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Application Of Magnetic-Assistant Fenton Reagent For Treatment Of Surfactant Simulative Wastewater



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ABSTRACT

The treatment of surfactant simulative wastewater by magnetic-assistant Fenton reagent system has been studied under different magnetic-assistant reaction time and the optimum dosage of Fenton reagent. The results showed that the removed rate of COD_{Cr} was 15% under the existence of magnetic field better than without the existence of magnetic field. © 2006 Trade Science Inc. - INDIA

KEYWORDS

Magnetic-assistant;
Fenton reagent;
Sodium dodecylbenzene;
Sulfonate.

INTRODUCTION

Environment was largely harmed by the surfactant. The foam was easily formed by the anion detergent in water. It debased the velocity and degree of reaeration. It made fish death or malformation. When its concentration was 10 mg·L⁻¹, the harvest of the rice decreased 50%. When its concentration was 45 mg·L⁻¹, all of rice was killed and nothing was harvested. Sodium dodecylbenzene sulfonate (DBS) which was hardly degraded by biochemical method was degradations, H₂O₂ was oxidant, FeSO₄·7H₂O was catalyst, magnetic field was the added field. The

effect and efficiency which the DBS was degraded by magnetic-assistant Fenton reagent catalytically oxidation method was researched. The mechanism of magnetic field co-operative effect was theoretically discussed.

EXPERIMENTAL

Instruments and reagents

Magnetic force mixer (Shandong, China), quick director for COD_{Cr} (Beijing, China), 30% H₂O₂ (AR), FeSO₄·7H₂O (AR), KC-70C magnetizer (Shanghai, Chian), SXG-1B teslameter (Shanghai, Chian)

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Simulative Wastewater

The simulative wastewater was confected by DBS and the distilled water. Its COD_{Cr} was 320 mg·L⁻¹ and concentration was 200 mg·L⁻¹.

TABLE 1: The quality of raw wastewater

Concentration (mg·L ⁻¹)	Chroma (times)	COD _{Cr} (mg·L ⁻¹)	pH value
200	0	320	5~6

Method

The experiment were performed in 250mL beakers according to the following steps:(1)take 100mL simulative DBS wastewater in a 250mL beaker on a stirred; (2) regulated the pH value of the aqua; (3) add definite dosage of FeSO₄·7H₂O and turn on the stirrer; (4) drip 30% H₂O₂ solution into the simulative DBS wastewater. After reaction had completed, regulated the pH value of the aqua to alkalescence, deposited some time, filtered the aqua and took the pure liquid to measure the COD_{Cr}.

The magnetic-assistant oxidation experiment was same to last. The discrimination was that the beaker of the kind of water was clipped in magnetic field in the magnetic-assistant oxidation experiment. The influence of the productivity and productive rate of hydroxyl radical was studied.

The influencing factors which affected the rate of COD_{Cr} removal were researched. These factor

included the dosage catalyst and oxidant, pH value, reaction time, magnetic-assistant reaction time, intensity of magnetic field.

Method of analysis

The removed rate of COD_{Cr} could be calculated by the formula as following:

$$\text{Removed rate of COD}_{Cr} = \left(1 - \frac{\text{COD}_{Cr}}{\text{COD}_{Cr_0}}\right) \times 100\%$$

Note: COD_{Cr₀}, COD_{Cr} respectively denoted chemical oxygen demand (K₂Cr₂O₇) of DBS simulative wastewater before and after treatment.

RESULT AND DISCUSSIONS

All kinds of influential factors of removal COD_{Cr} by common Fenton reagent

The main influential factors were dosage of H₂O₂, dosage of FeSO₄·7H₂O, pH and oxidation time.

