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Mechanism of Advanced Oxidation Technique with Iron to Remove COD

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Abstract. The research on the two advanced oxidation techniques of Fenton reagent and potassium ferrate is long-standing, and the basic principle of its reaction is also gradually clear. However, the mechanism of removal of COD by these two methods is not perfect. The mainstream view is that COD removal is mainly based on the complete oxidation of organics, followed by the flocculation of iron. It is believed that most of the organics are oxidized, and only a small part is precipitated with iron ions to achieve COD removal, but during the actual experiment founded it’s not like that. In this paper, the Fenton reagent oxidized glucose experimental analysis found that the simple reduction of COD by oxidation was very limited, but in the initial condition PH = 6, COD=428mg/L, with addition 1.67ml H$_2$O$_2$ (30%)/L, 1.36gFeSO$_4$·7H$_2$O/L. After 40min, the iron ions were difficult to flocculate and the effluent COD was 335mg/L. If a certain amount of Ca(OH)$_2$ were added, the iron ions are precipitated and the water COD was measured as 70mg/L, if the resulting precipitate regulated the acidity and the precipitate dissolved, the solution's COD rose again to 312mg/L. This shows that the latter has a much higher effect on reducing COD than the former thought little research has been done in this phenomenon.

1. Introduction
In recent years, more and more attention has been paid to environmental protection, and pollution emission standards have been continuously improved, that prompting us to further study new and highly efficient sewage treatment technologies. Advanced oxidation technology as a new and efficient COD removal technology has increased the research and application of organic wastewater treatment. Fenton reagent is a typical advanced oxidation reagent composed of H$_2$O$_2$ and Fe$^{2+}$. The main reason for its oxidation is that it produces highly oxidized HO· in the reaction system. The redox potential is as high as 2.8V, second only to fluorine(2.87V) [1]. The oxidation mechanism is mainly a series of chain reactions initiated by hydroxyl radicals, replacing hydrogen on organic carbon or attacking carbon-carbon bonds, converting macromolecules into small molecules. Basically speaking, the final oxidation of low valence carbon to positive tetravalent carbon completely degrades organics. Fenton process is relatively mature in foreign countries, and it has a good effect when combined with biological methods [2-4]. The mechanism of Fenton reaction is more complex and there are many influencing factors. The main factors are H$_2$O$_2$ dosage, Fe$^{2+}$ dosage, wastewater pH, reaction time and temperature [5-7]. Potassium ferrate is highly oxidizing and its oxidation potential is 2.20V and 0.72V in acidic and alkaline solutions [8], respectively. Therefore, potassium ferrate is used in a wide pH range. Potassium ferrate is used in acidic conditions, hexavalent iron is rapidly reduced to ferric iron, rapidly reducing the COD of wastewater [9].

The change in valence is essentially the gain or loss of electrons. The oxidation of organics is mainly caused by the shift of electron pairs. Since the oxidation of organics is the result of the shift of
electron pairs, it is advisable to examine Fenton reagent’s process and results of removal COD from gain and loss of electrons. Assuming that the oxidants are all used to oxidize organics. Table 1 below compares the results of some authors’ experiments with gain and loss of electrons.

| Wastewater type       | Method          | COD removal (mg/L) | Loss of electrons (mol/L) | Oxidizer dosage H₂O₂/K₂FeO₄ (mg/L) | Gain of electronic number (mol/L) | The author                  |
|-----------------------|-----------------|--------------------|---------------------------|-----------------------------------|----------------------------------|-----------------------------|
| Oilfield wastewater   | Fenton's method | 1785.1             | 0.223                     | 2822                              | 0.166                            | Tao Li et al. [9]           |
| Garbage permeate      | Fenton's method | 1401.0             | 0.175                     | 2720                              | 0.160                            | Yanjiao Gao et al.[10]      |
| Oilfield wastewater   | Fenton's method | 544.9              | 0.068                     | 113                               | 0.007                            | Zhongjie Zhang [11]         |
| Papermaking wastewater| Potassium ferrate| 1819.6             | 0.227                     | 10                                | 0.00015                          | Zongcheng Miao et al[12]    |
| Leather waste water   | Potassium ferrate| 3936.1             | 0.492                     | 20                                | 0.00030                          | Zongcheng Miao et al[12]    |
| Toluene solution      | Potassium ferrate| 1442.0             | 0.180                     | 30                                | 0.00045                          | Zongcheng Miao et al[12]    |

