there is absence of organic molecule; hydrogen

peroxide undergoes decomposition converting into Oxygen and water according to Equation (10).



C. DIFFERENT ROUTES OF OXIDATION REACTION.

The effluent constitutes of organic compound of varying nature. Depending upon the characteristics of compound, any of the below mentioned reaction are possible.

1. By radical addition: A radical organic compound is formed when a hydroxyl radical is added to an unsaturated aliphatic or aromatic compound. The radical organic compound formed can further be oxidised.
2. By hydrogen abstraction: Radical organic compound and water are formed by removal of a hydrogen atom. This initiates a chain reaction where the radical organic compound produces peroxy radical when reacted with oxygen. This reacts with another compound and this goes on.
3. By electron transfer: Higher valence ions are generated, a result of electron transfer. Oxidation of a monovalent

negative ion results in formation of a atom or a free radical.

4. By radical combination: A hydroxyl radical reacts with another hydroxyl radical or with other unlike radical to form a stable product.

III. PARAMETERS AFFECTING FENTON PROCESS & OPTIMUM CONDITIONS.

A. OPERATING PH

Speciation Factors of iron and hydrogen peroxide, makes Fenton process highly dependent on pH of the effluent. Speciation refers to development of new species from existing species. The optimum pH for Fenton reaction was found to be around 3. At relatively high pH, it is found that precipitates of Ferric hydroxide are produced and there is presence of relatively inactive iron oxohydroxides. Hence at high pH, the activity of fenton reagent is reduced as less hydroxyl radicals are generated due to presence of less free Ferric ions. The oxidation potential of Hydroxyl ion reduces with increase in pH.

At Low pH, precisely at pH value less than 3 there is decrease in degradation efficiency. At low pH, iron complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ exists. This complex iron species reacts slowly with hydrogen peroxide compared to other complex species. Due to high concentration of H^+ ions, hydrogen peroxide forms $[\text{H}_3\text{O}_2]^+$ oxonium ions which are stable. Hence the stability of hydrogen peroxide increases with reduction in pH and reduces its reactivity with ferrous ions.

It is very important to maintain the pH during the reaction, as the shift in balance on either side of optimum value will generate undesired complexes and product and ultimately reduce treatment efficiency and increase treatment cost.

B. FERROUS ION CONCENTRATION

The optimum concentration of ferrous ion needs to be evaluated at laboratory scale experiment. The amount of ferrous ion concentration required for the process will vary from effluent to effluent. Generally with the increase in ferrous ion concentration the degradation rate also increases. Although, unnatural increase in ferrous ion concentration will increase the iron salts in effluent ultimately increasing total dissolved salt content in effluent.

C. HYDROGEN PEROXIDE CONCENTRATION

Hydrogen peroxide dosage is very important for the overall degradation efficiency of the process. Generally, with the increase in dosage of Hydrogen peroxide, there is increase in degradation of pollutants. However, over a certain limit there are irreversible negative effects of the reagent. The unused proportion of Hydrogen Peroxide increases the Chemical Oxygen Demand (COD) of the effluent. Also, the excess quantity of hydrogen peroxide is harmful for the organism. This is particularly crucial where the process is used as a pre-treatment to biological treatment systems. The heart of any biological process is the bacteria and the excess hydrogen peroxide will destroy the system.

D. OPERATING TEMPERATURE

There are very limited studies available depicting the optimum temperature range. It is reported that, the degradation efficiency is increased between temperatures 10°C to 40°C . Above the temperature range, the utilization efficiency of hydrogen peroxide decreases. At temperature above $40\text{-}50^\circ\text{C}$, hydrogen peroxide decomposes into water and oxygen. If the temperature of the effluent exceeds the temperature range, cooling is recommended considering the fact that the process is exothermic in nature.

E. TYPE OF IRON (FERRIC OR FERROUS)

The majority of the degradation efficiency depends on hydrogen peroxide and concentration of pollutant as they are the one's taking part in the reaction. The reaction initiates quickly once peroxide and the pollutants are in sufficient quantity. It generally does not play a decisive role whether to use ferric or ferrous salts. However, where low dosage of Fenton's reagent is in application, it is recommended to use ferric ion salt. It also does not matter whether it is chloride or sulphate salt of iron. But chlorine may be generated in higher quantity with chloride salts of iron.

F. REACTION TIME

It is very difficult to analyse the completion of the reaction. The presence of residual peroxide will interfere with wastewater analysis. The required reaction time for completion of process majorly depends on concentration and strength of pollutants and catalyst dose. The reaction time may range from 30-60 minutes for simpler organic pollutants to several hours for complex waste water. During application generally the colour change is observed to assume the reaction progress. The effluent tends to get darken on Hydrogen Peroxide addition and as the reaction step propagates, the effluent gets lighter and clearer in colour.

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