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Treatment of Oily Wastewater with WPO and CWO

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ABSTRACT. Petroleum refining unavoidably generates large volumes of oily wastewater. The environmentally acceptable disposal of oily wastewater is a current challenge to the petroleum industry. Nowadays, more attentions have been focused on the treatment techniques of oily wastewater. Oily wastewater contained highly concentrated and toxic organic compounds. Wet peroxide oxidation (WPO) and catalytic wet oxidation (CWO) were applied to eliminate pollutants to examine the feasibility of the WPO/CWO of oily wastewater. The results indicated that more than 80% chemical oxygen demand (COD) removal from oily wastewater was achieved with CWO. Homogenous catalyst, $NaHCO_3$ and Na_2CO_3 and NaOH showed effective removal for pollutants in oily wastewater. Greater than 90% COD removal was achieved with WPO. It was concluded that WPO was a far more effective process for oily wastewater.

Key words: Oily wastewater, COD removal, Catalytic wet oxidation, Wet peroxide oxidation

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 sources 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 wastewater.[1–3] 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 from.[4–5] Given oily wastewater pollution and 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.

The CWO process removes organics by oxidising them to carbon dioxide and water, in the liquid phase, using oxygen or air in the presence of a catalyst. The addition of catalysts decreases the operating conditions, enhances the reaction rate, and shortens the reaction time.[6,7] A significant amount of research has been conducted on CWO and the development of catalysts for use in CWO over the last three decades.[8–18] But the use of alkali in CWO is few.[19–21] While the WPO process involves complete oxidation of organics in the liquid phase using hydrogen peroxide.[22] A number of studies have been carried out on WPO.[23–26]

The main aim for this paper is to investigate the removal of organics from oily wastewater with CWO and WPO. CWO of oily wastewater was investigated in detail to determine the effect of alkali, including NaOH, $NaHCO_3$ and Na_2CO_3. The effects of the operating condition on WPO of the oily wastewater, including temperature, initial COD, H_2O_2 excess (HE) and residence time, were studied.

EXPERIMENTAL

Materials and Methods

CWO experiments

CWO of the oily wastewater was carried out in a 0.6 L batch autoclave (*Fig.* 1). Firstly, water and oily wastewater was put into the reactor, and then the system was flowed by nitrogen to remove the air within the system; the valves around the reactor were closed when the air was removed entirely. Secondly, a specific amount of required catalyst (NaOH, $NaHCO_3$ and Na_2CO_3) was put into the reactor. Finally, pure O_2 was put into the reactor until the predefined pressure was reached, and the reaction started. Liquid samples (ca.15 mL) were periodically withdrawn from the reactor and analyzed.

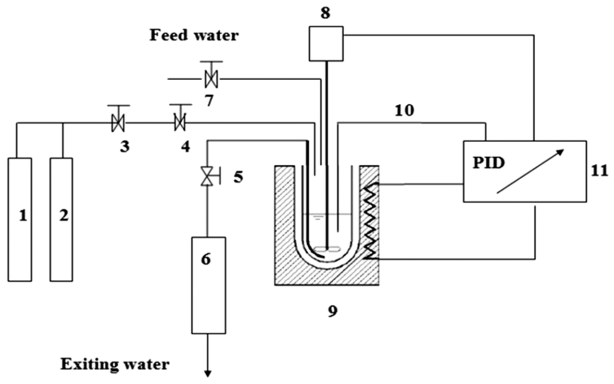

Figure **1.** Schematic diagram of the experimental setup.

WPO experiments

WPO experiments were carried out in the same reactor as described above using the same volume of oily wastewater. The required quantity of H_2O_2 was then delivered into the reactor using a high-pressure pump. Samples were withdrawn at pre-determined time periods.

Analytical methods

The COD of collected liquid are measured by potassium dichromate method of Chinese Standard 11914-89. HE is defined as equation 1.

$$HE = H_2O_{2,Excess} = \frac{(H_2O_2)_{in} - (H_2O_2)_{stoichiometric}}{(H_2O_2)_{in}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Catalytic Wet Oxidation of Oily Wastewater

Alkali catalyzed wet oxidation of oily wastewater

It is seen that from *Fig*. 2, concentration of NaOH, $NaHCO_3$ and Na_2CO_3 increased COD removal. The maximum COD removal was 88.70%, 83.90%, 80.60% in the presence of NaOH as opposed to 50.35% without adding NaOH, $NaHCO_3$ and Na_2CO_3. It is indicated that NaOH, $NaHCO_3$ and Na_2CO_3 are effective for remove a significant amount of COD in oily wastewater.

For oily wastewater treatment with the catalyst, during the process, NaOH, $NaHCO_3$ and Na_2CO_3 may promote the reaction of O_2, resulting in higher utilization of O_2 due to the high catalytic activity. Another reason is that increasing the amount of the catalyst can accelerate the generation of hydroxyl radicals, and promote hydroxyl radicals reacting with the intermediates of oily wastewater degradation.