As shown in Table 1, the number of electrons obtained by the oxidant in the reaction process is less than the number of electrons lost by the reducing organic matter, and the number of gain and loss electrons also differ greatly. For the Fenton method, there is also an H₂O₂ used to oxidize Fe²⁺. This shows that the principle of removing COD by iron-containing advanced oxidation technology is not only the oxidation-reduction reaction, but also the precipitation of iron salts to remove some of the organics. Moreover, the COD removal effect of the iron salt precipitation is not inferior to the COD removed by the oxidation process. For potassium ferrate, a small dose of oxidant removes a large amount of COD, indicating that the precipitation of iron salt plays an important role in the process. Tang et al. [14] found that Fenton removal of organics is a major process in two processes, oxidation and flocculation. Lìgia F et al. [15] and Carmen SD et al. [16] also found that the Fenton process is an combined oxidation with flocculation phase method, which has a certain degree of innovative attraction, and can reduce the economic cost. Through the above analysis, the following experiment was simply designed to examine the Fenton process to remove COD.

2. Experimental part
The experiment artificially formulated organic wastewater with distilled water and glucose.

2.1 Experimental materials
H₂O₂ (30%), FeSO₄·7H₂O, glucose, Ca(OH)₂ are all analytically pure, distilled water, sulfuric acid, high temperature rapid digestion instrument (CR 2200), visible spectrophotometer (Photolab 6100VIS), COD test reagent A, COD test reagent B, electrobalance, pH test paper.

2.2 Detection methods
The experiment was performed using the dichromate method [17].

2.3 Experimental process
2.3.1 Experiment 1
The artificial wastewater COD was first formulated to be 850 mg/L. Yiying G. et al [18] measured the best molar ratio of H₂O₂/FeSO₄·7H₂O when the wastewater was treated with Fenton’s reagent was 3 to 3.5:1. In this experiment, the molar ratio of H₂O₂/FeSO₄·7H₂O was 3:1.

The wastewater was first put into 15 sample glass bottles, each sample contains 500ml of wastewater, one was used as the original wastewater to measure COD, and the remaining sample were
step by step added with different volumes of H$_2$O$_2$ (30%) solution (detailed in Table 2 below) and then different quality of FeSO$_4$ · 7H$_2$O (detailed in Table 2 below) were added and stirred, the solution quickly turned reddish-brown, and no precipitation in the whole process. After 40 minutes of full reaction with a pipette accurately weigh 3ml of each sample into the COD detection reagent bottle, then the COD detection reagent bottle were placed into the high-temperature rapid digestion instrument. Heated and refluxed at 148°C for two hours, then the COD reagent bottle were removed and exposed at room temperature for at least ten minutes, followed by a gentle shaking the COD reagent bottle until liquid in the bottles were well mixed. Finally, the COD reagent bottles were cooled to room temperature and placed into the calibrated visible light spectrophotometer to measure the sequence.

2.3.2 Experiment 2

First, two cups of organic wastewater with the COD of 428 mg/L were prepared, and each of cup was 1 liter. Then take a cup of wastewater, 1.67 ml of H$_2$O$_2$ (30%) and 1.36 g of FeSO$_4$·7H$_2$O were added, and stir evenly. The solution was homogeneous and transparent yellow-brown. The pH of the solution was reduced. After 40 minutes, 3 ml of the sample was taken directly from the tan solution and the prepared COD was added A, B reagents, and then detection of COD. Next, 0.54 g of Ca(OH)$_2$ was added to the solution. The solution was rapidly stirred. The solution was gray-green floc and precipitated slowly. After the precipitate was completely collected, the supernatant was extracted and 3 ml of COD was detected. Finally, sulfuric acid was added to adjust the pH until the precipitate was completely dissolved, and a 3 ml sample was taken for detection of COD.

Taking the other bottle of wastewater, added 1.36g of FeSO$_4$·7H$_2$O and then added 0.54g of Ca(OH)$_2$. The precipitate was dark green. After the precipitation was complete, take 3ml of sample to detect COD.

