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Study on Advanced Treatment Process for Drilling Wastewater by Fenton Oxidation

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Abstract—Two factors including the dosage rate of H_2O_2 and the interference of Cl^- concentration were analyzed to optimize the Fenton process. Results showed that when the dosage rate of H_2O_2 was at 1mL/min the COD removal efficiency increased by 7% more than that of added instantly; Cl^- concentration had an inhibition effect on Fenton oxidation—when the Cl^- concentration was below 2500mg/L the effect was negligible and the highest COD removal efficiency was up to 92%, which had reached the secondary standards (DB12-356-2008) of Tianjin. It was indicated that the process was an effective method in the advanced treatment of drilling wastewater.

Keywords—Fenton process; $\cdot OH$; COD removal efficiency; Cl^- concentration

I. INTRODUCTION

Fenton oxidation is a common wastewater treatment process. Due to the advantages such as simple equipments, mild reaction conditions, easy operation and no secondary pollution and so on [1-3], Fenton oxidation process is widely used in pre-treatment of wastewater to improve its biodegradability [4] or in advanced treatment to improve its water quality [5], etc. Drilling wastewater was generated from the petroleum exploitation process on oil platform in Dagu bay of Tianjin. It contained complicated organic compounds, extremely high oil concentration and high salinity. Having been treated by “oil separation—flocculation pre-treatment—hydrolytic acidification—aerobic treatment” process, oil and COD load was significantly removed, but some water quality indexes of the effluent still couldn’t reach the discharge standards, so Fenton process was adopted in the experiment as an advanced treatment. Some water quality indexes of the wastewater were enumerated in TABLE I.

TABLE I. SOME WATER QUALITY INDEXES OF THE WASTEWATER

Index	oil concentration [mg/L]	pH	chromaticity [times]	COD [mg/L]	Cl^- [mg/L]
water quality	80	7.08~7.34	87~97	1646~1813	8367~10081
discharge standards	30	6-9	50	60	—

II. EXPERIMENTAL PART

A. materials

Drilling wastewater;

Reagents: 10% $FeSO_4$ solution; 30% H_2O_2 solution; 30% H_2SO_4 solution;

B. methods

Some wastewater (300mL) was put in a 500mL beaker stirred by magnetic stirrer; then a given amount of $FeSO_4$ was put in and regulated pH to acidity(its value was given in the following text); after that, some amount of H_2O_2 given in the text was injected into the solution; keep the mixture interchanging stir and regulated pH to neutral, finely some PAM was added in for getting the clean solution which was used to monitor COD and chromaticity.

III. RESULTS AND DISCUSSIONS

A. Conditions optimization in traditional Fenton process

Four factors include the ratio of H_2O_2/Fe^{2+} , the dosage of H_2O_2 , the initial pH and the oxidation time were investigated to obtain the optimum operating conditions. COD of the wastewater in all of these experiments were monitored and the results were shown in Fig.1.

(a)

(b)

(c)

(d)

Figure 1. The effect of the four factors in the traditional Fenton process on the removal efficiency

Fig.1 (a) showed that the process had the highest COD removal efficiency when the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was at 2:1. Beyond that, the removal efficiency was not high either the concentration of Fe^{2+} was too high or low, for Fe^{2+} was a essential catalyst for H_2O_2 generating $\cdot\text{OH}$. When the concentration of Fe^{2+} was too low, the reaction given in Eq. (1) responded slowly and less $\cdot\text{OH}$ were produced,

so Fenton process had a poor oxidation effect; on the other hand, high Fe^{2+} concentration caused swift decomposition of H_2O_2 and amount of $\cdot\text{OH}$ became O_2 before they oxidized

organic compounds in the wastewater, which could be verified by the phenomenon that lots of bubbles emitted from the beaker. On the other hand, the chromaticity was greatly removed and almost had no relation with the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, so in the following optimum experiments COD removal was discussed only. And the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was kept at 2:1.

Fig.1 (b) indicated that the COD removal efficiency increased gradually with the increasing dosage of H_2O_2 ; while the dosage was up to 8.2mL/L, the COD removal efficiency reached 43%.

It could be indicated from Fig.1 (c) that the optimum initial pH was 3 or 4 and took 4 considering the economic factors. In addition, the COD removal efficiency declined as pH increased or decreased, for in acidic solution the oxidation ability of $\cdot\text{OH}$ was so fortissimo that it could easily oxidize many difficultly decomposed organic substances which could be described as the following:

$\cdot\text{OH}$ reacted rapidly with organic substances in the wastewater and the rate constant was about $10^8 \sim 10^{10} \text{ mol}\cdot\text{s}^{-1}$, on the other hand, the stability of $\cdot\text{OH}$ could be strengthened in fortissimo acidic environment and correspondingly its oxidation ability declined, as a result, the removal of COD declined too.

Fig.1 (d) reflected the effect of the oxidation time on COD removal. It showed that Fenton process had a quick rate within 2h and the COD removal efficiency kept increasing as times elapsed. When the oxidation time was over 3h, the efficiency no longer changed.

The COD removal efficiency under the optimum conditions was merely about 45%. So optimization experiments were carried out to optimize the Fenton process in two respects, the dosage rate of H_2O_2 and the interferences of Cl^- in the solution respectively.

