TREATMENT OF OLEFIN PLANT SPENT CAUSTIC BY COMBINATION OF NEUTRALIZATION AND FENTON REACTION

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Abstract—Spent caustic from olefin plants contains much H_2S and some mercaptans, phenols and oil. A new treatment process of spent caustic by neutralization followed by oxidation with Fenton's reagent (Fe^{2+}/H_2O_2) was successfully developed. Over 90% of dissolved H_2S were converted to gas phase by neutralization at pH = 5 and $T = 70°$, and the vent gas stream could be introduced to sulfur recovery plant. The neutralized liquid was oxidized with OH· free radical, which was provided by a Fenton's reagent. The residual sulfides in the neutralized spent caustic were oxidized to less than 0.1 mg/L. The total COD removal of spent caustic is over 99.5% and the final COD value of the effluent can be lower than 100 mg/L under the following oxidation conditions: reaction time = 50 min, $T = 90°$, $Fe^{2+} = 100$ mg/L, and a stoichiometric $H_2O_2/COD = 1.1$. The value is better than the 800 mg/L value obtained by common WAO process. The optimum pH of the Fenton reaction is around 2 for this process, and the oxidation step can maintain a pH value in the range of 1.8–2.4. Moreover, the iron catalyst can be recycled without affecting process effectiveness thus preventing secondary pollution. © 2001 Elsevier Science Ltd. All rights reserved

Key words—spent caustic, Fenton's reagent, oxidation

INTRODUCTION

Spent caustic produced from olefins plants contains a large amount of hydrogen sulfide and some mercaptans, phenols and emulsified hydrocarbons (Table 1). As noted by William and Rothschild (1994), under the US Resource Conservation and Recovery Act (RCRA) definitions, spent caustic is classified as D003 (reactive sulfide) hazardous waste.

Current environmental regulations have a large impact on the spent caustic treatment system design. Conventional disposal methods of dumping in a deep well or the ocean are becoming environmentally unacceptable (Grover and Gomaa, 1993). Also, spent caustic contains high concentrations of toxic constituents such as phenols and hydrogen sulfide that hinder the conventional biological treatment even after neutralization and dilution.

Spent caustic can be treated by acid neutralization followed by steam stripping. After neutralization, stripping removes residual hydrogen sulfide and mercaptans. Residual mercaptans and sulfides in

the treated caustic generate odors that may be noticeable even when diluted with other plant wastes. The liquid effluent has high BOD and COD concentrations because the major portion of the organic constituents is unaffected by the stripping process.

Wet air oxidation (WAO) can treat spent caustic to lower than 1000 mg/L COD in 60 min at 202°C and 28 bar (William *et al.*, 1992). However the process is very expensive, and due to severe reaction conditions, safety is a major concern.

Fenton's reagent (Fe^{2+}/H_2O_2) can oxidize refractory pollutants at a low temperature and pressure (Lin *et al.*, 1999). But due to a high COD value of

Table 1. Characteristics of spent caustic generated from olefin plants

Item	Value
S^{2-} (mg/L)	14,000–21,000
NaOH wt%	5.8–7.5
COD (mg/L)	30,000–45,000
Phenols (mg/L)	300
Emulsified oil (mg/L)	150
Non-sulfide COD (mg/L)	2000
pH	13.5–13.7
Specific gravity	1.1
Temperature	40°C

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spent caustic, it consumes a large amount of H_2O_2. Also, because of a high concentration of H_2S (up to 20 g/L), its reaction with ferric ion causes a loss of iron catalyst activity.

In this study a new process was developed to treat olefin plant's spent caustic. The spent caustic was first neutralized with sulfuric acid to pH = 5.0. Fenton's reagent was then added to oxidize the solution. As a result, the spent caustic treatment becomes economical and effective.

EXPERIMENTAL

Experimental system

The experimental flow-sheet of the present study is shown in Fig 1. Spent caustic (20 mL/min) was neutralized continuously by adding 98 wt% sulfuric acid to obtain pH = 5 ± 0.2. The neutralizer was a glass container (600 mL) with 500 mL working volume. Then three streams: the neutralized spent caustic, a ferrous sulfate solution (3 g/L Fe^{2+}, 0.35–0.7 mL/min), and hydrogen peroxide (35 wt%, 0.48–0.6 mL/min) were pumped to the Fenton reactor, which was a 1.2 L glass container with flexible working volume (600–1000 mL). When the system reached a steady-state condition, samples of Streams 2, 8, and 12 (Fig. 1) were taken and analyzed.