3. Results and discussion

3.1 Experiment 1 results and discussion

| H$_2$O$_2$(30%) (ml/L) | Gain of Electronic number (mol) | COD reduction (mg/L) | Loss of electrons (mol) | FeSO$_4$·7H$_2$O (g/L) | Oxidizer utilization(%) |
|------------------------|-------------------------------|---------------------|-------------------------|-------------------------|-------------------------|
| 1.8                    | 0.0348                        | 122                 | 0.0153                  | 1.46                    | 44.0                    |
| 2.4                    | 0.0466                        | 212                 | 0.0265                  | 1.96                    | 56.9                    |
| 3.0                    | 0.0582                        | 246                 | 0.0307                  | 2.46                    | 52.7                    |
| 3.6                    | 0.0698                        | 264                 | 0.0330                  | 2.94                    | 47.3                    |
| 4.2                    | 0.0816                        | 289                 | 0.0361                  | 3.44                    | 44.2                    |
| 4.8                    | 0.0932                        | 351                 | 0.0439                  | 3.92                    | 47.1                    |
| 5.4                    | 0.1048                        | 369                 | 0.0460                  | 4.40                    | 43.9                    |
| 6.0                    | 0.1160                        | 385                 | 0.0481                  | 4.90                    | 41.5                    |
| 6.6                    | 0.1276                        | 415                 | 0.0519                  | 5.40                    | 40.7                    |
| 7.2                    | 0.1392                        | 416                 | 0.0520                  | 5.88                    | 37.4                    |
| 8.4                    | 0.1624                        | 454                 | 0.0568                  | 6.86                    | 35.0                    |
| 9.6                    | 0.1856                        | 574                 | 0.0718                  | 7.84                    | 38.7                    |
| 10.8                   | 0.2088                        | 602                 | 0.0753                  | 8.82                    | 36.1                    |
| 12.0                   | 0.2320                        | 686                 | 0.0858                  | 9.80                    | 37.0                    |
| 14.4                   | 0.2784                        | 718                 | 0.0898                  | 11.78                   | 32.3                    |
Iron ions did not precipitate during the experiment. The solution was yellow-brown and the dose was increased proportionally. The COD of the wastewater gradually decreased, and the COD decreased basically linearly. From the electron transfer investigation, it was found that when the raw water COD was 850 mg/L, the utilization of hydrogen peroxide first increased and then decreased slowly. When the effluent COD was high, the hydrogen peroxide utilization was about 50%. When the COD was reduced, the utilization of hydrogen becomes lower, and gradually decreasing from 50% to less than 40%. Especially when the COD was reduced to 132 mg/L, the utilization of hydrogen peroxide is only 32.3%. As the efficiency of oxidation decreases, it is desirable to use a large amount of oxidant to lower the COD.

3.2 Experiment 2 Results and Discussion

| Raw water | Before adding Ca(OH)₂ | After clarification with Ca(OH)₂ | Adjust pH to precipitate dissolution | Second cup of wastewater supernatant |
|----------|------------------------|----------------------------------|-------------------------------------|--------------------------------------|
| COD (mg/L) | 428                    | 335                              | 70                                  | 312                                  | 432                                  |

3.2.1 Electronic transfer

A total of 0.5g of H₂O₂ was added in this experiment. Assuming that all of them were used to oxidize organics, about 0.0294mol electrons could be obtained. Before the addition of Ca(OH)₂ precipitates, the COD was reduced by 93mg. Then the electrons needed to be lost about 0.0116mol electrons. The utilization of H₂O₂ was about 40%. Then added 0.54g Ca(OH)₂. After the iron ions were completely precipitated, the COD was reduced by 358 mg/L. The electrons were lost 0.0448 mol/L, which is 1.5 times that of the electrons that could be obtained by H₂O₂. It was assumed that H₂O₂ oxidizes all the divalent iron to three. The valence iron gets 0.0049mol electrons, which is 17% of the electrons of hydrogen peroxide. Nearly 43% H₂O₂ neither removes COD nor oxidizes ferrous iron. It can be seen that in the reaction before the Ca(OH)₂ was added, the utilization rate of H₂O₂ was low, and 0.5 g of H₂O₂ can only removed 93 mg of COD. In theory, the remaining 335 mg of COD needs to be completely consumed about 3.6 g of H₂O₂.

