UV-catalytic treatment of spent caustic from ethene plant with hydrogen peroxide and ozone oxidation

YU Zheng-zhe[1,2] , SUN De-zhi[2] , LI Chang-hai[2] , SHI Peng-fei[2] , DUAN Xiao-dong[2] , SUN Guo-rong[2] , LIU Jun-xin[1]

(1. Research Center for Eco-Environmental Sciences, CAS, Beijing 100085, China. E-mail: yuzhengzhe2002 @ sohu. com; 2. Department of Environmental Science and Engineering, Harbin Institute of Technology, Harbin 150001, China)

Abstract: The performance of UV/H_2O_2 , UV/O_3 and $UV/H_2O_2/O_3$ oxidation systems for treating spent caustic from an ethylene plant was investigated. In UV/H_2O_2 system, with the increase of H_2O_2 dosage, removal efficiencies of COD and the ratio of biochemical oxygen demand(BOD) to chemical oxygen demand(COD) of the effluent were increased and a better performance was obtained than the H_2O_2 system alone. In UV/H_2O_2 system, removal efficiency of COD reach 68% under the optimum condition, and BOD/COD ratio was significantly increased from 0.22 to 0.52. In UV/O_3 system, with the increase of O_3 dosage, removal efficiency of COD and BOD/COD ratio were increased, and a better performance was obtained than the O_3 system alone. Under the optimum condition, removal efficiency of COD was 54%, and BOD/COD ratio was significantly increased from 0.22 to 0.48. In $UV/H_2O_2/O_3$ system, COD removal efficiency was found to be 22.0% higher than UV/O_3 system.

Keywords: spent caustic; photochemical oxidation; UV/O_3 system; UV/H_2O_2 system; $UV/H_2O_2/O_3$ system

Introduction

Current process for ethylene production is not environment friendly where a large amount of spent caustic is discharged during the scrubbing of the cracking gas, which contains high concentration sulfide (ca. 3000 mg/L) and organic compounds (ca. COD = 3500 mg/L). Some techniques have been applied to treat the spent caustic, including chemical oxidation, neutralization and precipitation (Eater, 1963; Lim, 1984; Claude, 1998). However, low removal efficiency and second pollution are commonly involved in these techniques. Although wet air oxidation process can efficiently remove organic compounds in spent caustic, it is characterized by the too high cost and severe running conditions. So, a more thorough treatment is generally preferable.

In our study, three kinds of photochemical oxidation processes, including UV/H_2O_2 , UV/O_3 and $UV/H_2O_2/O_3$ processes, are adopted to degrade organic compounds in spent caustic, sulfide of which has been removed preliminarily, and some influential factors are also examined.

1 Materials and methods

The photochemical reactor employed in this work is shown in Fig. 1. It is a cylindrical stainless steel reactor of 80 mm inner diameter and 450 mm height, which is fixed with a low-pressure mercury vapor lamp in the axial position and quartz sleeve that houses the lamp and ultraviolet light source of 254 nm wavelength is adopted, power is 15 W. The O_3 was produced by an ozone generator and entered the bottom of the reactor to aerate through a microporous plate distributor at different rates. A solution of H_2O_2 with the spent caustic, which was taken from Daqing Petrochemical Company, is fed to the bottom of the reactor as well. Characteristics of the spent caustic after removing sulfide are given in Table 1.
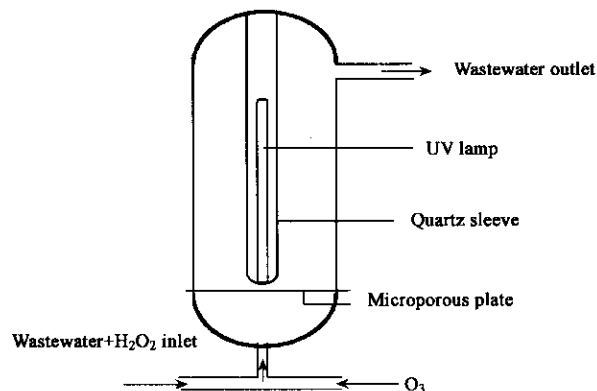

Fig.1 The UV reactor for treating spent caustic

Table 1 Characteristics of spent caustic after removing sulfide

Parameter	Concentration, mg/L
COD	3626
BOD_5	780
S^{2-}	95
NaOH	60000

GCMS-QP5050A is adopted to analyse the spent caustic components. Operation conditions: gasification and detection cell temperature are 250℃, process heat orders for column are 2 min at 40℃, 10 min at 160℃ and 12 min at 250℃. Extraction agent is 2-chloricmethane.

