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Wet peroxide oxidation of oilfield sludge



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Abstract Wet peroxide oxidation (WPO) of oilfield sludge was performed in a batch reactor. Effect of reaction parameters such as residence time, reaction temperature, HE (H_2O_2 excess) and initial concentration of oilfield sludge were investigated. The experimental results showed that WPO can effectively remove the organic compounds of the oilfield sludge, the residence time and reaction temperature are the main factors for COD removal of oilfield sludge. The initial concentration of the oilfield sludge and HE are also important. When the reaction temperature is 340 °C, initial concentration of the oilfield sludge is 4000 mg/L, the residence time is 9 min and the COD removal oilfield sludge could reach 88.68%. The COD removal increases with the rise of reaction temperature and residence time. The preliminary study of mechanism on the oilfield sludge by WPO is carried out. The result indicates that the oilfield sludge by WPO can be explained by free radical mechanism.

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1. Introduction

Wet 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 condition, so this can reduce energy consumption and equipment intensity. It has

gained 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). Oilfield sludge is the byproduct of petroleum production and also one of the main pollutants of petroleum. Output liquid from oil wells contains lots of sludge and sand. It is deposited in oil sedimentation cans. Large amounts of sludge contain water, crude oil and other hazardous substances in the bottom of sedimentation cans and containers such as crude oil storage tanks. Oilfield sludge is a kind of direct dump waste of resource, and it can pollute the environment. So the key to treat oilfield sludge is to remove oil from it (Kuriakose and Manjooran, 2001). This experiment uses sludge 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.

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2. Experimental

2.1. The reactor design

The general setup of the system including WPO reactor is shown in Fig. 1.

This is an intermittent reacting system for WPO. It includes a reactor, heater reactor, gas–liquid separator and other major equipment. Firstly water and oilfield sludge were 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. The reactor was heated, and hydrogen peroxide was added into the hydrogen peroxide container; when reactor temperature reached the scheduled value, hydrogen peroxide was injected into the reactor by using a high pressure pump. When the reaction residence time was attained, the reaction fluid was put into the gas–liquid separator, and the gas and the liquid were separated; opening the reactor vessel, the sediment was removed directly. Reaction pressure and reaction temperature were measured by a thermocouple and a pressure transducer. The entire system does not need high-pressure pump following the turbocharging system, the different reaction pressure was controlled by reaction temperature and by means of putting water into the reactor, and the high-pressure pump was used only when hydrogen peroxide was injected into the reactor. The reactor is made from 1Cr18Ni9Ti, and the reactor volume is 600 ml. The OE is defined as Eq. (1) (Cocero et al., 2002), in the present experiment, hydrogen peroxide is the oxidant, so Eq. (2) is used instead of Eq. (1).

$$OE = O_{2,Excess} = \frac{(O_2)_{in} - (O_2)_{stoichiometric}}{(O_2)_{in}} \times 100 \quad (1)$$

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

3. Results and discussion

3.1. Influence of residence time on COD removal

Reaction residence time has a significant impact on the COD removal rate, since the rate increases with the rise of residence time. It is, therefore, crucial to choose a suitable residence time. In this experiment, the residence time varies from 1 to 9 min.

Fig. 2 shows that the COD removal of the oilfield sludge is affected by residence time. The initial concentration of the oilfield sludge is 1000 mg/L, HE is 0.86. COD removal of the oilfield sludge increases with the rise of residence time, which is shown in Fig. 2, when the residence time was up to 9 min, the COD removal of the oilfield sludge increased gently. So the appropriate residence time was 9 min.

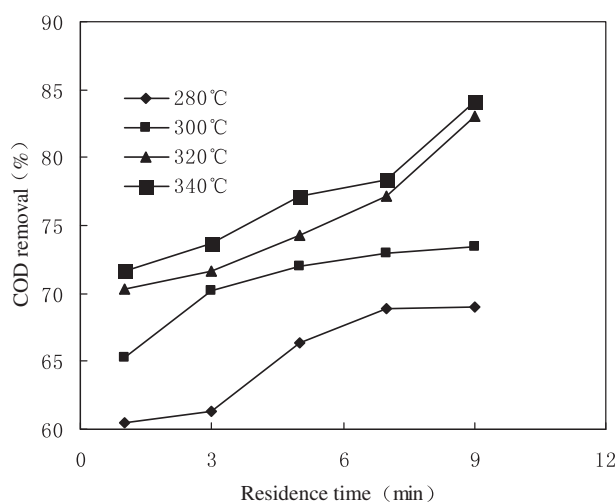


Figure 2 Influence of residence time on COD removal.