3.2.2 Flocculation precipitation

However, it was found in the experiment that when Ca(OH)₂ was added, the divalent trivalent iron ions in the solution quickly formed gray-green flocs and gradually sank. After the solution was clarified, the measured COD was only 70 mg/L. Which was found by reading many literatures, most of the literature considered that iron hydroxide or ferrous hydroxide itself reduces the flocculation adsorption, but there is no direct evidence to prove how this precipitation method actually removes...
organic matter in such a flocculation process. It was judged based on the characteristics of flocculation and sedimentation. In theory, advanced oxidation technology is to oxidize macromolecule organics into small molecule organics, functional groups can be oxidized from hydrocarbons, alcohols, aldehydes, acids all the way to smaller organic molecules or inorganic substances such as water and carbon dioxide. Generally small molecules are not conducive to flocculation and adsorption, followed by the second cup of experimental samples can be seen that such flocculation did not have any effect on glucose molecules, so the flocculation is not the only cause of COD reduction. Founding in the Fenton’s reaction process the solution was acidic, and it can be judged that a large amount of organic acid has been produced in the solution. Some studies have found that the combination of Fenton reagent and oxalic acid or EDTA has a synergistic effect. This synergistic effect may be the cause of organic flocculation. It is thought that these generated organic acids promote the Fenton reaction on the one hand and form chemical bonds with iron hydroxide or ferrous hydroxide on the other hand and then precipitate.

3.2.3 Oxidation
The precipitation-adjusted acidity re-dissolves in the solution COD almost back to the previous value, indicating that the organic material was not oxidized but only precipitated with iron, and this precipitate reduced the COD by 265 mg, and the reduced COD during oxidation was 93 mg. The COD that can be reduced by iron ion precipitation was much higher than the COD that was reduced in the oxidation process. A large number of studies have found that, when pH = 3, Fenton reagent has the strongest oxidizing ability and the best effect of reducing COD. The first thing that happens in the test was the oxidation reaction. The glucose was in the form of a ring in the solution and has certain difficulty. The results show that Fenton reagent oxidizes organics to organic acids and that it is an organic acid structure that is easily co-precipitated with iron salts. Although the oxidation process reduces small COD, it is the key to the next step in the precipitation of iron ions. The bedding allows the next step to remove more COD with less reagents.

4. Conclusion
Based on previous experiments, from the point of view of electron transfer, many experiments including Fenton’s experiment and potassium ferrate oxidizing organic matter found that the number of electrons obtained by the oxidant is much lower than that of the organics, thus it is believed that iron ions precipitate removal COD has played a greater role. The organics can be precipitated in a chemical bond to remove COD.

(1) The use of Fenton to remove COD hydrogen peroxide will gradually reduce the utilization rate. The lower the COD the more hydrogen peroxide will be consumed for each 1 mg of COD reduction. Therefore, the removal of COD by simple oxidation requires the use of a large amount of oxidants. This increases the cost of Fenton oxidation and hinders its promotion.

(2) The removal of COD by Fenton method or potassium ferrate method is not only its strong oxidizing ability, but also iron ion precipitation to remove COD. Iron ions precipitation to remove COD is much higher than its oxidative removal of COD. So advanced oxidation techniques like this removal of COD is divided into two key processes, first oxidation, post-precipitation, and the effect of precipitation to remove COD is greater than oxidation.

(3) The precipitation of this iron ion did not remove glucose, and its flocculation effect is limited. The oxidation of glucose by Fenton reagent also did not produce easily flocculated macromolecules. The solution was found to be acidic during the test. Therefore, the iron ion precipitation was combined with a large amount of organic acid substances to precipitate and achieve the purpose of reducing COD.

Therefore, we can study the use of strong oxidants to first modify the organic functional groups, and it is easy to chemical precipitation with iron ions in alkaline conditions, so as to achieve the purpose of removing organic matter, reduce the amount of oxidants, and reduce processing costs.
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