

Waste Water Treatment by Fenton Process

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Abstract:

Fenton is considered to be one of the most effective advanced treatment processes in the removal of many hazardous organic pollutants from refractory/toxic wastewater. It has many advantages, but drawbacks are significant such as a strong acid environment, the cost of reagents consumption, and the large production of ferric sludge, which limits Fenton's further application. The development of Fenton applications is mainly achieved by improving oxidation efficiency and reducing sludge production. This chapter presents a review on fundamentals and applications of conventional Fenton, leading advanced technologies in the Fenton process, and reuse methods of iron containing sludge to synthetic and real wastewaters are discussed. Finally, future trends and some guidelines for Fenton processes are given.

Key Words:

Fenton ,Fenton-like, Fenton Sludge, Reuse, Application.

1.INTRODUCTION

The presence of many organic pollutants in wastewater, surface water, and groundwater may result from contaminated soil, agricultural runoff, industrial wastewater, and hazardous compounds storage leakage. These organic pollutants, such as volatile phenols, benzene, and benzene derivatives, are considered highly toxic and low biodegradable. In some instances, conventional treatment methods such as biological processes are not sufficient to remove them. In order to improve water quality,

advanced treatment is needed to remove the refractory organics.

Fenton is an effective advanced treatment process. The hydroxyl radical ($\cdot\text{OH}$) can be generated from the reaction between aqueous ferrous ions and hydrogen peroxide (H_2O_2), and it can destroy refractory and toxic organic pollutants in wastewater. Fenton discovered the Fenton reaction in 1894, and he reported that H_2O_2 could be activated by ferrous (Fe^{2+}) salts to oxidize tartaric acid. However, its application as an oxidizing process for destroying toxic organics was achieved until the late 1960s. Fenton was mainly used to treat wastewater by radical oxidation and flocculation. H_2O_2 is catalyzed by ferrous ions to decompose into $\text{HO}\cdot$ and to trigger the production of other radicals, which can fully oxidize organic matters. The hydroxyl radical ($\cdot\text{OH}$) has a strong oxidation capacity (standard potential = 2.80 V versus standard hydrogen electrode) . Hydroxyl radicals can effectively oxidize refractory organic pollutants in wastewater and even completely mineralized them into CO_2 , water, and inorganic salts . Meanwhile, the iron complex produced in the treatment of wastewater by Fenton will play the role of flocculant.

The conventional Fenton continuous flow process configuration, as illustrated in , including acid regulation, catalyst mixing, oxidation reaction, neutralization, and solid-liquid separation. Fenton has many advantages, such as its high performance and simplicity (operated at room temperature and atmospheric pressure) for the oxidation of organics and its non-toxicity (H_2O_2 can break down into environmentally safe species like H_2O and O_2). However, Fenton also has some inherent disadvantages, which limit its application and promotion. For example, strict pH range, high H_2O_2 consumption, and the accumulation of ferric sludge that affects the oxidation efficiency . In order to overcome these disadvantages, the enhancement of

the Fenton process has attracted much attention from researchers. Both heterogeneous and homogeneous catalysts were used to replace Fe^{2+} , including ferric oxide, iron minerals, and nano zero-valent iron.

2. Fenton process

Currently, two mechanisms have been proposed to explain the degradation of organic matters by Fenton reaction. One is the Harber-Weiss mechanism, which considered that active oxide species $\cdot\text{OH}$ are generated to degrade organics in Fenton reaction. The other is the mechanism of high iron oxide intermediates, which was proposed by Bray and Gorin. They suggested that the strong oxidizing iron substances (FeO^{2+} , FeO^{3+}) were produced in Fenton reaction, rather than $\cdot\text{OH}$. With the development of spectroscopy and chemical probe method, it is generally accepted that the formation of $\cdot\text{OH}$ initiates the Fenton oxidation.

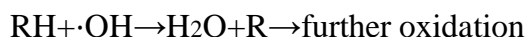
The traditionally accepted Fenton mechanism is represented by [Eqs. \(1\)–\(7\)](#).



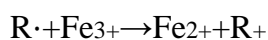
E1



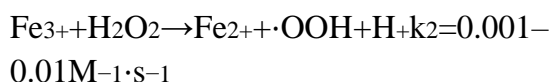
E2



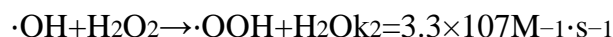
E3



E4



E5



E6



E7

According to the above equation, ferrous iron (Fe^{2+}) was rapidly oxidized to ferric ions (Fe^{3+}), while Fe^{2+} is regenerated from the so-called Fenton-like reaction between Fe^{3+} and H_2O_2 at a very slow rate. [Equation \(1\)](#) is usually considered as the core of the Fenton reaction.