1. Effect of the dosage of H₂O₂ on COD_{Cr} removal

100mL sample, the dosage of FeSO₄·7H₂O was 300mg, pH value was 3, oxidation time was 90 min, change the volume of H₂O₂

From figure 1, it can be seen that removed rate of COD_{Cr} reached 86.9% when the volume of H₂O₂ was 0.5mL. On the contrary the removed rate of COD_{Cr} descended when the volume of H₂O₂ was

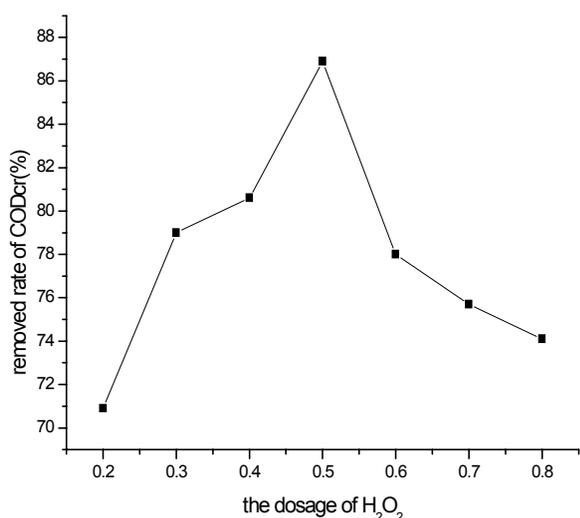


Figure 1: Effect of H₂O₂ dosage on COD_{Cr} removal

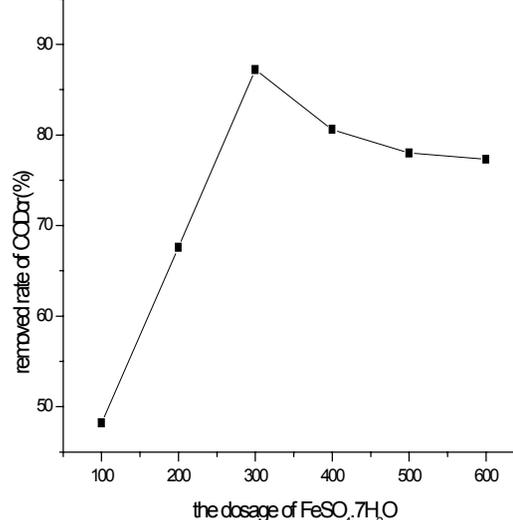


Figure 2: Effect of FeSO₄·7H₂O dosage on COD_{Cr} removal

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continuously increased. The reason was that when volume of H_2O_2 was low, increased volume of H_2O_2 made concentration of $\bullet OH$ which was generated by H_2O_2 increased. But when volume of H_2O_2 was high, superfluous H_2O_2 did not generate more $\bullet OH$ and Fe^{2+} was oxidized to Fe^{3+} in the beginning. It made the oxidation reaction was catalyzed by Fe^{3+} not Fe^{2+} . On the one hand volume of H_2O_2 was consumed and generation of $\bullet OH$ was restrained, on the other hand CODcr of filtrate was increased because of reducibility of H_2O_2 ^[2]. According to these reasons, the optimum volume of H_2O_2 was 0.5mL.

2. Effect of the dosage of $FeSO_4 \cdot 7H_2O$ on CODcr removal

100mL sample, the volume of H_2O_2 was 0.5mL, pH value was 3, oxidation time was 90 min, change the dosage of $FeSO_4 \cdot 7H_2O$.

It was essential to generate $\bullet OH$ which was catalyzed by Fe^{2+} . Under no Fe^{2+} conditions, H_2O_2 hardly generated $\bullet OH$. Reaction speed of $Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + \bullet OH + OH^-$ was very slow when concentration of Fe^{2+} was very low. Therefore dosage of $\bullet OH$ was very small, reaction speed was very slow and degradation was restrained. When the dosage of Fe^{2+} was superfluous, it could deoxidize H_2O_2 and it was oxidized to Fe^{3+} . On the one hand superfluous Fe^{2+} consumed H_2O_2 , on the other hand it increased chromaticity of filtrate^[2]. From Fig.2, it can be seen that the removed rate of CODcr reached 87.2% when the dosage of $FeSO_4 \cdot 7H_2O$ was 300mg. On the contrary total removed rate of CODcr descended when the dosage of $FeSO_4 \cdot 7H_2O$ was continuously increased. The reason was that CODcr of filtrate was increased because of reducibility of Fe^{2+} . According to these reasons, the optimum the dosage of $FeSO_4 \cdot 7H_2O$ was 300mg.

