Treatment of ultrahigh chemical oxygen demand chemical wastewater by Fenton oxidation

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Abstract—The article focuses on the Fenton oxidation process for the treatment of ultrahigh COD chemical wastewater from chemical plants. Optimum pH was determined as 2.0 and 10.0 for the first (oxidation) and second stage (coagulation) of the Fenton process, respectively. 0.465gFeSO₄·7H₂O, H₂O₂(30%)2ml, the mole ratio of H₂O₂:Fe²⁺=10:1, adjust the pH of the solution to 10 , after 1.5 hours of agitation, then add 5% PAM2ml to the solution, filtrate, extract, filtrate the clear liquid and dilute it three times, take 200ml of the diluted liquid, and add 0.465gFeSO₄·7H₂O, H₂O₂(30%)2ml, the mole ratio of H₂O₂:Fe²⁺=10:1, adjust the pH of the solution to 10 , after 1.5 hours of agitation, then add 5% PAM2ml to the solution, static stratification. For chemical wastewater, when the molar ratio H₂O₂/Fe²⁺ is 10:1, the removal rate of COD is the highest, provided 86.21–86.45% COD removal.

1. Introduction
In the treatment of refractory organic wastewater, Fenton method has been widely studied and applied, compared with other advanced oxidation techniques (AOPs) , Fenton method has the advantages of fast reaction, easy operation and automatic flocculation. Fenton reagent is a combination of Fe²⁺ and H₂O₂, which can react to form hydroxyl radical ·OH with high oxidation activity. ·OH can degrade and mineralize most organic matters, especially for organic wastewater which is toxic, difficult to oxidize and degrade with common oxidant or biochemically. Therefore, Fenton reagent method has been widely concerned by environmental workers, and has been widely studied, applied and developed in wastewater treatment research. The present paper is basically about research on the optimum process of Fenton oxidation process for the treatment of ultra-high chemical oxygen demand (COD) chemical wastewater from chemical plant.

2. Related work
In 1894, the French scientist Fenton [1] discovered that Fe²⁺ could effectively catalyze the oxidation of malic acid by H₂O₂. Later research showed that the combination of Fe²⁺ and H₂O₂ was an effective oxidant for many kinds of organic compounds. In memory of this great scientist, the reagent composed of Fe²⁺ and H₂O₂ was named Fenton reagent, and the reaction using this reagent was called Fenton reaction. The reaction mechanism of Fenton reagent is [2,3]:

\[
\begin{align*}
Fe^{2+} + H_2O_2 &\rightarrow Fe^{3+} + OH^- + \cdot OH \\
Fe^{2+} + \cdot OH &\rightarrow Fe^{3+} + OH^- \\
Fe^{3+} + H_2O_2 &\rightarrow Fe^{2+} + HO_2^- + H^+
\end{align*}
\]
\[ \text{HO}_2^+ + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} + \cdot \text{OH} \]  
(4)

\[ \text{RH} + \cdot \text{OH} \rightarrow \text{R}^+ + \text{H}_2\text{O} \]  
(5)

\[ \text{R}^+ + \text{Fe}^{3+} \rightarrow \text{R}^{2+} + \text{Fe}^{2+} \]  
(6)

\[ \text{R}^+ + \text{O}_2 \rightarrow \text{ROO}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  
(7)

Fe\(^{2+}\) reacts quickly with H\(_2\)O\(_2\) to form \(\cdot\)OH, while Fe\(^{3+}\) is also formed during the reaction. Fe\(^{3+}\) can react with H\(_2\)O\(_2\) to form Fe\(^{2+}\), and the resulting Fe\(^{2+}\) reacts with H\(_2\)O\(_2\) to form \(\cdot\)OH. It can be seen that Fe\(^{2+}\) is a good catalyst in the reaction process. The resultant \(\cdot\)OH can be further reacted with the organic compound RH to produce organic radical R\(^+\), R\(^+\) further oxidation, which breaks the carbon chain of the organic compound and finally oxidizes to CO\(_2\) and H\(_2\)O, thus greatly reducing the chemical oxygen demand (COD) of the wastewater\[4\]. At present, phenol compounds, polychlorinated biphenyls, nitrobenzene and dinitrochlorobenzene have been successfully degraded by Fenton reagent. The effects of pH, Fe\(^{2+}\), H\(_2\)O\(_2\) dosage and temperature on the degradation efficiency have been investigated, to study the properties of chemical kinetics. The treatment of organic wastewater by Fenton reagent has been studied extensively. Fenton reagent has obvious advantages in the removal of organic pollutants in wastewater. Recently, the applications and mechanisms of Fenton reagents and Fenton-like reagents such as light/Fenton, light/H\(_2\)O\(_2\)/ferric oxalate complex, microwave/Fenton and ultrasound/Fenton-like reagents have been widely studied\[5\]. And what's more, the optimum process parameters of Fenton oxidation for Berberine hydrochloride wastewater treatment were obtained by orthogonal test\[6\].