The Fenton process is usually operated under the solution pH value of 3. The oxidation activity of $\cdot\text{OH}$ is related to the solution pH. The oxidation potential of $\cdot\text{OH}$ increases and the oxidation capacity is enhanced with decreasing pH. In addition, the activity of Fenton reagent is reduced with increasing pH due to the lack of active Fe^{2+} , in which the formation of inactive iron oxohydroxides and ferric hydroxide precipitate. Meanwhile, auto-decomposition of H_2O_2 appears at high pH.

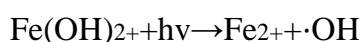
At very low pH values, iron complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and stable oxonium ion $[\text{H}_3\text{O}_2]^+$ exist, which reduces the reactivity between Fe^{2+} and H_2O_2 . Therefore, the efficiency of the Fenton process to degrade organic compounds is reduced both at high and low pH. In addition, there are many competitive reactions in the Fenton reaction system. In Fenton oxidation, the reaction rate is dependent on the iron dosage, while the extent of mineralization is directly related to the concentration of oxidant.

It is important to understand the mutual relationships between Fenton reagent in terms of $\cdot\text{OH}$ production and consumption. These relationships were investigated and classified them into three categories according to the quantity of the $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ ratio (initial concentration of Fe^{2+} versus initial concentration of H_2O_2). Their results showed that $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ ratio and organics can affect the competition in Fenton reaction paths.

The main disadvantages for the application of the Fenton process are the relatively high cost of H_2O_2 and the high amount of ferric sludge produced in the neutralization step of the treated solution before disposal. These drawbacks and the more increasingly stringent water regulations are a challenge to develop solutions addressed to improve the Fenton technology. On one hand, the energy was introduced into Fenton to enhance the $\cdot\text{OH}$ generation, such as photo-Fenton, electro-Fenton, and so on. On the other hand, iron-based catalysts and reuse of Fenton sludge were developed as a Fenton-like reaction.

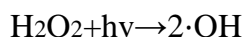
3. Photo-Fenton process

The classic Fenton reaction efficiency was affected by the conversion rate from Fe^{3+} to Fe^{2+} . Recent methods have promoted the in situ circulation from Fe^{3+} to Fe^{2+} . A combination of hydrogen peroxide and UV radiation with Fe^{2+} or Fe^{3+} oxalate ion [photo-Fenton (PF) process] produces more $\cdot\text{OH}$ compared to the conventional Fenton method. The hydroxy- Fe^{3+} complexes after Fenton reaction mainly exists in the form of $\text{Fe}(\text{OH})^{2+}$ at pH 2.8–3.5. The photochemical regeneration of Fe^{2+} by photo-reduction (Eq. (8)) of ferric Fe^{3+} occurs in the photo-Fenton reaction. The newly generated Fe^{2+} reacts with H_2O_2 and generates $\cdot\text{OH}$ and Fe^{3+} , and the cycle continues:



E8

Direct photolysis of H_2O_2 (Eq. (9)) produces $\cdot\text{OH}$, which can be used for the degradation of organic compounds, and in turn increases the rate of degradation of organic pollutants.



E9

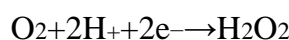
However, photo-Fenton gives a better degradation of low concentration organic pollutants. Because the high concentration organic pollutants could reduce the absorb radiation of iron complex, which needs a longer radiation time and more H_2O_2 dosage.

Excess H_2O_2 can easily capture $\cdot\text{OH}$. In order to improve the efficiency of photo-Fenton, several organic ligands such as EDTA, EDDS, oxalate, and other organic carboxylic acid were added and complexed with Fe^{3+} under photocatalysis. The positive effects achieved by these ions can be attributed to the following aspects: (i) iron-ligands having higher ability compete for UV light in a wide wavelength range compared to other Fe^{3+} -complexes, and promoting the reduction of ferric ion to ferrous ion and accordingly, regeneration of higher amounts of $\cdot\text{OH}$, (ii) Promoting H_2O_2 activation and $\cdot\text{OH}$ radical generation, (iii) improving iron dissolution at pH 7.0, and (iv) operating over the broad range of the solar radiation spectrum.

Compared with the classic Fenton, photo-Fenton has many advantages. A photo-induced $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycle could decrease the dosage of catalyst in Fenton, which effectively reduce the formation of iron sludge. Meanwhile, solar or UV light can increase the utilization of H_2O_2 , and possess photolysis on several small molecule organics. However, photo-Fenton has many disadvantages, such as low utilization of visible light, the required UV energy for a long time, high energy consumption, and cost.

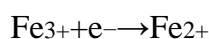
3.2 Electro-Fenton process

Electrochemical processes can be combined with Fenton processes (EF processes) during WW treatment to improve the Fenton processes. Fe^{2+} and H_2O_2 were produced by the electrochemical method as Fenton reagent. The electro-Fenton process follows the reaction shown below, where H_2O_2 can be generated in situ via a two-electron reduction of dissolved oxygen on the surface of the cathode in an acidic solution when the electrochemical process is applied (reaction Eq. (10)).



