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Combined Air Oxidation and Activated Sludge Process for the Treatment of Refinery Spent Caustics

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Liquid hydrocarbon spent caustics generated in the oil refining process of a refinery contained a high concentration of toxic materials and refractory organic wastewater. In this study, the spent caustics were detoxified with a combination of air oxidation and biological treatment processes, as opposed to the direct biological treatment method. Further, the combined processes enabled the conversion of sulfate up to 95.5 % when the total sulfur load was 1.5 kgS/ (m^3 d). The study indicated that the detoxification of sulfides to thiosulfates in the oxidation process enabled successful biological treatment and the combined air oxidation and biological treatment processes can effectively improve the oxidation rate of conversion, thereby reducing elemental sulfur generation rate. Furthermore, the combined processes can effectively shorten reaction time, thus increasing reaction load.

Keywords: Spent caustic, Air oxidation, Biological treatment, Sulfide, Sulfate, Sequencing batch reactor.

INTRODUCTION

Liquid hydrocarbon spent caustics contained a high concentration of toxic chemicals and refractory organic wastewater, which were the primary odor sources in petroleum refineries. If the untreated caustics were directly discharged into a sewage treatment plant, the biochemical system would be difficult to operate normally, leading to serious secondary pollution[1]. Therefore, there is an urgent need to develop a suitable method for spent caustic disposal.

Currently, the effluent quality of spent caustics cannot be guaranteed to meet discharge standards with the direct biological treatment method. In case of the insufficient dissolved oxygen and a high sulfide load, sulfides can be biologically oxidized into a large amount of elemental sulfur and less sulfate, resulting in water turbidity and low effluent quality. Sulfate is the preferred end product because it does not represent COD (Chemical Oxygen Demand) and can be discharged into the environment[2]. Moreover, the H^+ generated from the formation of sulfate can be neutralized with alkaline solutions to save acid consumption. Therefore, sulfides must be oxidized into sulfates to a feasible extent.

Although chemical oxidation is usually expensive for complete mineralization, its combination with a biological treatment is widely preferred to reduce operating costs[3]. This research adopted a combination of air oxidation and biological treatment methods to deal with spent caustics. Air oxidation can oxidize most of the sulfide to nontoxic thiosulfate and thiosulfate can be further oxidized to sulfate by biological treatment. In addition, most of studies used the air-oxidation method for detoxification of caustics[4]. In order to test the detoxification effect, scholars used spent caustics containing methyl mercaptan (CH_3-S) as sample and rapid oxidation of methyl mercaptan to dimethyl disulfide (CH_3-S-S-CH_3) occurred, the toxicity of which is 1/40 of that of the precursor compound. In addition, detoxification was favorable to the further biodegradation of spent caustics.

Because in practice, such as at refineries, sulfide influent concentration may vary in time, formation of elemental sulfur may be difficult to prevent. Therefore, there are more potential advantages with the combined method than with a single process to ensure complete sulfate formation at all times. The current study focused on the combined air oxidation and biological treatment process of spent caustics and compared with the direct biological treatment method to demonstrate the feasibility and superiority of the combined processes.

EXPERIMENTAL

The experimental system comprised two types of cylindrical bench-scale reactors. Reactor 1 (R1) serves as an oxidation reactor and reactor 2 (R2) serves as an SBR (sequencing batch reactor). The influent first entered R1 and then the effluent from R1 entered R2. The final effluent water from R2 was discharged. The activated sludge in the bioreactor R2 was obtained from the secondary clarifier of a refinery wastewater

treatment plant. A pre-experiment was conducted to ensure that the activated sludge was acclimated by the synthetic sulfide wastewater under halo-alkaline conditions[5]. The working volume of R1 was 1 L and that of R2 was 2 L. In addition, the working volume of SBR used in the direct biological experiment was 3 L. The reaction system is shown in Fig. 1.