2 Results and discussion

2.1 COD removal by UV/H_2O_2 system

To research the interaction between UV and H_2O_2 , UV, H_2O_2 and UV/H_2O_2 systems are adopted separately to treat the spent caustic, with which H_2O_2 is added with the ratio of 0.8 by H_2O_2/COD. The results are shown in Fig. 2.

It can be seen from Fig.2 that though the COD removal rate is quite low when UV or H_2O_2 is used individually, combination of UV with H_2O_2 (i. e. UV/H_2O_2 system) can
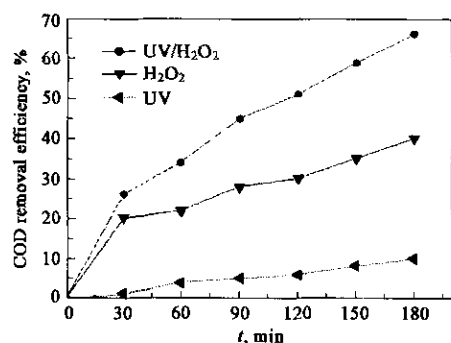
Fig.2 COD removal by using different AOPs

result in a better COD removal efficiency. This shows the necessity of H_2O_2 addition to the individual UV system, and the COD removal efficiency for UV/H_2O_2 system is better than that of the sum of individual UV or H_2O_2 system, it can been explained that there is a better synergetic action between UV and H_2O_2 systems.

To make a survey of H_2O_2 utilization ratio and the influence of addition amount of H_2O_2 on COD removal, the addition amount of H_2O_2 is changed in the system of H_2O_2. The relationship between COD removal and the addition amount of H_2O_2 is shown in Table 2 and Fig.3.

Table 2 COD removal efficiency in different modes of oxidation system

H_2O_2/COD ratio	UV/H_2O_2 process	
	COD, mg/L	COD removal/H_2O_2, mg/g
Sample	3626	
1.5(H_2O_2 process only)	2132	275
0.6	1667	675
0.8	1160	850
1.5	1087	466
2.5	979	294

It is evident from the data that the highest utilization ratio of H_2O_2 removing COD is recorded at H_2O_2/COD ratio 0.8 in UV/H_2O_2 system. And this value is even higher than what is obtained when a high ratio of 1.5 by H_2O_2/COD was supplied in H_2O_2 process alone. Better COD removal efficiency at low dosage of H_2O_2 is thought to be synergetic action of UV irradiation with H_2O_2. In that case, more hydroxyl radicals are generated in the reaction system.

It is also evident from experimental results that when amount of H_2O_2 is increased from 1.5 to 2.5 by H_2O_2/COD ratio in UV/H_2O_2 system, no significant raise of COD removal could be observed in comparison to COD removal at the ratio of 0.8 by H_2O_2/COD. The hydroxyl radicals generated from the photolysis of H_2O_2 are main species responsible for COD removal. But H_2O_2 also reacts with hydroxyl radicals and hence acts as an inhibiting agent against the oxidation of organic compounds. In addition, H_2O_2 itself absorbs light in the system consequently, thus the light intensity available for organic compounds is reduced at higher H_2O_2 concentration (Sundstrom, 1986; Steensen, 1997; Tahir, 2002). Hence an optimum amount of H_2O_2 is necessary. Fig. 3 shows effect of H_2O_2/COD ratio on COD removal efficiency in UV/H_2O_2 process, oxidation time of which was controlled at 180 min. Therefore from both Table 2 and Fig. 3, with consideration of

processing efficiency and economy, it is appropriate when the addition amount of H_2O_2 is 0.8 by H_2O_2/COD in the system of UV/H_2O_2.
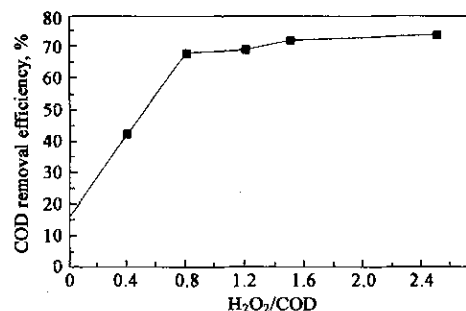
Fig.3 The effect of H_2O amount on COD removal