3. Materials and methods

3.1. Wastewater

The wastewater for this experiment is provided by Chengdu Yuanzhan Chemical Co., Ltd. The sewage mainly comes from the resin esterification in the production process, the main ingredients are styrene, propylene glycol, maleic anhydride, diethylene glycol, ethylene glycol, dipropylene glycol, neopentyl glycol, phthalic anhydride and other organic solvents. According to the analysis of the water quality, the pH value of the wastewater is 5-6, the acidity is slight, and the COD concentration is about 90000mg/L. The designed water volume of this experiment is 5M\(^3\)/d. The company's existing treatment method is to be incinerated by the corresponding units, the treatment cost is about 500 RMB/ton. The sewage discharge standard of the factory is the People's Republic of China the reuse of urban recycling water-water quality standard for industrial use (GB/T19923-2005). The discharge standard requires that the COD must reach the standard limit of 60 mg/L before it can be reused.

3.2. Methodology

The main method of this study is to obtain a set of best feasible, economic and reasonable reaction small test process parameters through various experimental factors, dosage of reagent, reaction time, reaction temperature.

3.3. Experimental procedure

The experiments were conducted in batch reactors and 200 mL wastewater samples were used in the experiments. The sample was heated up to the determined temperature (50 °C). The pH of the heated sample was adjusted to the required value with sulphuric acid (1 M) and sodium hydroxide (10 M). Required amounts of Fe\(\text{SO}_4\cdot7\text{H}_2\text{O}\) and H\(_2\)O\(_2\) were added to the sample. The solution was stirred. Thirty minutes were allowed for the completion of the reaction. Then, another 30 min were allocated for precipitation.

The supernatant was then decanted. The pH of the decanted supernatant was then adjusted to the desired value to initiate coagulation. Two hours were allowed for precipitation. After precipitation, the
supernatant was decanted for COD measurement for the selected samples (those treated with optimal dosage).

3.4. Materials
All chemicals and reagents used were analytical grade. The Chengdu Kelong chemical reagent Co., Ltd supplied FeSO₄·7H₂O, H₂O₂ solution of 30%, NaOH and H₂SO₄, which were used during experiments. Polyacrylamide (PAM) was purchased from Henan Gongyi Taihe County water treatment materials Co., Ltd. The wastewater was collected from the outlet of esterification workshop of Chengdu Yuanzhan Chemical Co., Ltd and transported to the laboratory by 25 kg plastic bucket.

3.5. Analytical methods
COD of the samples were measured according to the People's Republic of China National Standard for determination of Chemical oxygen demand (HJ828-2017). If a water or wastewater sample includes hydrogen peroxide, the standard COD test will be interfered since the dichromate ions react with H₂O₂ in an acidified solution [7,8,9]. Because of this reason, COD measurements were performed only after the Fenton’s coagulation stage. Since H₂O₂ is unstable in basic solution, after raising the pH above 7 for the initiation of Fenton’s coagulation, it decomposes to give oxygen and water and lose its oxidation ability [6] so that no interference is of importance. pH measurements were performed using a laboratory table-top pH meter (Model PHS-3C, Shanghai Leici instrument Co., Ltd. China). The stirrer is high power electric stirrer (Model MYP2011-50, Shanghai Meiyingpu instrument and meter manufacturing Co., Ltd. China).

4. Results and discussion

4.1. The optimum technological parameters studies with Fenton oxidation process
Experiments were carried out in five broad categories, known as One-time Fenton method (Test number 1-12), two-time Fenton method (Test number 13), triple dilution + one-time Fenton method (Test number 14), triple dilution + two-time Fenton method (Test number 15) and one-time Fenton + triple dilution + one-time Fenton method (Test number 16). All the experiments took the same sample size, all the experiments had the same initial pH and settling pH as well as the same dosage of flocculant. The sample size is 200 ml, the initial pH is 2.0 and the secondary pH is 10.0, the dosage of flocculant is 5% PAM 2 ml. The basic procedure of the experiment is to take water sample, adjust pH, then add FeSO₄·7H₂O, and H₂O₂ (30%), adjust the pH of the solution, after agitation, then add flocculant to the solution, static stratification. The COD of the supernatant was measured. The information of the actual dosage and time step of each type of experimental process is shown in Table 1.

| Number | DM | FeSO₄ | H₂O₂ | MT | T | FeSO₄ | DM | H₂O₂ | MT | T | COD |
|--------|----|-------|------|----|---|-------|----|------|----|---|-----|
| 1      | 1  | 0.233g| 1ml  | 10:1| 2h| ----  | 1  | ----  | ----|   | 76423|
| 2      | 1  | 0.465g| 2ml  | 10:1| 2h| ----  | 1  | ----  | ----|   | 74152|
| 3      | 1  | 0.465g| 2ml  | 10:1| 3h| ----  | 1  | ----  | ----|   | 88282|
| 4      | 1  | 0.61  | 2ml  | 8:1 | 2h| ----  | 1  | ----  | ----|   | 68282|
| 5      | 1  | 0.61  | 2ml  | 8:1 | 3h| ----  | 1  | ----  | ----|   | 82413|
| 6      | 1  | 0.97  | 4ml  | 10:1| 2h| ----  | 1  | ----  | ----|   | 72728|
| 7      | 1  | 0.97  | 4ml  | 10:1| 3h| ----  | 1  | ----  | ----|   | 73054|
| 8      | 1  | 1.22  | 4ml  | 8:1 | 2h| ----  | 1  | ----  | ----|   | 76423|
| 9      | 1  | 1.22  | 4ml  | 8:1 | 3h| ----  | 1  | ----  | ----|   | 72185|
The variations of removal rate in the treatment of the all kinds of wastewater experiment are shown in Fig.1.

