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Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Wet peroxide oxidation of oilfield sludge

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Received 25 February 2011; accepted 4 June 2011 Available online 15 June 2011

KEYWORDS

Wet peroxide oxidation; Batch reactor; Oilfield sludge; Removal 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 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

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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).

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

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

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