The initial operating conditions of R2 were as follows: The operating cycle was 24 h and hydraulic retention time (HRT) was 2 days. Further, 50 % of the full volume was replaced during the filling period with freshly prepared wastewater in each cycle. The temperature was controlled at 30 °C in a water bath. Moreover, the aeration rate was controlled by the respective flowmeters of the reactors. The initial aeration rate of reactor R1 was 0.1 L/min whereas dissolved oxygen (DO) was set to be more than 4 mg/L by adjusting the aeration quantity of R2.

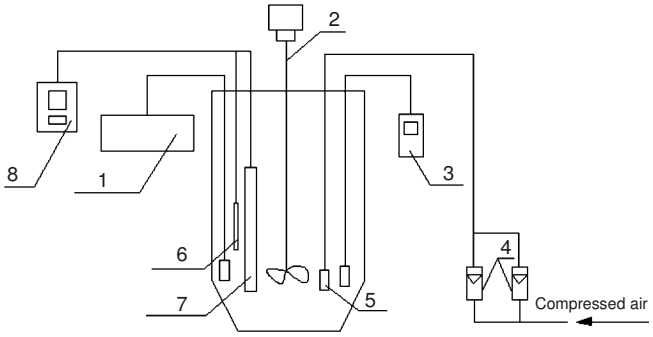

Fig. 1. Reaction system: 1: pH meter; 2: stirrer; 3: DO tester; 4: rotameter; 5: aeration device; 6: thermoelectric coupling; 7: heating rod; 8: temperature controller

Influent preparation: Influent used in the experiment was divided into synthetic wastewater and liquid hydrocarbon spent caustic samples. Because of the possible uncertainties owing to the complicated composition of spent caustics obtained directly from a refinery, most of the studies used a synthetic spent caustic of simpler composition for research convenience [6,7].

The pH value was controlled by adding H_2SO_4 (1 mol/L) or NaOH (0.5 mol/L). Table salt (NaCl) was added to the influent flow to obtain desired total dissolved solids (TDS) for growth of haloalkaliphilic sulfide-oxidizing bacteria. Nutrients were also added to R2 to provide essential trace elements for microbial proliferation. The initial pH value was adjusted to be 10.5 ± 0.1.

The liquid hydrocarbon spent caustic samples were obtained from the catalytic cracking unit of Fushun Petrochemical Company and the spent caustics were characterized by high concentrations of sulfide (9180 mg/L) and TDS (> 23000 mg/L), with the concentration of COD exceeding 63300 mg/L. The initial pH value was adjusted to be 10.5 ± 0.1 and the caustics were treated with a dilution ratio of 3.

Experimental program: The experiment was divided into two parts. The first part involved the study of the synthetic spent caustics. The study focused on the final effluent quality and sulfide oxidation of R1 with different influent sulfide concentrations. The influence of aeration rate and HRT was also studied in consideration of the effluent of R1 and the final effluent. Next, the effect of treatment of liquid hydrocarbon spent caustic samples was studied. The detailed experimental operation parameters are shown in Table 1.

Analysis: Sulfide, COD, alkalinity and TDS were analyzed according to standard methods[8]. Thiosulfate and sulfate were determined using gas chromatography (ICS-1000, Dionex). The pH value was measured with a portable pH meter (Delta 320, METTLER).

RESULTS AND DISCUSSION

Influence of influent sulfide concentration on sulfide oxidation with combined processes: The variation of effluent of R1 with influent sulfate concentration is shown in Fig. 2. The results indicated that the sulfide was mainly oxidized to nontoxic thiosulfate, which is consistent with the findings of other research, which showed that the main oxidation product of sulfide was thiosulfate in salinity and alkalinity[9]. When the influent sulfate concentration was 0.06 mmol/L, the effluent sulfate concentration was 2 mmol/L with a conversion rate of 3.2 %, indicating that a small amount of sulfide was oxidized to sulfates in the pre-oxidation process. Moreover, the formation of elemental sulfur was not observed in this experiment. Furthermore, when the influent sulfide concentrations were 200 mg/L (6.25 mmol/L) and 500 mg/L (15.6 mmol/L), the oxidation rate of sulfides was 100 % because the maximum oxidation efficiency of the pre-oxidation system was not exceeded. However, when the influent sulfide concentrations were 31.25, 46.9 and 62.5 mmol/L, the sulfur oxidation rate decreased to 89.1, 70.1 and 49.8 %, respectively, because the maximum oxidation efficiency was exceeded.