2.2 COD removal by UV/O_3 system

UV, O_3 and UV/O_3 systems are adopted separately to treat the spent caustic. The results are shown in Fig. 4.
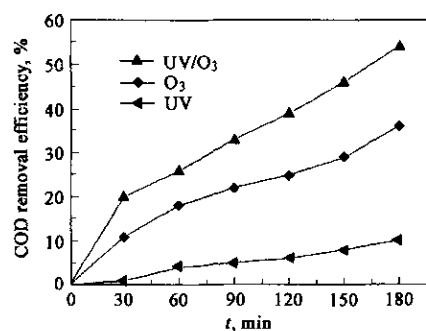

Fig.4 COD removal by using different AOPs

It can be seen from Fig.4 that combination of UV with O_3 (i.e. UV/O_3 system) is much better to degrade COD of spent caustic than the individual UV or O_3 system, and the COD removal efficiency for UV/O_3 system is better than that of the sum of individual UV or H_2O_2 system, it proves the synergetic action of UV irradiation with O_3 in UV/O_3 system. To make a survey of O_3 utilization ratio and the influence of addition amount of O_3 on COD removal, the addition amount of O_3 is changed into the system of UV/O_3. The results are indicated in Table 3 and Fig.5. It is evident that the COD removal was increased with the increase of O_3 addition, but it was also observed that the increase of COD removal is not significant when the O_3 addition is greater than 0.6 g/L. COD removal per gram ozone for different modes of oxidation (different O_3 dose) was calculated. The highest COD removal per gram of ozone dose was observed at 0.6 g/L in the system UV/O_3. For a better experimental result and economic consideration, it can be concluded from Table 3 and Fig.5 that the better loading of O_3 is 0.6 g/L.

2.3 COD removal by $UV/H_2O_2/O_3$ system

To certify the advantage of the $UV/H_2O_2/O_3$ system, UV/H_2O_2, UV/O_3 and $UV/H_2O_2/O_3$ systems are adopted separately to treat the spent caustic, during which H_2O_2 is

added with the ratio of 0.8 by H_2O_2/COD and O_3 0.6 g per liter spent caustic. The experimental results are indicated in Fig. 6.

Table 3   COD removal efficiency in different modes of UV/O_3 oxidation system

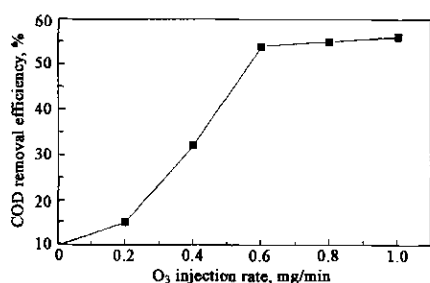| Experimental mode, g/l.	COD, mg/L	COD removal/O_3, g/g
Sample	3626	
0.8 (O_3 process)	2501	1.4
0.8	1631	2.5
0.6	1667	3.3
0.4	2454	2.9
0.2	3101	2.6

Fig.5   The effect of O_3 amount on COD removal
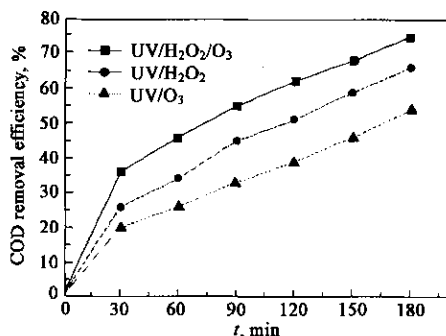

Fig.6   COD removal by using different AOPs

It is evident that the best efficiency of COD removal can be achieved in the UV/H_2O_2/O_3 combined process. The order of COD removal efficiency in different processes is: UV/H_2O_2/O_3 > UV/H_2O_2 > UV/O_3. It is also proved that the efficiency of COD removal is not so ideal by the processes of UV, H_2O_2, or O_3 alone. Compared to individual process, the efficiency of UV/H_2O_2/O_3, UV/H_2O_2 and UV/O_3 processes is largely enhanced, which means that the combination of H_2O_2 or O_3 and UV is very necessary. Among them, the efficiency of COD removal reaches up to 68% in the system of UV/H_2O_2 and 54% in the system of UV/O_3 and 76% in the process of UV/H_2O_2/O_3 within 180 min, which indicates that UV, H_2O_2 and O_3 have additivity together.