3. Effect of oxidation time on CODcr removal

100mL sample, the volume of H_2O_2 was 0.5mL, the dosage of $FeSO_4 \cdot 7H_2O$ was 300mg, pH value was 3, change oxidation time.

From figure 3, it can be seen that removed rate of CODcr reached 86.5% when oxidation time was 60 min. It also can be seen that removed rate of CODcr increased indistinctively when oxidation time was increased. According to practical application

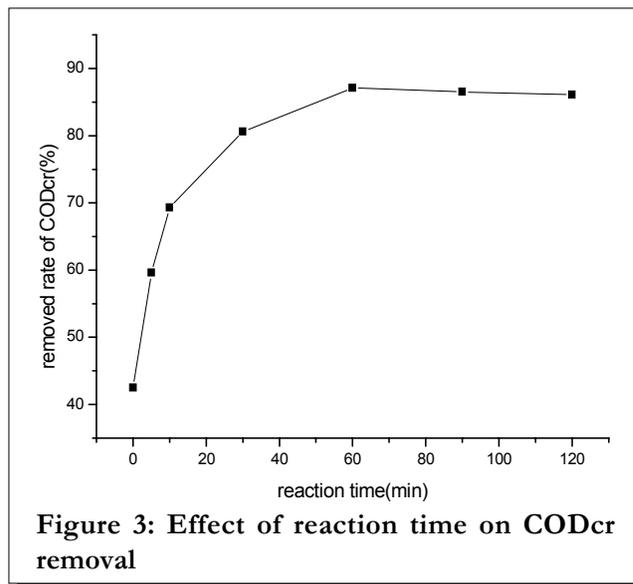


Figure 3: Effect of reaction time on CODcr removal

and economic aspects, the optimum oxidation time was 60 min.

4. Effect of pH on CODcr removal

100mL sample, the volume of H_2O_2 was 0.5mL, the dosage of $FeSO_4 \cdot 7H_2O$ was 300mg, oxidation time was 60 min, change pH value.

Under the acidic condition, Fe^{2+} catalyzed H_2O_2 produced $\bullet OH$. But under the neutral or alkaline condition Fe^{2+} did not catalyze H_2O_2 produced $\bullet OH$. According to classical Fenton reagent theory, the generation of $\bullet OH$ was restrained because of pH value being increased and Fe^{2+} existed in form of $Fe(OH)_2$ with pH value being continuously increased, Fe^{2+} lost its catalysis. When pH value under 3, reaction of $Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + \bullet OH + OH^-$ was restrained when concentration of H^+ was very high. Catalytic reaction was restrained because $Fe(III)$ was not deoxidized to $Fe(II)$ namely Fe^{2+} and Fe^{3+} of coordination balance system was directly destroyed by changing pH value. It weakened the oxidation of Fenton reagent^[2]. From figure 4, it can be seen that removed rate of CODcr reached the highest point when pH value was 3. But removed rate of CODcr obviously descended with pH value continuously being increased. The reason was that under pH value being 3 condition, composition of ferryl iron was created and it was the actually catalytic ingredient in the Fenton reagent reaction^[3].

5. Effect of the added sequence of oxidant, cata-

TABLE 2: Effect of the addition order of pH, catalyst and oxidant on COD_{Cr} removal

Added sequence	Firstly regulated pH value finally added the oxidant and catalyst	Firstly added the oxidant and catalyst finally regulated pH value
Removed rate of COD _{Cr} (%)	94.6	87.1

TABLE 3: Effect of the addition order of catalyst and oxidant on COD_{Cr} removal

Added sequence	Firstly regulated pH value finally added the oxidant and catalyst	Firstly regulated pH value finally added the catalyst and oxidant
Removed rate of COD _{Cr} (%)	94.6	94.2

lyst and pH value on COD_{Cr} removal

100mL sample, the volume of H₂O₂ was 0.5mL, the dosage of FeSO₄·7H₂O was 300mg, oxidation time was 60 min, pH value was 3, change the sequence of oxidant, catalyst and pH value

From TABLE 2, it can be seen that removed rate of COD_{Cr} reached 94.6% when pH value was firstly regulated, the oxidant and catalyst was finally added. It was higher 7.5% than which the oxidant and catalyst was firstly added, pH value was finally regulated. The reason was that the hydrolysis of FeSO₄·7H₂O was restrained in the acidic condition. It can exerted its catalysis in maximum.