The variation of the effluent from R2 is shown in Fig. 3. Sulfides and thiosulfates were not detected in the final effluent after biological reaction indicating that the two-step oxidation process completely converted sulfide to sulfate, which was allowed to be discharged into the environment, with a conversion efficiency of over 98 %.

As shown in Fig. 4, for the same sulfur load (including S^{2-} and $S_2O_3^{2-}$), the effluent still contained a certain concentration

TABLE-1
EXPERIMENTAL OPERATION PARAMETERS

Stage	Pre-oxidation reactor R1			Biological reactor R2	
	Influent sulfide concentration (mg/L)	Aeration rate (L/min)	Period (h)	Aeration rate (L/min)	Period (h)
Synthetic wastewater	2002000	0.1	24	0.3	24
	2000	0.1–0.4	24	0.3	24
	2000	0.4	4–48	0.3	24
	2000	0.4	12	0.5	4–24
Spent caustic samples	1300–1400	0.4	12	0.3	24

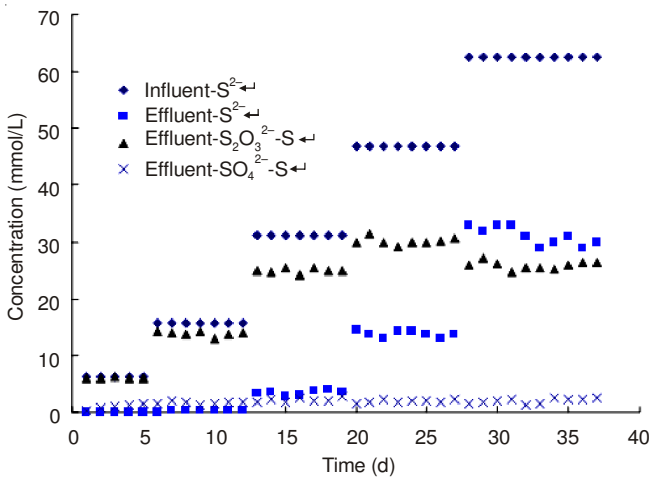

Fig. 2. Variation of influent and effluent of R1

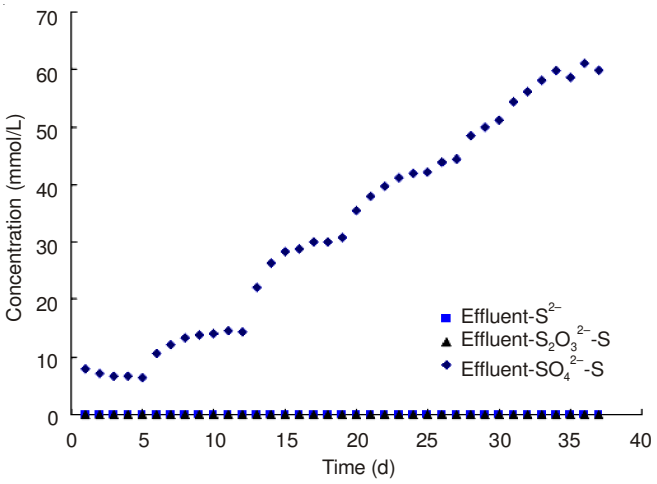

Fig. 3. Variation of effluent from R2

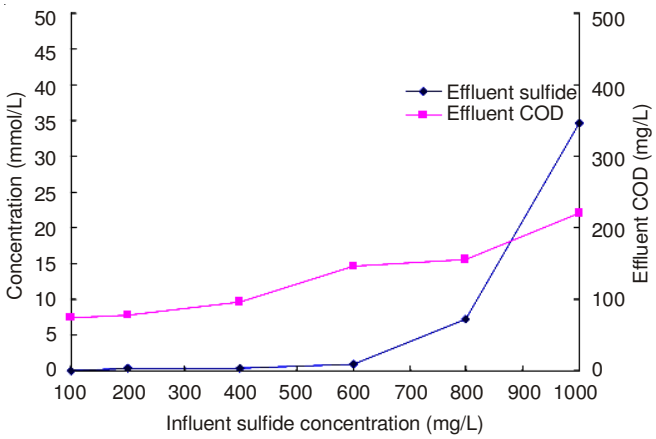

Fig. 4. Variation of effluent from the direct biological treatment method

of sulfides, with a mixture of elemental sulfur in water, when direct biological treatment was employed. Whereas with the proposed method, the effluent was free of sulfur and turbidity was low, indicating that almost no elemental sulfur was generated. Moreover, the treatment effect of air oxidation and biological method was more stable and was not affected by