Research and Application of Flocculant for Oilfield Wastewater Treatment Based on Fracturing Wastewater

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Abstract. In view of the characteristics of high viscosity, high turbidity and high oil content in the oilfield fracturing operation wastewater, the Fenton oxidation-flocculation treatment method is used to reinject the fracturing wastewater, and the pH value, Fenton reagent and flocculation of the wastewater The dosage of agent and the time interval of adding flocculant to the effect of fracturing wastewater oxidation and flocculation treatment. The results show that: according to the conditions of 30% hydrogen peroxide (volume percentage) dosage of 0.2% and FeSO₄ dosage of 20mg / L Fenton oxidation was carried out for 30min, and then flocculation treatment was carried out under the conditions of PAC dosage of 70mg / L, PAM dosage of 3mg / L, and stirring speed of 100r / min for 30min, then into the SBR reactor for 8h aeration and sedimentation for 1h, then treated The COD of post-fracturing wastewater decreased from 4132.92mg / L to 190.38mg / L, and its removal rate could reach 95.4%. The combined process has far better treatment effect on wastewater than the single micro-electrolysis, Fenton oxidation or flocculation process, and the method is simple and easy to use, and the utilization rate of the agent is high.

1. Introduction
Oilfield fracturing operation is one of the main measures to increase the production of oil and gas wells in the tertiary oil recovery of oilfields, and is widely used in various oilfields. With the increase in the exploitation of oilfields, the amount of fracturing flowback wastewater (referred to as fracturing wastewater) has increased year by year. The wastewater contains a large number of suspended particles, petroleum, residual thickeners, cross-linking agents, pH adjusters, bactericides and other chemical additives. It has complex components, high organic content, high toxicity, and poor biodegradability. Directly discharged after treatment will cause great harm to soil, water, plants and the environment.

The treatment methods of oilfield wastewater at home and abroad mainly include biological method, electrochemical method, membrane separation method and coagulation precipitation method. Conventional waterflood produced water treatment process treats polymer produced water, on the one
hand increases the settling time and reduces the filter speed of the filter, thereby increasing the size of the ground buildings and increasing infrastructure investment; on the other hand, the polymer will also interfere with flocculation. The use effect of the agent makes the treated water quality not reach the original water quality standard (mainly the oil content and suspended solids content seriously exceed the standard). Polyaluminum ferric sulfate is prepared with ferrous sulfate as raw material and sodium nitrate as catalyst, and it has a good treatment effect on oily wastewater. Polyferric aluminum chloride sulfate is prepared from bauxite, activated calcium silicate, hydrochloric acid, sulfuric acid, etc., and has the excellent performance of polytron and polyalanine. The flocculant is better than oxychlorination in treating oily wastewater aluminum. The composite inorganic polymer flocculant not only has the excellent performance of polyalanine and polytron inorganic polymer flocculant, but also has the characteristics of greater polymerization degree and higher alkalinity [1].

2. Flocculant

2.1. Organic flocculant
Organic flocculants are the most commonly used flocculants in the treatment of oily sewage. Compared with inorganic flocculants, organic flocculants have the advantages of low dosage, strong flocculation capacity, small scum generation and high treatment efficiency. Organic flocculants commonly used in the treatment of oily sewage include polyacrylamide (PAM), CG-A, UP-20, etc. Polyacrylamide is the most widely used organic flocculant in the world. It is divided into cationic, anionic and non-ionic polymers. Among them, cationic polymers are the best for oily sewage treatment; CG-A is a natural modified organic polymer flocculant and has a good treatment effect on oily sewage in oil fields. UP-20 is a polyquaternary flocculant and is often used as a flotation agent for heavy oil [2].

2.2. Inorganic flocculant
The initial research and development for the treatment of oily sewage is mainly a compound flocculant, which is composed of several inorganic flocculants or inorganic and organic flocculants. Mainly include PAC + CG-A, PAC + CG-A + NaOH, PAC + PAM, etc. The application effect is better, such as the cationic organic polymer flocculant ZDMC and the inorganic polymer flocculant PAFC to form a compound flocculant, which can deal with the oily sewage of Maoming Petrochemical Company. The amount of slag formation is reduced by 26.5%; or the compounding agent S-2040 + PAC + PAM or S-2040 + PACS is used to treat heavy oil wastewater, and the oil content, machine impurities, and bacteria in the effluent after treatment are all lower than the quality of oilfield reinjection water Standard, can be used as reinjection formation water, Figure 1 is the principle of inorganic flocculants in the treatment of fracturing wastewater.