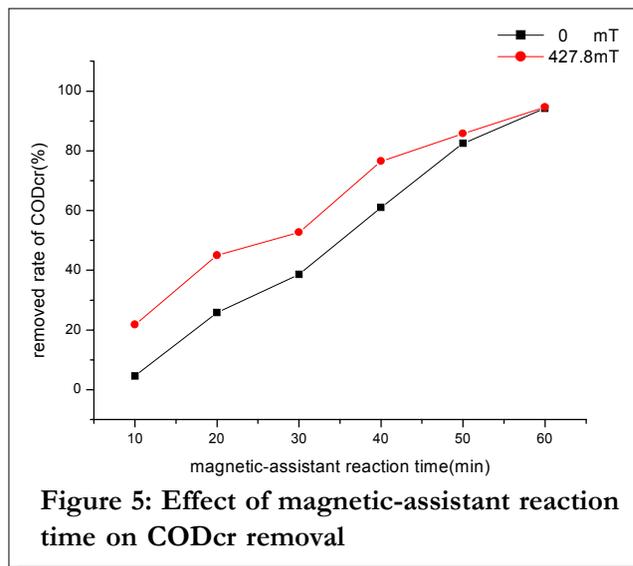
From TABLE 3, it can be seen that removed rate of COD_{Cr} reached the close value when pH value was firstly regulated, the added sequence of oxidant and catalyst was changed. The result showed that the added sequence of oxidant and catalyst was not affected removed rate of COD_{Cr} if pH value was firstly regulated.

Magnetic-assistant oxidation experiment

1. Effect of magnetic-assistant reaction time on COD_{Cr} removal

100mL sample, the volume of H₂O₂ was 0.5mL, the dosage of FeSO₄·7H₂O was 300mg, pH value was 3, intensity of magnetic field was 427.8mT, change magnetic-assistant reaction time

From figure 5, it can be seen that removed rate

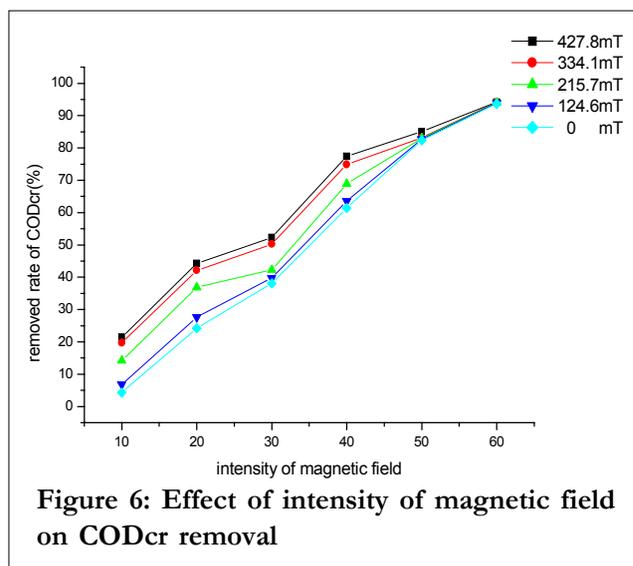


of COD_{Cr} in intensity of magnetic field being 427.8mT was higher than that without magnetic field at different magnetic-assistant reaction time. But with the magnetic-assistant reaction time increasing, removed rate of COD_{Cr} in intensity of magnetic field being 427.8mT was close to which without magnetic field. The result showed that the productive rate of hydroxyl radical was improved, but the productivity of hydroxyl radical was not improved.

2. Effect of intensity of magnetic field on COD_{Cr} removal

100mL sample, the volume of H₂O₂ was 0.5mL, the dosage of FeSO₄·7H₂O was 300mg, pH value was 3, change the intensity of magnetic field

From figure 6, it can be seen that removed rate



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of COD_{Cr} increasing with the intensity of magnetic field increasing at different magnetic-assistant reaction time. But with the magnetic-assistant reaction time increasing, removed rate of COD_{Cr} in different intensity of magnetic field were close to each other. The result showed that the productive rate of hydroxyl radical from Fenton reagent increased when the intensity of magnetic field was augmented.

