

## An Effective Process for Removing Organic Compounds from Oily Sludge

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**ABSTRACT.** Wet air oxidation (WAO) of oily sludge was carried out using  $\text{Fe}^{3+}$  as catalyst, placed in a 0.5 L batch autoclave in the temperature range of 250-330 °C. Experiments were conducted to investigate the effects of temperature, the initial COD, reaction time, concentration of catalyst and  $\text{O}_2$  excess (OE) on the oxidation of the oily sludge. The results showed that in the WAO 88.4% COD was achieved after 9 min reaction at temperature of 330 °C, OE of 0.8 and the initial COD of 20000 mg/L. Temperature was found to have a significant impact on the oxidation of oily sludge. Adding a catalyst significantly improved the COD removal. Homogenous catalyst,  $\text{Fe}^{3+}$ , showed effective removal for pollutants. COD removal was 99.7% in the catalytic wet air oxidation (CWAO) over  $\text{Fe}^{3+}$  catalyst. The results proved that the CWAO was an effective pretreatment method for the oily sludge.

**Key words:** Wet air oxidation, Catalytic wet air oxidation, Oily sludge, COD removal

### INTRODUCTION

Oily sludge is byproduct of petroleum product and one of main pollutant of petroleum, outputs liquid from oil wells contains lots of sludge and sand, and it is deposited in oil sedimentation cans. There are a large number of sludge containing water, crud-oil and other hazardous substances in the bottom of sedimentation cans and containers such as crude oil storage tanks. Oily sludge is directly dumps waste of resource, and it pollutes the environment. So it is the key to treat oily sludge that crude oil is removing oil from oily sludge.<sup>1</sup> Oily sludge treatment is mainly to use a biological method<sup>2,3</sup> at present, or it is made into the highway materials,<sup>4</sup> supplement fuels,<sup>4</sup> solidification materials,<sup>4</sup> industrial ceramics materials<sup>5</sup> and so on. The treatment and disposal of oily sludge represents major challenges for petroleum industries. The oily sludge consumes a high portion of budget of oil production plant and refiner. Several conventional technologies, such as landfill, biological treatment, incineration and so on, for the treatment and disposal of oily sludge have been implemented. Various treatment options are compared in terms of their effectiveness, ease of operation, and cost. Of the technologies mentioned above, landfill is a cheap and straightforward treatment method for oily sludge. However, without volume reduction and appropriate treatment before disposal, oily sludge will reduce the service-life of landfill sites and may result in an

odor problem and create the risk of contamination, particularly of ground water, thus causing adverse health effects. Biological treatment of organic pollutants is a promising, reliable, simple and cheap technology over chemical and physical processes.<sup>6-8</sup> However, it is reported as being very difficult or non-practical because it takes a relatively long time to treat and the removal rate is low.<sup>9-11</sup> Incineration is a valuable means of waste disposal with the advantage of being highly effective in reducing the volume of waste. Unfortunately, incinerators generate large volumes of off gases containing polycyclic aromatic hydrocarbons. Furthermore, the auxiliary fuel must be added to the incinerator to keep the incineration temperature constant.<sup>12</sup> As mentioned above, no technology currently has reached a satisfactory solution from the environmental and highly effective point of view. Consequently, there is a need for environmentally benign technologies capable to effectively neutralize the oily sludge and reduce its adverse impacts on the environment.

Wet air oxidation (WAO) has been proven as one of the efficient technologies to eliminate highly concentrated, toxic and hazardous organic compounds to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and other innocuous end products under high temperature and high pressure using oxygen as the oxidant, and without the emissions of  $\text{NO}_x$ ,  $\text{SO}_2$ , HCl, dioxins, furans, fly ash, etc..<sup>13</sup> Such conditions lead to very high investment costs, because reinforced materials are needed to support the strong pressures, and special metal alloys, which are much

more expensive than commonly used stainless steel alloys, must be employed to avoid corrosion which is highly favored under these conditions. In spite of this, there has been a strong effort on the research and development of catalysts in order to bring down pressure and temperature to milder values-catalytic wet air oxidation (CWAO).<sup>14</sup> The CWAO has gained some attentions. The addition of catalysts decreases the operating conditions, enhances the reaction rate, and shortens the reaction time.<sup>15</sup> A significant amount of research has been conducted on CWAO and the development of catalysts for use in CWAO over the last three decades.<sup>16-24</sup>

The purpose of the present study was to investigate the performance of the WAO and CWAO of oily sludge, and to examine the feasibility of the technology as a pre-treatment for biological remediation to reduce toxic organic compound. The effect of the operating conditions on COD removal of the oily sludge, including temperature, the initial COD of the oily sludge, reaction time, concentration of catalyst and OE, was studied.

## EXPERIMENTAL

### Materials and methods

**Characteristics of the oily sludge:** Oily sludge used in the experiments was obtained in sedimentation cans from the Second Oil Production Plant of Daqing Oilfield Company Ltd., China. The sludge contains 42.8% crude oil, 55.4% water and 1.8% sediment.