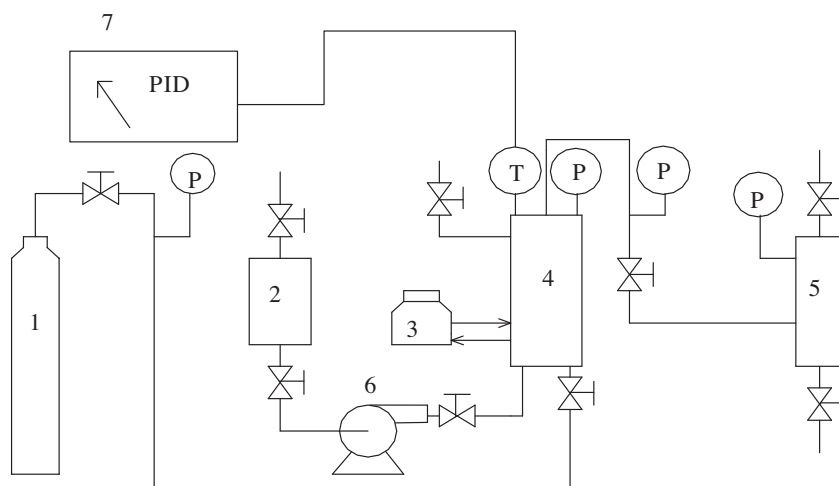


Figure 1 The setup of WPO process, (1) nitrogen storage bottle, (2) hydrogen peroxide container, (3) heater, (4) reactor, (5) gas–liquid separator, (6) high pressure pump, (7) control instrument.

3.2. Influence of reaction temperature on COD removal of oilfield sludge

The highest design temperature of reactor was 500 °C, which was based on the range of reaction temperatures [280, 340 °C]. An experimental result shows that obvious changes in the removal of COD occurred when the reaction temperature changed in an increment of 20 °C.

The experiments were conducted under isothermal and isobaric conditions at temperatures of 280, 300, 320, and 340 °C, respectively. Steady-state temperature fluctuations along the reactor were ± 3 °C in maximum. Result was shown in Fig. 2.

Fig. 2 shows that the COD removal of the oilfield sludge is affected by reaction temperature. Fig. 2 indicates the COD removal radiate upward trend with the rise of reaction temperature. COD removal is low at low reaction temperature (280–300 °C), but COD removal rate increases quicker than that of under high reaction temperature (320–340 °C). When the residence time is 9 min, HE is 0.86, and reaction temperature increases from 300 to 320 °C, COD removal increases from 73.44% to 83.03%, while it increases from 83.03% to 84.06% when temperature increases from 320 to 340 °C. So the appropriate temperature for COD removal of the oilfield sludge is between 320 and 340 °C.

3.3. Influence of HE on COD removal of oilfield sludge

Fig. 3 shows that COD removal is affected by HE. The initial concentration of the oilfield sludge is 1000 mg/L and the residence is 9 min. The COD removal increases with the rise of HE, which is shown in Fig. 3. The COD removals increasing trend becomes gentle when HE is over 0.8, so the appropriate HE is 0.8.

3.4. Influence of initial concentration of oilfield sludge on COD removal of oilfield sludge

Fig. 4 shows that COD removal is affected by initial concentration of the oilfield sludge. The reaction temperature is 340 °C, HE is 0.86, and the residence time is 9 min. The COD removal increases with increasing initial concentration of the oilfield sludge, which is observed from Fig. 4. When ini-

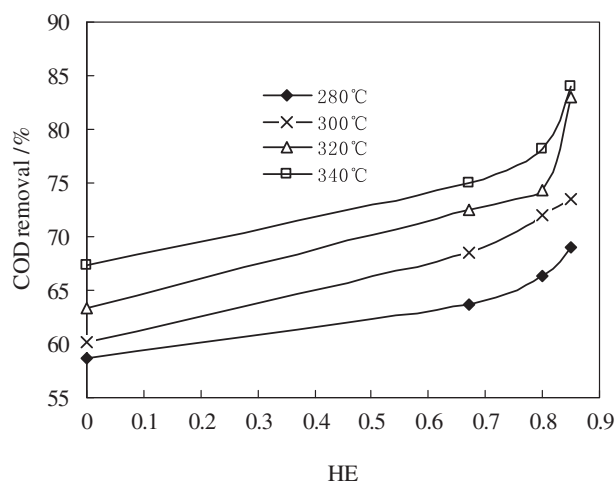


Figure 3 Influence of HE on COD removal.