Mechanism

The hydroxyl radical was formed by the Fe²⁺ and H₂O₂ quick reaction. It had strong oxidation ability. When Fe³⁺ existed, Fe³⁺ slowly reacted with H₂O₂ formed Fe²⁺, then in succession Fe²⁺ quickly reacted with H₂O₂ formed •OH. The newly formed •OH had strong oxidation ability which electrolyzed oxidizing was 2.8V. It was only lower than F₂ which electrolyzed oxidizing was 2.87V.

DBS was the ramifications of benzene. It with passive groups was difficultly oxidized by the normal oxidant. But •OH could quickly oxidize them. Its velocity of oxidation was quicker than only H₂O₂. The reason was that under the acidic condition Fenton reagent rapidly generated •OH. It had a stronger oxidation which could effectively decompose organic pollutions. The conjectural oxidation procedure was as follows: First, the passive groups of intermediates were substituted by •OH, it made aromatic rings active. Then the aromatic rings were decomposed and generated low fatty acid compounds. At last they were turned into CO₂ and H₂O.

A lot of study about UV-Fenton system was reported and it was applied in practice. The electrical Fenton which based on Fe/C micro-electrolysis technology was attached importance to because of its broadly application range and low cost. But wastewater was not treated by magnetic-assistant advanced oxidation technology. For example magnetic-assistant Fenton reagent was not reported.

Hydroxyl radical was obviously affected by magnetic field. It was found by people long before. Forming hydroxyl radical reaction was the main reaction in Fenton oxidation reaction, so magnetic-assistant Fenton reagent method was speculated to improve the velocity of oxidation degradation of contamination and didn't consume excess electric resource. But

UV or ultrasonic needed added electric resource, so magnetic-assistant Fenton reagent method was easily applied.

Under not sur-magnetic field condition, a magnetic field which being from the molecular interior (is called partial magnetic field) could provide the magnetic moment for the change of the spinning condition of the free radical. Under sur-magnetic field condition, the Larmor spinning velocity of the spinning vector of the free radical can be changed. The difference of the spinning velocity of two spinning vectors ($\Delta\omega$) can be expressed by the formula^[4].

$$\Delta\omega = \left(\frac{\Delta g \mu_B H_0}{h} \right) \pm (a_1 - a_2) I$$

In the formula, $\Delta g = |g_1 - g_2|$, g_1 , g_2 respectively notes the g value of two free radicals alone electron, g value is related with the system nature, μ_B is a Bohr's magneton, h is the Planck constant, H_0 is the intensity of sur-magnetic field, a_1 , a_2 are ultra fine coupling constants of two free radicals, I is the nuclear spin quantum number. The transformation speed which the two spinning vectors of free radicals from S state to T₀ state is decided by $\Delta\omega$ value. According to above formula, the above transformation speed can increase with Δg or H_0 enhancing^[5]. Speaking of the DBS simulative wastewater, Δg is a definite value in the microscopic structure, therefore the difference of the Larmor spinning velocity ($\Delta\omega$) is only decided by the intensity of macroscopic sur-magnetic field. According to Δg mechanism, the bigger H_0 will be, the shorter transformation time from S state to T₀ state will be, the quicker transformation speed from S state to T₀ state will be, Namely the more little singlet state total will be, the smaller possibility of re-combination will be, the quicker the rate of chemical reaction will be. This is the degeneration process mechanism of magnetic Fenton reagent.

CONCLUSIONS

- (1) The added magnetic field improved the productive rate of hydroxyl radical, but didn't improve the productivity of hydroxyl radical from Fenton reagent.
- (2) The productive rate of hydroxyl radical from

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TABLE 4: Index of sample before and after treatment

Index	COD _{Cr} (mg·L ⁻¹)	pH
Original sample	320	5~6
Fenton reagent oxidation	18.6	7
Magnetic-assistant Fenton reagent oxidation	17.3	7

Fenton reagent increased with the intensity of magnetic field augmenting.

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