![Figure 1. The principle of inorganic flocculant in the treatment of fracturing wastewater](image-url)
3. Experimental research

3.1. Reagents, materials and instruments
30% (w) H₂O₂ solution, concentrated sulfuric acid, NaOH, hydrochloric acid: analytically pure. Cationic polyacrylamide (CPAM): relative molecular mass 8 × 10⁶, analytically pure, produced by Tianjin Damao Chemical Reagent Factory; activated carbon: nutshell-based, first-class product, carbon element mass fraction not less than 21%, average particle size 3mm, produced by Shenyang Chemical Reagent Factory; iron shavings: iron shavings in a mold processing workshop of a heavy machinery factory, which are irregularly curled. Wastewater: fracturing wastewater from CNOOC's operation area. See Table 1 for wastewater quality [3].

| colour          | Density / (g · cm⁻³) | pH  | BOD₅ / (mg · L⁻¹) | COD / (mg · L⁻¹) |
|-----------------|----------------------|-----|-------------------|------------------|
| Deep yellow     | 1.12                 | 6.6 | 1435              | 3116.0           |
| Turbidity / NTU | Chroma / degree      |     |                   |                  |
| 106             | 420                  | 70.38 | 4.31               | 3980             |

3.2. Micro electrolysis experiment
Before filling with iron filings, wash with 4% (w) NaOH solution repeatedly to remove oil, and then soak and activate with 4% (w) dilute hydrochloric acid for 40 min to remove surface oxides. Activated carbon needs to be soaked in wastewater for 72 hours before use to reduce the effect of adsorption on the experiment. According to the previous experimental results, the iron filings and activated carbon were mixed uniformly in a mass ratio of 1:1, and then filled in a self-made cylindrical micro-electrolysis reactor. After adjusting the initial wastewater pH with 4% (w) dilute sulfuric acid, a dynamic experiment was conducted.

3.3. Fenton oxidation experiment
According to site conditions, the Fenton oxidation reaction temperature was set to room temperature (25°C). Take 200mL of micro-electrolysis water with a beaker and adjust the pH of Fenton oxidation with dilute sulfuric acid. Under magnetic stirring, add 30% (w) H₂O₂ solution to perform Fenton oxidation reaction.

3.4. SBR treatment of fracturing wastewater
The SBR pool is made of plexiglass, the size is: length × width × height = 200mm × 100mm × 300mm, the effective volume is 3.5L. The concentration of cultured and domestic sludge in the pond is controlled at about 2500mg / L. The experiment temperature is 20 ~ 25 °C, aeration pump aeration, supernatant is drained by the discharge pipe. Under the experimental conditions, SBR operation includes four stages of instantaneous water inflow, aeration, settlement and drainage, in which the settlement time is 1h, and the appropriate aeration time is determined by the index of COD removal rate [4].

3.5. Results

3.5.1. Fenton oxidation treatment results of oilfield fracturing wastewater: 1) Influence of pH. Adjust the pH value of fracturing wastewater in the range of 2.0 ~ 7.0, add H₂O₂ and FeSO₄ according to the mass concentration of 0.2% (volume fraction) and 20mg / L, react for 10min, and stand for 30min, then take the supernatant to measure its light transmittance and turbidity Degree, the measurement results are shown in Table 2.
Table 2. Effect of wastewater pH on turbidity and light transmittance of fracturing wastewater

| PH  | Turbidity / NTU | Transmittance/% | Experimental phenomena                                      |
|-----|-----------------|-----------------|-------------------------------------------------------------|
| 2.0 | 41.2            | 89.3            | The generated flocs are large and the density is low,        |
|     |                 |                 |                                                             |
| 3.0 | 32.4            | 90.2            | The resulting flocs are large, dense, and sink quickly; the |
|     |                 |                 | supernatant is translucent                                 |
| 4.0 | 39.6            | 87.5            | The flocs generated are small, low density, and sink slowly;|
|     |                 |                 | the supernatant is muddy                                   |
| 5.0 | 118.0           | 60.4            | No obvious change in water                                 |
| 6.0 | 127.0           | 59.0            | No obvious change in water                                 |
| 7.0 | 119.0           | 61.8            | No obvious change in water                                 |

It can be seen from Table 2 that under acidic (pH 2 ~ 4) conditions, the flocs generated in the fracturing wastewater oxidized by Fenton reagent are large, but the pH is different, the density of the generated flocs is different, and the effect is best when the pH is 3. When the pH of the wastewater is higher than 5.0, the treatment effect of Fenton reagent on fracturing wastewater is not obvious, indicating that Fenton reagent has a strong oxidizing ability to fracturing wastewater under acidic conditions. This is mainly because acidic conditions are beneficial to OH in Fenton system. When the pH is too low (<3.0), the rate of Fe²⁺ catalysing the decomposition of H₂O₂ is accelerated, which is beneficial to the generation of O₂, and the concentration of OH⁻ is reduced; when the pH is increased (> 3.0), the rate of H₂O₂ decomposition is slowed down, and OH⁻ is The concentration is reduced. Therefore, the treatment effect is best when the pH is 3.0. Under alkaline conditions, H₂O₂ will self-decompose, and the catalyst Fe²⁺ is converted to [Fe (HO₂)]²⁺ and Fe(OH)₂, which is not conducive to OH⁻. Therefore, when performing Fenton oxidation treatment on the fracturing wastewater, the pH value of the wastewater should be controlled at about 3.0, as shown in Figure 2 is the effect of the initial wastewater pH on the COD removal rate of the micro-electrolysis section.

