Original Article

Studies on affecting factors and mechanism of oily wastewater by wet hydrogen peroxide oxidation

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Abstract Wet hydrogen peroxide oxidation of oily wastewater is performed in a batch reactor at reaction temperature between 280 °C and 320 °C, the reaction time between 30 and 90 min. Effect of reaction parameters such as reaction time, reaction temperature, H2O2 excess (HE) and initial concentration of oily wastewater is investigated. The results of orthogonal test indicate that reaction temperature is the main factor and the reaction time is the secondary factor. When the reaction temperature is 300 °C, initial concentration of oily wastewater is 1160 mg/L, the reaction time is 30 min, HE is 0.75 and the COD removal of oily wastewater could reach 70%. It will not produce pollutants and it complies with the cleaner production. The preliminary study of mechanism on oily wastewater by WPO is carried out. The result indicates that oily wastewater by WPO can be explained by free radical mechanism.

1. Introduction

With industrial development, increasing the amount of oil used, but due to various technical and management development lags behind other reasons are not perfect makes a lot of oil into the water, forming pollution. Oily wastewater source is very broad, the oil in the oil industry, oil refining, oil storage, transportation and petrochemical industries in the production process will generate a lot of oily wastewaters (Ahmed et al., 2007; Machín-Ramírez et al., 2008; Chen and He, 2003). Oily wastewater pollution is mainly manifested in the following aspects:

(1) Affecting drinking water and groundwater resources, endangering aquatic resources; (2) endangering human health; (3) atmospheric pollution; (4) affecting crop production; (5) destructing the natural landscape, and even probably because of coalescence of the oil burner safety issues arising. Given oily wastewater pollution China provides the maximum allowable emission of oily wastewater concentration of 10 mg/L. Therefore, oily wastewater treatment is urgently needed in today's field of environmental engineering problems. Oily wastewater
treatment does not have mature technology to be followed, which is an environmental protection problem of problematic petroleum enterprises. Therefore, finding the technology of oily wastewater treatment can help them overcome their difficulties, and also seek an effective treatment method for highly concentrated and refractory wastes.

Wet hydrogen peroxide oxidation (WPO) is a kind of advanced oxidation technology developed on the basis of wet air oxidation (WAO). The WPO technology uses hydrogen peroxide as oxidant and is carried out under mild conditions; therefore energy consumption and equipment intensity can be reduced. It has gained a wide attention of scholars at home and abroad in recent years (Qiao et al., 2007; Li et al., 2007; Tang et al., 2006; Carriazo et al., 2005; Neamtu et al., 2004). This paper studies the oily wastewater treatment by WPO, and explores the optimum reaction conditions for oily wastewater by WPO with orthogonal experiment. Finally, reaction mechanism of oily wastewater by WPO is analyzed, which will provide guidance for subsequent catalytic wet hydrogen peroxide oxidation.

2. Experiment

2.1. WPO experiment

WPO experiments were carried out in the reactor as described in Fig. 1. The required quantity of H$_2$O$_2$ (2 mL) was then delivered into the reactor using a high-pressure pump. Samples were withdrawn at pre-determined time periods (1 min, 3 min, 5 min, 7 min and 9 min). The general setup of the system including the WPO reactor is shown in Fig. 1.

2.2. Analytical methods

The diluted sludge and COD of the collected liquid are measured by the potassium dichromate method of Chinese Standard 11914–89. The O$_2$ excess (OE) is defined as Eq. (1) (Cocero et al., 2002) and HE is defined as Eq. (2).

\[
OE = \frac{(O_2)_{in} - (O_2)_{stoichiometric}}{(O_2)_{in}} \times 100
\]

\[
HE = \frac{(H_2O_2)_{in} - (H_2O_2)_{stoichiometric}}{(H_2O_2)_{in}} \times 100
\]

3. Results and discussion

3.1. Results of the orthogonal test

Four parameters such as reaction temperature (A), initial concentration of oily wastewater(B), reaction time (C) and HE (D) are selected, and each factor is selected for three different levels, they are 280, 300, 320 °C; 1000, 1080, 1160 mg/L; 30, 60, 90 min; 0, 0.75, 0.86. The experiment is carried out by L$_9$(3$^4$) orthogonal table shown in Table 1.

As can be seen in Table 1, when the reaction temperature is 300 °C, initial concentration of oily wastewater is 1160 mg/L, the reaction time is 30 min, HE is 0.75, and COD removal of oily wastewater could reach 70%. When the reaction temperature is 300 °C, initial concentration of oily wastewater is 1080 mg/L, the reaction time is 90 min, HE is 0, and the COD removal of oily wastewater could reach 60%. Experimental parameters influencing on COD removal by range analysis in orthogonal experiment were concluded, and the order is that reaction temperature > reaction time > HE > initial concentration of oily wastewater.