the proportional variation of influent sulfide and thiosulfate. Because the sulfide was partly converted into thiosulfate, the toxicity to microorganisms was reduced and thus the efficiency of biological treatment was increased, thus improving water quality. Therefore, the combined air oxidation and biological treatment process can be applied more effectively for higher sulfide loads when compared with the direct biological treatment method.

Process of sulfide oxidation in R1: The sulfide oxidation process in R1 is shown in Fig. 5. It can be seen that the sulfide was primarily oxidized to thiosulfate in R1. The aeration rate was controlled to be 0.4 L/min and the sulfide load was constant at 1.5 kgS/(m^3 d). Therefore, the amount of oxidation of sulfides in R1 depends entirely on the reaction time, which follows first-order reaction kinetics[10]. Hence, the sulfide oxidation rate increases as the reaction time increases. For example, for a sulfide concentration of 500 mg/L (15.6 mmol/L), when the reaction time was 1, 2, 4, 8, 12 and 24 h, the corresponding sulfide oxidation rates were 10, 19, 44, 74, 92 and 100 %, respectively. It can also be seen from Fig. 5 that there is a good linear relation within the 0-12 h range and the main factor affecting the correlation coefficient is the oxidation of small amount of sulfate. In addition, the pH of the system decreased rapidly from 13.1 to 9, thus preventing consumption of acid for the subsequent biological treatment.