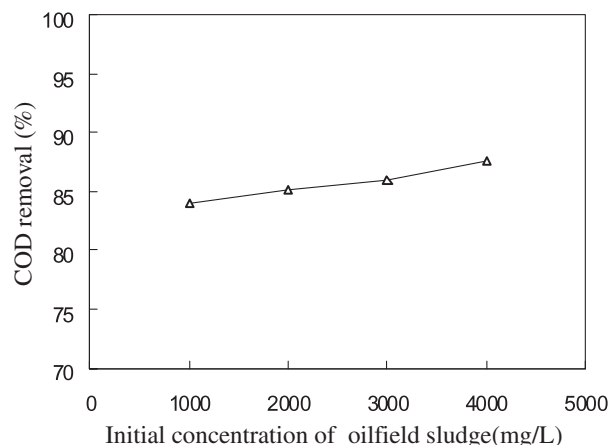


Figure 4 Influence of initial concentration of oilfield sludge on COD removal.

tial concentration of oilfield sludge reaches 1000 mg/L, the COD removal can be up to 84.06%. When the initial concentration of oilfield sludge is 1000–4000 mg/L, the oil removal changes gently, i.e., increasing from 84.06% to 88.68%. Because WPO reaction is an exothermic reaction, initial concentration of oilfield sludge should be chose between 1000 and 4000 mg/L.

4. Mechanism

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



M is a homogeneous boundary or heterogeneous boundary.



Peroxide is usually decomposed to smaller molecule compounds, and the rupture promptly carries out then stops until formic acid or acetic acid generates. Formic acid or acetic acid is converted to CO_2 and H_2O finally. It is generally thought that Eq. (1-3) is the rate determining step.

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



M is a homogeneous boundary or heterogeneous boundary. Generated $\cdot\text{OH}$ 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) speculated that decomposition reaction of hydrogen peroxide is determined by the following pathway:





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).



It is seen that oxygen and water can also generate hydrogen peroxide during the reaction. That means whatever the initial state is the system of O_2 and H_2O or H_2O_2 and H_2O is, 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.

5. Conclusions

The decomposition of the oilfield sludge was studied under isothermal and isobaric conditions at 280, 300, 320, and 340 °C, and residence time from 1 up to 9 min, HE from 0 to 0.86, initial concentration of oilfield sludge from 1000 to 4000 mg/L. The results showed that WPO can effectively remove organic

compounds of the oilfield sludge, the COD removal is up to 88.68% when the conditions are not very harsh in the circumstances. Reaction temperature, residence time, HE and initial concentration of the oilfield sludge are the important factors that affect COD removal, and the appropriate reaction temperature is 320–340 °C, the residence time is 9 min, HE is 0.8, and initial concentration of the oilfield sludge is 1000–4000 mg/L. The oilfield sludge by WPO can be explained by free radical mechanism.

References

- Carriazo, J., Guélou, E., Barrault, J., Tatibouët, J.M., Molina, R., Moreno, S., 2005. *Water Res.* 39, 3891.
- Cocero, M.J., Alonso, E., Sanz, M.T., Fdz-Polanco, F., 2002. *J. Supercrit. Fluids* 24, 37.
- Kuriakose, A.P., Manjooran, S.K.B., 2001. *Surf. Coat. Technol.* 24, 132.
- Lee, D.S., 1996. *Environ. Sci. Technol.* 30, 3487.
- Li, Y., Liu, J.L., Dong, G.H., Wang, J., 2007. *J. Safe. Environ.* 7, 31.
- Neamtu, M., Zaharia, C., Catrinescu, C., Yediler, A., Macoveanu, M., Kettrup, A., 2004. *Appl. Catal. B: Environ.* 48, 287.
- Qiao, S.J., Zhao, A.P., Xu, X.L., Zhao, H.H., Zhang, Z.M., Wen, F., Qiao, M., 2007. *J. Safe. Environ.* 7, 35.
- Takagi, J., Ishigure, K., 1985. *Nucl. Sci. Eng.* 89, 177.
- Tang, W.W., Zeng, X.P., Hu, Z.H., 2006. *Acta Scientiae Circumstantiae* 26, 1265.
- Tsang, W., Hampson, R.F., 1986. *J. Phys. Chem. Ref. Data* 15, 1087.
- Wang, J. 2007. Xi'an, Northwest University. CHINA 1-60.