4. Discussion

WPO process is carried out via considering water as the medium and physical properties of water and hydrogen peroxide change under high temperature and high pressure. Hydrogen peroxide is decomposed into oxygen. Solubility of the oxygen decreases with the rise of temperature from room temperature.


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to 100 °C, but oxygen of this nature changes under high temperature condition. When the temperature is more than 150 °C, oxygen solubility increases with the rise of temperature instead, and its solubility is more than the solubility under temperature condition. Meanwhile, the mass transfer coefficients of oxygen in water also increase with the temperature increasing. Therefore, oxygen of this nature will be beneficial to the oxidation reaction under high temperature.

We can conclude experimental parameters influencing on COD removal by range analysis in orthogonal experiment, and the order is that reaction temperature > reaction time > HE > initial concentration of oily wastewater. Its possible causes are that increasing temperature will lead to reaction rate constant greater during the WPO process, which is helpful for decomposition of organic compounds. Oily wastewater is quickly decomposed into CO2 and H2O with the reaction time increasing. When HE increases, it can make oxygen concentrations relatively increasing. It is beneficial to oxidation reaction from the reaction kinetics. The initial concentration of oily wastewater is higher; it is easier to oxidate and decompose. Organic compounds are completely oxidized into CO2 and H2O using the WPO method to treat oily wastewater, and inorganic hybrid element forms inorganic salts and settles at the bottom of reactor.

5. Mechanism

Wang Jin (2007) advocated the reaction mechanism of WPO is the same as WAO, they are radical reactions. The reaction mechanism of WPO is below:

$$\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\cdot\text{OH} \quad (3)$$

M is a homogeneous boundary or heterogeneous boundary.

$$\text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{O}_2 \quad (4)$$

$$\text{RH} + \cdot\text{OH} \rightarrow \cdot\text{R} + \text{H}_2\text{O} \quad (5)$$

$$\cdot\text{R} + \text{O}_2 \rightarrow \cdot\text{ROO} \quad (6)$$

$$\cdot\text{ROO} + \text{RH} \rightarrow \cdot\text{ROOH} + \cdot\text{R} \quad (7)$$

Peroxide is usually decomposed to small molecule compounds, and the rupture promptly carries out then stops until generating formic acid or acetic acid. Formic acid or acetic acid is converted to CO2 and H2O finally. It is generally thought that Eq. (5) is the rate determining step.

When hydrogen peroxide is in redox reaction, the reaction is below:

$$\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\cdot\text{OH} \quad (8)$$

M is a homogeneous boundary or heterogeneous boundary. Generated .OH has a very strong oxidation, and it can react with organic compounds then is oxidized, so it plays a critical role in the whole oxidation process (Lee, 1996). In addition, Takagi and Ishigure (1985) speculate that decomposition reaction of hydrogen peroxide is under the following pathway:

$$\text{H}_2\text{O}_2 \rightarrow 2\cdot\text{OH} \quad (9)$$

$$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{HO}_2 \quad (10)$$

$$\cdot\text{OH} + \cdot\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \cdot\text{O}_2 \quad (11)$$

$$\cdot\text{OH} + \cdot\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \cdot\text{O}_2 \quad (12)$$

It is seen that oxygen is one product of hydrogen peroxide. At the same time, there are reactions below in oxygen and water systems (Tsang and Hampson, 1986).

$$\text{H}_2\text{O} + \text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{HO}_2 \quad (13)$$

$$\cdot\text{OH} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}_2\text{O}_2 \quad (14)$$

$$\text{H}_2\text{O}_2 + \text{O}_2 \rightarrow \cdot\text{HO}_2 + \cdot\text{HO}_2 \quad (15)$$

It is seen that oxygen and water can also generate hydrogen peroxide by reaction. That means whatever initial state is the system of O2 and H2O or H2O2 and H2O, it will be transformed into a mixing system. To sum up, free radical reaction mechanism can explain the process of grease compounds in the oxidation and degradation by WPO very well.

6. Conclusions

The primary objective of this work was the studies on affecting factors and mechanism of oily wastewater by WPO. The main results obtained are the following:

Oily wastewater is selected and its decomposition by WPO is investigated. When the reaction temperature is 300 °C, initial concentration of oily wastewater is 1000 mg/L, the reaction time is 10 min, HE is 4 and the COD removal of oily wastewater could reach 70%. Organic compounds can be completely oxidized to CO2 and H2O. It will not produce pollutants and it complies with the cleaner production.

We can conclude experimental parameters influencing on COD removal by range analysis in orthogonal experiment, and reaction temperature is the main factor then the reaction time is the secondary factor. Oily wastewater by WPO can be explained by free radical mechanism.

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References