### Experimental procedure

The WAO and CWAO of the oily sludge were carried out in a 0.5 L batch autoclave (Model GSHA-0.5, Weihai, China; Fig. 1). The reactor was equipped with a magnetically driven stirrer ensuring good mass transfer from the gas to the liquid phase and to a catalyst. Firstly, water and oily sludge was put into the reactor, and then nitrogen flowed through the system and removed the air within the system; the valves around the reactor were closed when the air was removed entirely. Secondly, homogenous catalyst was introduced into the reactor. Finally, pure O<sub>2</sub> was introduced into the reactor until the predefined pressure was reached, and the reaction started as "zero time". Liquid samples (ca. 10 mL) were periodically withdrawn from the reactor and analyzed.

### Analytical

The diluted sludge and COD of the collected liquid are measured by potassium dichromate method of Chinese

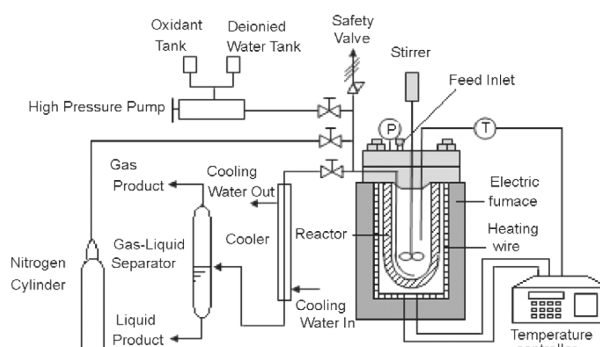


Fig. 1. Schematic diagram of the experimental setup.

Standard 11914-89. The OE is defined as equation 1.

$$OE = O_{2, Excess} = \frac{(O_2)_{in} - (O_2)_{stoichiometric}}{(O_2)_{in}} \quad (1)$$

### Homogenous catalyst

The metal salt used in the experiments was analytical grade, and was not further purified. The experiments were performed with FeCl<sub>3</sub>·6H<sub>2</sub>O as catalyst to investigate the effect of the homogenous catalyst on the conversion of organic compounds in the oily sludge.

## RESULTS AND DISCUSSION

### WAO of the oily sludge

**Effect of the temperature:** In the WAO of organic compounds, the temperature is an important parameter affecting the removal of pollutants. Generally, the higher operating temperature, the higher pollutant removal and the reaction rate are obtained. Fig. 2 showed COD removal of the oily as the function of reaction time at a series of reaction temperatures (250, 270, 290, 310 and 330°C). When the temperature increased from 250 to 330°C, COD removal significantly increased from 71.62 to 88.4% after 9 min reaction. Therefore, temperature had a significant impact on the oxidation of oily sludge.

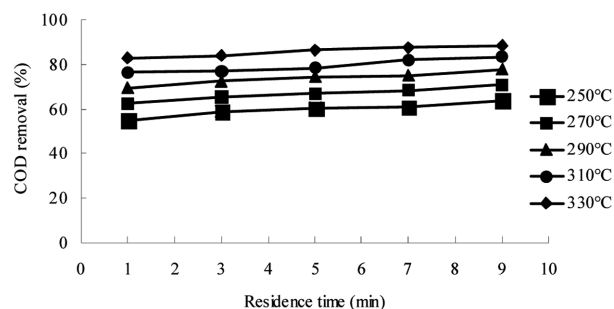


Fig. 2. Effect of the temperature.

This phenomenon can be explained in two ways. On the one hand, oxidation of organic matter is an irreversible process, the reaction rate constant will increase when the temperature increases, which accelerates the reaction rate. Eventually, it leads to increasing oxidation rates of organic matter degradation; on the other hand, the density of water becomes smaller when the temperature increases in the case of constant pressure, reducing the concentration of the reactants, which will cause the reaction rate slowed down, but increase of the rate constant caused by increase of the temperature is much greater than range of the concentration reduced, so it is shown that COD removal increases with increasing temperature.

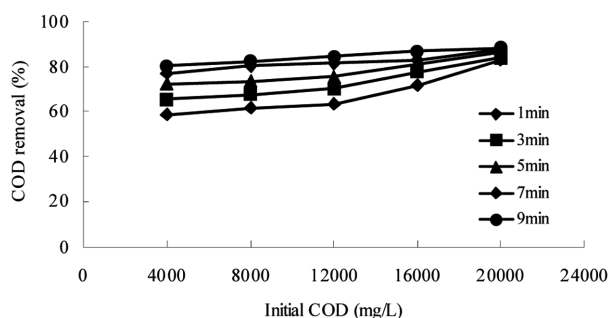
#### Effect of reaction time

The oily sludge conversion experiments were conducted at 250-330 °C for 9 min. *Fig. 2* showed COD removal for WAO of oily sludge at different temperatures. The result appeared that the reaction time had a significant effect on oily sludge conversion. Within each set of isothermal experiments, the COD removal increased rapidly during the first 1 min of reaction and slowed down afterwards.