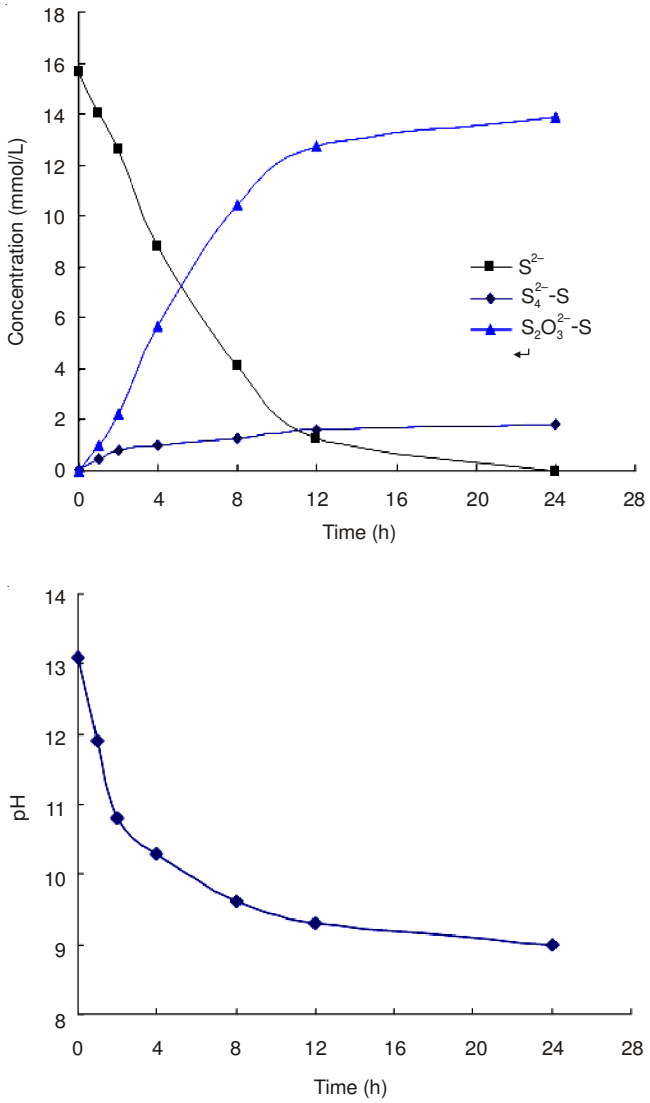

Fig. 5. Sulfide oxidation process in R1

Influence of aeration rate on sulfide oxidation in R1: The variation of sulfide oxidation with different aeration rates is shown in Fig. 6. The aeration rate can clearly be seen to affect sulfide oxidation. With a constant sulfide load, an increase in aeration rate accelerated the sulfide oxidation process because the oxygen concentration in water increases as the aeration rate increases and thus the sulfide oxidative ability was enhanced. For aeration rates of 0.1, 0.2 and 0.4 L/min, the sulfide oxidation rates for 12 h were 29.6, 48.6 and 80.1 %, respectively and the rates for 24 h reaction time were 47.2, 75.1 and 100 %, respectively. Therefore, the reaction time can be shortened by increasing aeration rate, which indicates that the reaction load can be enhanced. Therefore, the aeration rate was increased to 0.4 L/min in subsequent experiments.

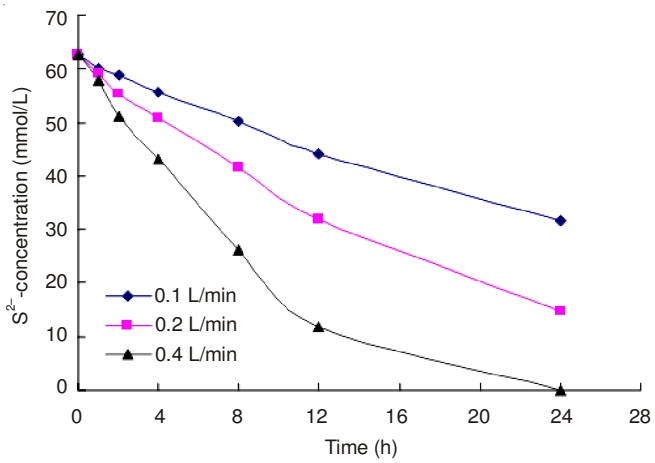

Fig. 6. Influence of airflow rate on sulfide oxidation in R1

Influence of HRT on sulfide oxidation of the effluents of R1 and R2: When the aeration rate was increased to 0.4 L/min, the sulfide oxidation rate increased to 80.1 % within the first 12 h, as shown in Fig. 6. It can be also seen in Fig. 2 that the ratio of sulfide to thiosulfate has minimal effect on the final effluent of the biological treatment step. Therefore, the aeration time of R1 can be selected to be 12 h because over aeration causes energy wastage with little effect on the subsequent biological treatment step.

The variation of effluent of R2 for an aeration rate of R1 of 0.4 L/min and R1 aeration time of 12 h with different HRTs is shown in Table-2. In case of the sufficient aeration in R2, when aeration time was reduced from 20 h to 6 h, the removal rate of sulfides and thiosulfates varied minimally and almost all the sulfur compounds were converted to sulfates. Therefore, the pre-oxidation process reduced the toxicity to microorganisms, thus strengthening microbial oxidation ability, which can significantly shorten the reaction time of the biological treatment process. When compared with the direct biological treatment method, the combined air oxidation and biological treatment method can save up to approximately 22 % of total reaction volume[11].