The neutralizer and Fenton reactor were operated at ambient pressure, and were equipped with an electromagnetic stirrer. Temperature-controlled hot plates were used to maintain the desired temperature.

In this system, metering pumps were used to transport sulfuric acid and hydrogen peroxide solutions, and peristaltic pumps were used to transport other solutions. All connecting tubing was made of Teflon material.

Experimental procedure

Neutralization. The experimental spent caustic was obtained from a naphtha cracking plant of Chinese Petroleum Corporation, Kaohsiung, Taiwan. Three batches of spent caustic samples were obtained at different time and they were used in the neutralization tests.

With the exothermic neutralization reaction, the reactor temperature reached about 70°C under adiabatic conditions. This is also the reaction temperature observed in the full-scale neutralization unit of a naphtha cracking plant of Chinese Petroleum Corporation in Taiwan. Due to a greater heat loss in the laboratory reactor, the temperature of 70°C was maintained by a thermal plate.

According to Pitsinigos and Lygeros (1989), the equilibrium and the Henry's law constants in equations (1) and (2) at 70°C, are $K_1 = 2.7 \times 10^{-7}$ g mol/L, $H = 1.617 \times 10^4$ mmHg/g mol/L.

$$H_2S_{(aq)} \underset{K_1}{\rightleftharpoons} HS^-_{(aq)} + H^+_{(aq)} \qquad (1)$$
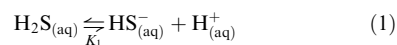
$$P_{H_2S} = H \cdot H_2S_{(aq)} \qquad (2)$$

When the neutralization was carried out at pH = 5 and temperature at 70°C, the HS^- to H_2S ratio is 2.7×10^{-2}. This means that over 97% of dissolved H_2S exists in molecular H_2S form. As a result, further reduction of pH below 5 has little effect on the H_2S removal. It should be noted that if only H_2O and H_2S are considered without accounting for other impurities, the equilibrium H_2S concentration in the liquid phase is 1115 mg/L.

pH effect on Fenton reaction. Phenol is a component in the spent caustic and it is more difficult to oxidize than H_2S. Thus, phenol was used to test the pH effect.

The batch reactor was a 300 mL glass container, and the solution was mixed with a magnetic stirrer. The initial pH value was adjusted with 1 N NaOH or 1 N H_2SO_4 solution. A 150 mL solution containing 500 mg/L phenol, 100 mg/L Fe^{2+}, but with various initial pH, was allowed to react at room temperature by adding 1 mL 35 wt% H_2O_2. During reaction, samples were taken and analyzed at different times.

Oxidation. According to Walling (1975) and Huang *et al.* (1993), the hydroxyl radical is one of the strongest oxidant, and it can be produced by Fenton's reagent (Fe^{2+}/H_2O_2) as
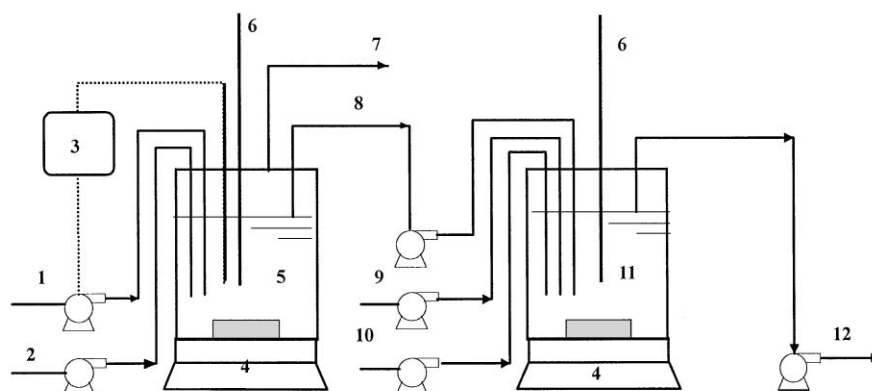
1. 98 wt% H_2SO_4.
2. spent caustic feed.
3. pH controller.
4. heating plate stirrer.
5. neutralizer.
6. thermometer.
7. vent gas.
8. feed to oxidation reactor.
9. 35 wt% H_2O_2.
10. ferrous sulfate solution.
11. oxidation reactor.
12. effluent

Fig. 1. Experimental schematic diagram.