B. Optimization of dosage rate of H_2O_2

The dosage rate of H_2O_2 strongly influenced Fenton process efficiency. Experiments were carried out with different dosage rate of H_2O_2 and the COD were monitored which was showed in TABLE II and Figure 2.

TABLE II. OPTIMIZATION EXPERIMENTS ON OXIDATION TIME

serial number	1	2	3	4	5	6	7
dosage rate of H_2O_2 [mL/min]	added instantly	0.5	1	2	4	6	8
COD [mg/L]	955	809	814	831	877	899	928
COD removal efficiency [%]	43.0	51.7	51.4	50.5	48.8	46.3	44.0

Figure 2. The effect of the dosage rate of H₂O₂ (a) and the dilution times on the removal efficiency of COD

Results showed that the COD removal efficiency declined as the dosage rate of H₂O₂ increased at the beginning. When H₂O₂ was added quickly in, most ·OH could generate ·OH in the catalysis of Fe²⁺, however, overquick dosage rate of H₂O₂ caused maldistribution of H₂O₂, which reacted with ·OH [6]:

The reactions consumed some H₂O₂ and ·OH, so the COD removal efficiency declined; when the dosage rate of H₂O₂ was between 0.5 and 1 mL/min, most H₂O₂ reacted with Fe²⁺ and the COD removal efficiency was raised about 52%. When the dosage rate of H₂O₂ was controlled at 1 mL/min the COD removal efficiency could be increased by 7% more than that of injected instantly and the effluent COD load was about 815 mg/L, which still hadn't reached the discharging standard. The reason of the low efficiency might be repressed by the high Cl⁻ concentration in the wastewater. The Cl⁻ which could reacted easily with ·OH, would inhibit Fenton process [7]. The process could be described in (6) and (7).

Cl⁻ could contest for ·OH with organic compounds in the wastewater, as a result, some ·OH couldn't oxidize organic compounds and the effect of Fenton process was restrained. On the other hand, Cl⁻ could react with Fe³⁺ and generate complex compounds:

These complex compounds of Fe³⁺ could neither react with H₂O₂ nor be reduced to Fe²⁺, so they restrained the generation of ·OH and the effect of Fenton process [8].

In order to reduce the inhibiting effect of Fenton, the drilling wastewater was diluted by domestic sewage to reduce the Cl⁻ concentration.

C. The influence of the Cl⁻ concentration

The wastewater was diluted multiple by the domestic sewage with other factors fixed as followed: H₂O₂/COD=2, H₂O₂/Fe²⁺=2:1, the initial pH=4, the oxidation time=3h, then COD and chromaticity of the effluent were monitored and shown in TABLE III and Figure3.

Results in Fig.3 showed that when the wastewater was diluted by 1 times, the COD removal efficiency increased slowly, which indicated that the inhibition effect of Cl⁻ (the concentration was 5000mg/L) was still prominent; as the increasing of the dilution times, the inhibition effect of Cl⁻ got weaken and the COD removal efficiency increased correspondingly; when the dilution times was larger than 3, the COD removal efficiency increased significantly, it raised

TABLE III. THE EFFECT OF THE DILUTION TIMES ON FENTON PROCESS

serial number	1 #	2 #	3 #	4 #	5 #	6 #	7 #
dilution times	0	1	2	3	4	5	6
COD before oxidation[mg/L]	1674	837	558	419	335	279	239
chromatics before oxidation [times]	92	46	31	23	18	15	13
dosage of H ₂ O ₂ [mL/L]	8.2	4.1	2.7	2.0	1.6	1.4	1.2
dosage of FeSO ₄ ·7H ₂ O [g/L]	13.69	6.85	4.56	3.42	2.74	2.28	1.96
COD[mg/L]	815	386	130	33	25	18	14
COD removal efficiency [%]	51.3	53.9	76.7	92.1	92.5	93.5	94.1
chromatics[times]	15	7	5	4	2	—	—
chromatics removal efficiency[%]	84	85	83	83	89	99	99

Figure 3. The effect the dilution times on the removal efficiency of COD

over 92% and the COD of the effluent was below 60mg/L; but kept diluting, the COD removal efficiency was stable. Experiment results showed that the optimum dilution times of the effluent was 3; the Cl^- concentration would be about 2500mg/L.

IV. CONCLUSIONS

- 1) In the traditional Fenton process, the optimum reaction conditions were ascertained: the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was 2:1, the dosage of H_2O_2 was 8.2mL/L, the initial pH was 4, the oxidation was 3h and the COD removal efficiency was about 45% .
- 2) The dosage rate of H_2O_2 affected the Fenton process to a certain extent. When the rate was 1mL/min, the COD removal efficiency was about 52%, 7% higher than that of the traditional process.
- 3) The Cl^- concentration in the drilling wastewater affected the Fenton process strongly: when the concentration was more than 2500mg/L, the inhibition effect was prominent; when the concentration was below 2500mg/L, the effect was negligible. Under this condition the COD removal efficiency was over 92% and COD of the effluent could be below 60mg/L, which had reached the secondary standards (DB12-356-2008) of Tianjin. The Fenton process was proved to be an effective advanced process to treat the drilling wastewater.

ACKNOWLEDGMENT

This work was financed by Tianjin education committee

(Grant no. SW 2008 0001). The study on technology of pollutant treatment and its comprehensive utilization for high yield pulp cotton stalk and paper making.

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