Biodegradation of liquid hydrocarbon spent caustic samples: After the synthetic wastewater experiment, the liquid hydrocarbon spent caustic samples with a dilution ratio of 3 were investigated. The variation of concentration of spent caustics at a high loading rate using the direct biological treatment is shown in Table-3 and that with the combined air oxidation and biological treatment process is shown in Table-4. It can be seen from Table-3 that the conversion of SO_4^{2-} reduced to 81.9 % when the total sulfur load was 1.5 kgS/(m^3 d) because sulfide was partly converted to elemental sulfur, which was observed by the turbidity of water. However, as shown in Table-4, sulfides are not detected in the treated effluent when the combined air oxidation and biological treatment process was used and the conversion rate of sulfate was 95.5 %. In addition, almost all the sulfides were converted to sulfates showing that the two-step treatment process can effectively reduce elemental sulfur thus improving water quality.

TABLE-3
VARIATION OF CONCENTRATION OF SPENT CAUSTICS BY DIRECT BIOLOGICAL TREATMENT

Parameter	Influent (mmol/L)	Effluent (mmol/L)	Removal (%)
S^{2-}	21.2	n.d.	100
$S_2O_3^{2-}$	21.3	n.d.	100
$C_2H_6S_2$	5.54	n.d.	100
$C_3H_8S_2$	1.68	n.d.	100
$C_3H_8S_2$	0.65	n.d.	100
SO_4^{2-}	76.1	142.3	SO_4^{2-} onversion rate (%) 81.9
Total sulfur load		1.5 kg S/(m^3 d)	

TABLE-4
VARIATION OF CONCENTRATION OF SPENT CAUSTICS BY COMBINED PROCESSES

Parameter	Influent (mmol/L)	Effluent (mmol/L)
S^{2-}	42.9	n.d.
$S_2O_3^{2-}$	42.6	n.d.
$C_2H_6S_2$	11.08	n.d.
$C_3H_8S_2$	3.36	n.d.
$C_3H_8S_2$	1.31	n.d.
SO_4^{2-}	16.3	168.8

Conclusion

This study investigated the effect of air oxidation and biological treatment on synthetic wastewater and spent caustic samples and showed that the combined processes improved

TABLE-2
INFLUENCE OF HRT ON EFFLUENTS OF R1 AND R2

HRT (h)	R2 influent S^{2-} (mmol/L)	R2 influent $S_2O_3^{2-}$ (mmol/L)	R2 influent SO_4^{2-} (mmol/L)	Effluent S^{2-} (mmol/L)	Effluent $S_2O_3^{2-}$ (mmol/L)	Effluent SO_4^{2-} (mmol/L)
20	11.9	48.1	2.1	0	0	61.7
12	12.2	47.8	2.4	0	0	62.0
8	11.9	48.0	1.9	0	0	61.6
6	12.0	48.2	2.6	0.1	0	62.1
4	11.9	48.1	2.0	1.8	3.3	55.9

the removal efficiency of sulfide in the treatment of spent caustics. For the synthetic wastewater, sulfides were primarily oxidized to thiosulfates in R1 and the oxidation rate depended on the aeration rate, HRT and sulfide load. After the air-oxidation step, the wastewater sulfides and thiosulfates were almost completely oxidized to sulfates in bioreactor R2. When compared with the direct biological treatment method, the effluent from the combined processes was characterized with lesser sulfides and elemental sulfur for the same total sulfur load. Furthermore, the combined method can effectively shorten the reaction time, thus increasing the reaction load. In addition, through the treatment of liquid hydrocarbon spent caustic samples, the conversion rate of SO_4^{2-} was effectively improved by the combined air oxidation and biological treatment method. Because the generation rate of the elemental sulfur declined, the treated effluent quality was better than that obtained with the direct biological treatment method.

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