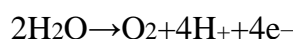
E10

Also, the produced ferric ion from Eq. (1) can be reduced to Fe^{2+} by electrochemical regeneration of Fe^{3+} ions on the cathode surface:



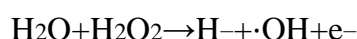
E11

Water was oxidized to oxygen at the anode (Eq. (12)):



E12

$\cdot\text{OH}$ was also generated at the surface of a high-oxygen overvoltage anode from water oxidation:



E13

Compared with tradition Fenton reaction, electro-Fenton has certain advantages, including (i) the production of H_2O_2 in situ via an electrochemical processes is beneficial for an increase in the organics degradation efficiency, a decrease in the cost, and a reduction in the risks associated with transportation; (ii) ferrous ion is regenerated through the reduction of ferric ions on the cathode, which reduces the production of iron sludge; and (iii) realizing the diversification of organics degradation pathway, such as Fenton oxidation, anodic oxidation, flocculation, and electric adsorption .

Electro-Fenton gives a better degradation of alachlor than the tradition Fenton. However, electro-Fenton processes have some problems with respect to H_2O_2 production. The production of H_2O_2 is slow because oxygen has low solubility in water and the current efficiency under reduced pH ($pH < 3$) is low. In addition, the efficiency of the electro-Fenton process depends on electrode nature, pH, catalyst concentration, electrolytes, dissolved oxygen level, current density, and temperature .

The application of modified iron source as heterogeneous catalysts in Fenton reactions

The Fenton reaction in which iron salts are used as a catalyst is defined as a homogeneous Fenton process. Nevertheless, there are some disadvantages, including (i) the formation of ferric hydroxide sludge at pH values above 4.0 and its removal, (ii) difficulty in catalyst recycle and reuse, (iii) high energy consumption, and (iv) limitation of operating pH range. Therefore, the application of modified iron source as heterogeneous catalysts in Fenton reaction to overcome the shortcomings of homogeneous catalysis has been widely studied. Different heterogeneous catalysts have been used in Fenton reactions, including zero valent iron , iron pillared clays, and iron minerals. [Figure 2](#) shows various types of heterogeneous Fenton-like catalysts.

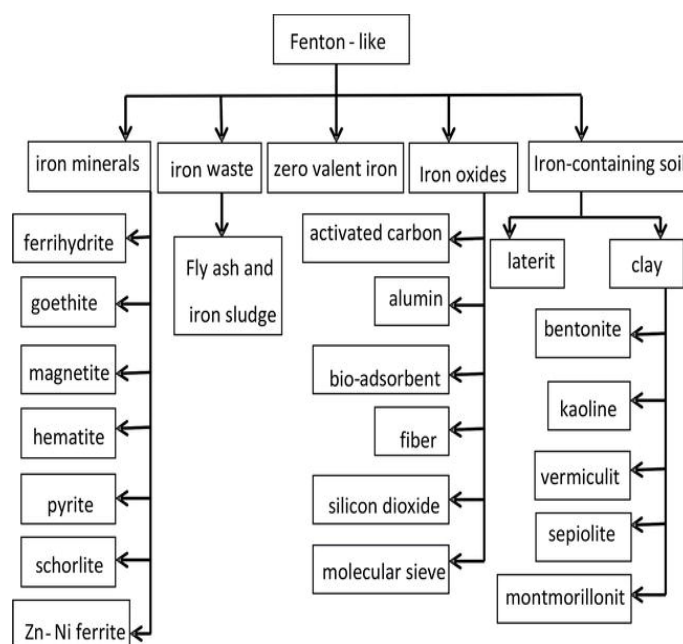


Figure 2.

Iron-containing catalysts.

3. CONCLUSIONS

Conclusions

During the last few years, many research efforts have been made toward the improvement of the Fenton process. Hybrid methods such as photo-Fenton, electro-Fenton, and sono-Fenton are not economically viable techniques to degrade large volumes of effluent disposed of by the industries. Most experimental studies have been conducted at the laboratory scale; thus, a more detailed investigation is required for the Fenton process to be considered feasible for industrial treatment plants. Further research on the advancement of the Fenton process is needed to demonstrate the economic and commercial feasibility of this process.

Although heterogeneous catalysts demonstrate considerable advances for the elimination of contaminants, there are still drawbacks related to the low oxidation rates, which appeared when pH values above four along with iron leaching, leading to an increase in the H_2O_2 consumption. Future studies should address the stability of the process for broader

operational conditions to avoid metal leaching of into the reaction solution and their negative effects on the environment. These combined methods and heterogeneous systems expected to reduce the production of Fenton sludge. However, the high cost of combined methods, the leaching of active iron, and the decay of active catalytic sites should limit the reduction of Fenton sludge.

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