4.2. Optimum process parameters and discussions

In the acidic conditions, the formation rate of free radicals from hydrogen peroxide is greater, the certain experimental results show that when the pH value of 2.0, COD removal rate is the highest. Too high or too low pH is not conducive to the removal of COD. According to the reaction formula(Fe²⁺+H₂O₂→Fe³⁺+OH⁻+•OH), when pH is too high, Fe³⁺ can easily form colloidal Fe (OH)₃ or amorphous precipitation Fe₂O₃·nH₂O which can inhibit the reaction and reduce the amount of free radicals, thus leading to the reduction of catalytic activity of the system. On the contrary, if pH value is too low, the reaction will still be inhibited and the catalytic reaction will be blocked. In view of the economical consideration, the experiment optimum pH value is 2.0[10].

With the increase of the concentration of hydrogen peroxide, the removal rate of COD in wastewater increases firstly, and then remains unchanged or decreases slightly. When hydrogen peroxide concentration is low, with the increase of additive amount, the amount of hydroxyl radicals also gradually increased, fenton reagent oxidation ability strengthens gradually, but at high concentration of hydrogen peroxide, fenton reaction system in excess hydrogen peroxide not only cannot produce a large number of hydroxyl free radicals, but in the initial stages of reaction Fe²⁺ oxidation as Fe³⁺. The reaction is carried out under the oxidation of Fe³⁺, which not only consumes a certain amount of hydrogen peroxide, but also inhibits the production of hydroxyl radicals [11], and the oxidation capacity of the Fenton system decreases on the contrary. At the same time, the excess hydrogen peroxide in the reaction may affect the density of the effluent, and 8 ml is the optimal dosage for the experiment due to the cost.

Based on the above researches, the optimum process parameters of The Fenton reaction are as

| DM | MT | T | COD removal rate |
|----|----|---|-----------------|
| 10 | 1  | 1.94g| 8ml | 10:1 | 2h | 668717 |
| 11 | 1  | 1.94g| 8ml | 10:1 | 3h | 78282 |
| 12 | 1  | 2.44g| 8ml | 8:1  | 3h | 67848 |
| 13 | 1  | 0.465g| 2ml | 10:1 | 2h | 64162 |
| 14 | 3  | 0.465g| 2ml | 10:1 | 3h | 17847 |
| 15 | 3  | 0.465g| 2ml | 10:1 | 1.5h| 12413 |
| 16 | 1  | 0.465g| 2ml | 10:1 | 1.5h| 12195 |

Note: DM represents dilution multiple, MT represents mole ratio of H₂O₂:Fe²⁺, T represents agitation time, COD has an unit of mg/L.
follows: 0.465g FeSO₄·7H₂O, H₂O₂(30%)2ml, the molar ratio of H₂O₂: Fe²⁺=10:1, adjust the pH of the solution to 10, after 1.5 hours of agitation, then add 5% PAM2ml to the solution, filtrate, extract, filtrate the clear liquid and dilute it three times, take 200ml of the diluted liquid, and add 0.465g FeSO₄·7H₂O, H₂O₂(30%)2ml, the molar ratio of H₂O₂: Fe²⁺=10:1, adjust the pH of the solution to 10, after 1.5 hours of agitation, then add 5% PAM2ml to the solution, static stratification. Admittedly, this is just a laboratory study parameter. This parameter must be optimized in the process of small-scale test, pilot-scale test and production so as to obtain a set of process with high COD removal efficiency, stable operation and economic feasibility.

5. Conclusions

The results in the use of Fenton’s reagent indicated that the overall treatment efficiency was best at an initial pH of 2.0 and second stage (coagulation) pH of 10.0. For all chemical products, average COD removal efficiency was highest when the ratio of H₂O₂/Fe²⁺ was around 10:1. At a constant H₂O₂/Fe²⁺ molar ratio of about 10:1. The experimental results show that under suitable reaction conditions, the removal rate of COD is as high as 90% in the treatment of chemical wastewater by Fenton’s oxidation method, and the BOD₅/COD of the wastewater increases from 0.08 to 0.41, which greatly improves the biodegradability of the wastewater. The effluent can be directly bio-treated in the next stage of the biochemical treatment system. The overall process flow is pretreatment+Fenton oxidation+coagulation precipitation+dilution+Fenton oxidation+coagulation precipitation+SBR. Fenton oxidation was an effective treatment method for the non-biodegradable portions of the chemical wastewater.

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