Figure 2. The effect of initial wastewater pH on the COD removal rate of the micro-electrolysis section

2) The amount of iron filings. Iron filings and activated carbon are added to the fracturing wastewater, which constitutes countless tiny primary batteries, which can undergo electrolytic reactions. The products produced by the electrode reaction react with the organic matter in the wastewater to destroy the molecular structure and change the shape, thereby achieving degradation
and pollution the purpose of the object. When the initial wastewater pH is 3.0 and the micro-electrolysis time is 80 minutes, the effect of iron filings on the COD removal rate in the micro-electrolysis section is shown in Figure 2. It can be seen from Figure 2: With the increase of the amount of iron filings, the COD removal rate increases first and then decreases; when the amount of iron filings increases from 0.5g / L to 1.5g / L, the COD removal rate is the largest, and then there is a certain reduction. Therefore, the optimal amount of iron filings was determined to be 1.5g / L [5].

3.5.2. Fracturing wastewater oxidative flocculation treatment experiment. 1) Screening of oxidants. Taking CODCr removal rate as an indicator, hydrogen peroxide and Fenton reagent are used as oxidants to oxidize the fracturing wastewater, so as to screen out the oxidants that have strong oxidative degradation effect on the organic matter in the wastewater. Since Fenton reagent has a pH of 3.0, and the molar ratio of Fe^{2+} and H_{2}O_{2} should be 0.02 to 0.3, the oxidation effect is better. When using Fenton reagent to treat fracturing wastewater, first adjust the pH of the wastewater to about 3.0.

2) Fenton reagent oxidation-flocculation orthogonal experiment. Using the CODCr removal rate as an indicator, a three-factor three-level orthogonal test was used to study the treatment effect of Fenton reagent H_{2}O_{2}, ferrous sulfate (FeSO_{4}) and PAC dosage on fracturing wastewater, and the results of variance analysis (see Table 3).

| source  | Degrees of freedom | sum of square | AdjSS | AdjMS | F    | P     |
|---------|-------------------|--------------|-------|-------|------|-------|
| FeSO_{4} | 2                 | 59.79        | 59.79 | 29.89 | 13.53 | 0.069 |
| H_{2}O_{2} | 2               | 15.44        | 15.44 | 7.72  | 3.49  | 0.222 |
| PAC     | 2                 | 118.7        | 118.7 | 59.35 | 26.87 | 0.036 |
| error   | 2                 | 4.42         | 4.42  | 2.21  |       |       |

3) Fenton oxidation-flocculation treatment effect of fracturing wastewater. According to the above test results, Fenton oxidation-flocculation treatment was carried out on the fracturing wastewater under the appropriate dosage of FeSO_{4}, H_{2}O_{2}, PAC and PAM of 20mg / L, 0.2%, 70mg / L and 3mg / L, respectively. After the wastewater quality analysis. The CODCr of the treated water was reduced from 4132.9mg / L (down to 1426.9mg / L, the removal rate was high, reaching 65.48%, but the CODCr value was still far higher than the national second-level discharge standard [6].

3.5.3. Optimization of conditions in the flocculation section. Iron-carbon micro-electrolysis and Fenton oxidation result in a large amount of Fe^{2+} and Fe^{3+} in the wastewater, and the iron compound itself is a very good coagulant. Under acidic conditions, iron ions are hydrolysed to form Fe (OH)_{2}^{2+}, Fe (OH)_{3}^{3+}, Fe (OH)_{4}^{4+} and other positively charged polynuclear cations. However, the floes produced by a single iron salt are small and not easy to settle. Usually, when the floes are formed, an appropriate amount of organic polymer flocculant is added to the system, so that the charged particles in the water sample are adsorbed by neutralization, net catching, and bridging Reaction with polynuclear cations produces floes, which removes large particles of pollutants by flocculation to achieve the effect of purifying water quality. The influence of CPAM addition on the COD removal rate of the flocculation section is shown in Figure 3. It can be seen from Figure 3: With the increase of CPAM addition, the COD removal rate increases first and then decreases; when the CPAM addition amount is 120mg / L, the COD removal rate is the highest, reaching 24.6%. Therefore, the optimal CPAM dosage was determined to be 120 mg / L. At this time, the wastewater COD decreased from 903.6mg / L to 681.3mg / L, and the total COD removal rate was 78.1% [7].
4. Conclusion

The compound flocculants used in the treatment of oily wastewater in oilfields are mainly a combination of several inorganic flocculants or inorganic/organic flocculants. In the application of traditional flocculants, flocculants have been added to enhance the flocculation effect. Using activated silicic acid as a coagulant for ferrous sulfate has achieved good results in the treatment of oily wastewater. Polysilicon acid (PSi), as an anionic flocculant, has a strong binding and aggregation ability. Compounding various forms of PSi with cationic Fe salt polymer can enhance its aggregation ability and also improve the stability of PSi.

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