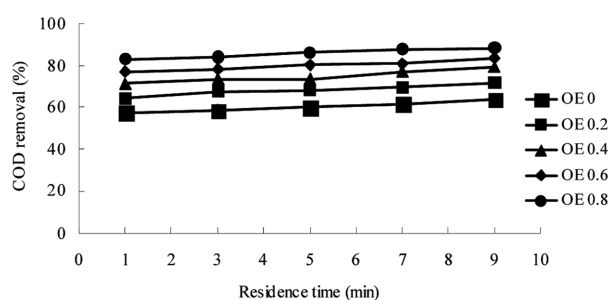
This is because the reaction rate is not only related to temperature but also with reactant concentration, the concentration of organic matter in oily sludge continues to decrease with the reaction proceeding, thus the reaction rate decreases. In addition, intermediates of more difficult degradation are generated, so the reaction rate decreases.

#### Effect of the initial COD of the oily sludge

The effect of initial COD on WAO of oily sludge was investigated between 4000 and 20000 mg/L as shown in *Fig. 3*. It can be observed from *Fig. 3* that the initial COD had influence on the COD removal to some extent. An increasing initial COD from 4000 to 12000 mg/L resulted in the slow increase in the COD removal rate. However, COD removal rate increased from 63.31 to 83.08% as ini-



*Fig. 3.* Effect of the initial COD of the oily sludge.



*Fig. 4.* Effect of OE.

tial COD increased from 12000 to 20000 mg/L under the condition of reaction time of 1 min.

This is because the increasing concentration of oil sludge increases the percentage of activated molecular in unit volume and higher effective collision and reaction probability of particles increases. Thereby it speeds up the oxidation rate and promotes oxidation effect of organic matter. Therefore, wet air oxidation is more suitable for treating high concentrations of oily sludge.

#### Effect of OE

A series of experiments were conducted to determine the effect of OE on WAO of oily sludge at given COD concentration. The experimental results are presented in *Fig. 4*. As can be seen in *Fig. 4*, COD removal increased with increasing OE. Approximately 88.4% of COD was removed when OE is 0.8.

It can be seen that partial pressure of oxygen has a direct impact on the oxidation rate within a certain range. When OE increases, the dissolved oxygen increases in the solution and could be helpful for the formation of strong oxidation species ( $O_2^{\cdot-}$ ,  $HO_2^{\cdot}$ , etc.). Therefore, high OE can accelerate the oxidation of the organic pollutant, leading to achieving higher organic compounds conversion in the WAO.

#### CWAO of the oily sludge

**Effect of homogenous catalyst:** *Fig. 5* showed COD removal in the CWAO of the oily sludge over  $Fe^{3+}$  as catalyst at temperature of 330 °C, OE of 0.8, initial COD of 20000 mg/L and reaction time of 9 min. Approximately COD removals are 99.7% (*Fig. 5*), using  $Fe^{3+}$  as catalyst after 9 min reaction.  $Fe^{3+}$  displayed high activity in the CWAO of the oily sludge (*Fig. 5*). The result indicated that the CWAO over  $Fe^{3+}$  catalyst effectively increased the removal of organic compounds in the oily sludge and there was significant advantage of increasing concentration of catalyst from 50 to 200 mg/L.

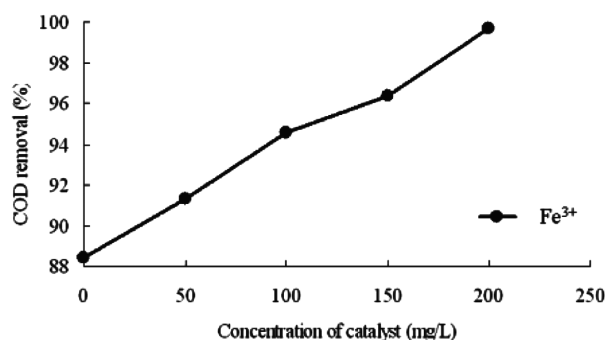


Fig. 5. Effect of homogenous catalyst.

This phenomenon may be caused by several reasons. One reason is that due to the high catalytic activity of  $\text{Fe}^{3+}$  may promote the reaction of  $\text{O}_2$ , resulting in higher utilization of  $\text{O}_2$ . 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 sludge degradation.

## CONCLUSION

To consider “wet air oxidation” as a pretreatment method to convert bioreistant organics to more readily biodegradable intermediates, knowledge of the impact of the operating conditions such as temperature, the initial COD, reaction time, catalyst type, concentration of catalyst and OE ( $\text{O}_2$  excess), is required. Experimental results indicated that in the WAO process, 88.4% chemical oxygen demand (COD) was obtained after 9 min reaction at temperature of 330 °C, OE of 0.8 and the initial COD of 20000 mg/L. Temperature was found to have a significant impact on the oxidation of oily sludge. Adding a catalyst significantly improved the COD removal. Homogenous catalyst,  $\text{Fe}^{3+}$ , showed effective removal for pollutants. COD removal was 99.7% in the CWAO over  $\text{Fe}^{3+}$  catalyst. Four concentration of  $\text{FeCl}_3$  catalyst as 50, 100, 150, 200 mg/L were tested. It was found that there was significant advantage of increasing concentration of catalyst from 50 to 200 mg/L. The present study proved that the CWAO was an effective method as a pretreatment of the oily sludge.

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