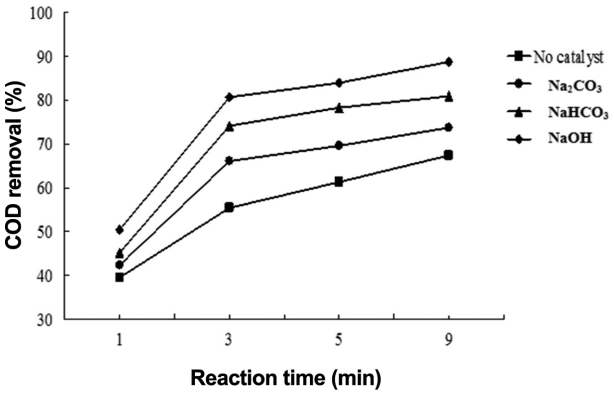

Figure **2.** Effect of catalysts on COD removal.

Wet Peroxide Oxidation of Oily Wastewater

Effect of temperature

The effect of temperature on COD removal via WPO was investigated. The results are shown in *Fig*. 3. It can be seen that rising temperature increased COD removal of oily wastewater. When temperature reached 340 °C, COD removal reached 90.15 and 99.10% after 1 and 9 min, respectively.

In the WPO of organic compounds, the reaction temperature is an important parameter affecting the removal of pollutants. As expected, the higher operating temperature is, the higher reaction rate and COD removal of oily wastewater are obtained.

Effect of residence time

Fig. 3 indicated that residence time has a significant effect on conversion of oily wastewater. Within each set of isothermal experiments, the COD removal increased rapidly during the first 1 min and slowed down afterwards.

During the process of WPO of organic compounds, at first the reaction rate is quick. Concentration of organic matter in oily wastewater continues to decrease with the reaction proceeding, thus the reaction rate decreases. In addition, non biodegradable intermediates are generated, so the reaction rate decreases. Therefore, the COD removal

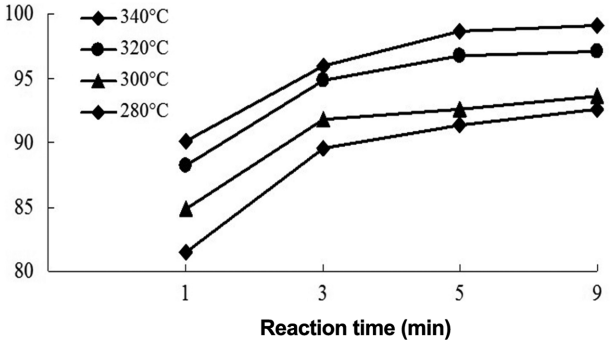

Figure **3.** Effect of temperature on WPO of oily wastewater. Conditions: residence time 1 to 9 min, HE 0.75, initial COD 18000 mg/L.

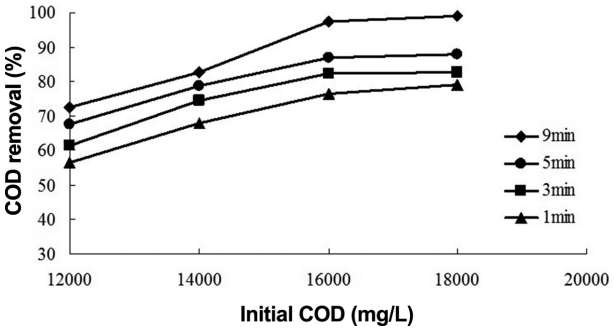

***Figure* 4.** Effect of initial COD on WPO of oily wastewater.

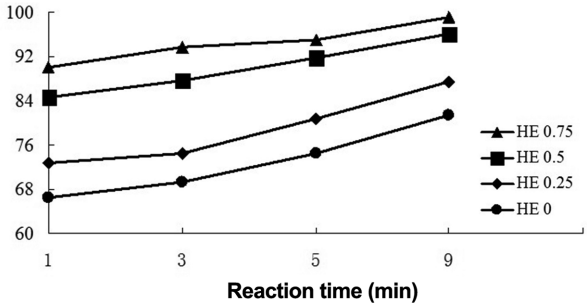

***Figure* 5.** Effect of HE on WPO of oily wastewater. Conditions: temperature 340 °C, residence time 1 to 9 min, initial COD 18000 mg/L.

increased rapidly at first and slowed down afterwards.

Effect of initial COD

The investigation on the effect of initial COD on WPO of oily wastewater was implemented and the results are shown in *Fig*. 4. It can be observed from *Fig*. 4 that the initial COD had influence on the COD removal to some extent. When initial COD varied from 12000 to 16000 mg/L, COD removal rapid increased. However, initial COD was beyond 16000 mg/L, and COD removal increased slowly. For example, COD removal increased from 97.30 to 99.10% as initial COD increases from 16000 to 18000 mg/L when residence time was 9 min.

Effect of HE

Lots of experiments were conducted to investigate the effect of HE on WPO of oily wastewater. The experimental results are presented in *Fig*. 5. As can be seen in *Fig*. 5, COD removal increased when HE increased. 99.10% of COD was removed when HE was 0.75.

CONCLUSION

The WPO and CWO of oily wastewater are investigated. The results showed that greater than 80% chemical oxygen demand (COD) removal from oily wastewater was achieved via CWO. Homogenous catalyst, $NaHCO_3$ and Na_2CO_3 and NaOH showed effective removal for pollutants. Greater than 90% COD removal was achieved via WPO. It was concluded that WPO was a far more effective process for removing organic compounds from oily wastewater.

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