COD removal per gram ozone for different modes of oxidation(different O_3 dose) could not be calculated for the system UV/H_2O_2/O_3 due to the presence of two oxidizing agents in the reaction mixture at the same time. Effect of change in H_2O_2 and O_3 addition and change of temperature on COD removal is tested. The orthogonal experiment is adopted

to optimize the reaction conditions of the UV/H_2O_2/O_3 system. Table 5 and Table 6 show that the level of factor and experimental results.

It could be seen from Table 5 that the rate of hydrogen peroxide doses was the most important effect factor on COD removal efficiency, and the COD removal efficiency of No.5 was the highest, compared to the other experiment. The better temperature was 30℃ among three level according to the calculated value of k of Table 5. The COD removal was increased with the increase of rate of hydrogen peroxide doses, but it was also observed that the increase of COD removal is not significant when the ratio of H_2O_2/COD increase from 0.8 to 1.2, so the ratio of 0.8 by H_2O_2/COD was better, this observation is in accordance with the UV/H_2O_2 oxidation system. In addition, the COD removal has a slightly increase with the increase of loading of ozone, therefore it is appropriate when the addition amount of ozone is 0.6 g/L on basis of Table 3 and Table 4. The range change reflected the effect of varied factors on COD removal. The bigger the value of the factor is, the more remarkable influence is on COD removal. It can be known from Table 3 that the effect order of varied factors on COD removal was BAC.

Table 4   Level of factor

	A Temperature, ℃	B Loading, H_2O_2/COD	C Loading, O_3, g/L
1	20	0.4	0.2
2	30	0.8	0.4
3	40	1.2	0.6

2.4   The effect of different modes of oxidation system on BOD/COD ratio

Different rates of hydrogen peroxide doses were supplied to the oxidation experiments in order to get the highest degradation efficiency of the UV/H_2O_2 system. BOD/COD ratio(0.22) of the spent caustic was improved by the application of UV/H_2O_2 oxidation systems and made up to the level, which is suitable for biological treatment. Reduction in COD levels was accompanied by an increase in BOD. Degradation efficiency of UV/H_2O_2 system could be attributed to the direct oxidation by H_2O_2, the direct photolysis by UV light, and the indirect oxidation by OH' produced from H_2O_2 excited by UV-light. The result showed that the mode UV/H_2O_2(0.8 time) has a higher degradation level in comparison to the mode H_2O_2 alone. So it could be argued that it is better to use less amount of H_2O_2 in combination with UV than to use high dosage of H_2O_2 without UV. Table 3 shows BOD/COD ratio of the effluent in different modes of UV/H_2O_2 system.

BOD/COD ratio was found to be increased further when UV/O_3/H_2O_2 system was applied in comparison to the UV/O_3 system without H_2O_2. According to data, low dosage of ozone (0.6 g/L), with the combination of UV, showed comparable results with that of the high dosage of ozone (0.8 g/L). It could be inferred that applying higher ozone doses might not be necessarily advantageous for the enhancement of biodegradability and short contact time was sufficient to achieve the specific biodegradability potential of the effluent. Higher doses of ozone will only contribute to the increased

residual amount of ozone in the effluent. Experiments done by Weichgrebe *et al*. also confirmed that higher ozone rate is only benefited at the lower energy output. In $UV/H_2O_2/O_3$ system, expected enhancement of the reaction rate by the addition of H_2O_2 did not occur since the organic compounds can also be destroyed rapidly via direct molecular attack of ozone. This observation is in accordance with the recent studies conducted with H_2O_2/O_3 combination for the treatment of industrial wastewater(Table 6).

Table 5   The orthogonal experimental results and analysis

	A Temperature, ℃	B H_2O_2/COD	C O_3, g/L	COD removal efficiency, %
1	20	0.4	0.2	46
2	20	0.8	0.4	67
3	20	1.2	0.6	69
4	30	0.4	0.4	52
5	30	0.8	0.6	76
6	30	1.2	0.2	72
7	40	0.4	0.6	47
8	40	0.8	0.2	68
9	40	1.2	0.4	70
k_1	182	145	186	$k_i = \sum_{i=1}^{3} COD$
k_2	200	211	189	removal efficiency
k_3	185	211	192	i = level
k_1	60.7	48.3	62.0	$k^i = k_i/3$
k_2	66.7	70.3	63.0	
k_3	61.7	70.3	64.0	
Range R	18	66	6	

Table 6   BOD/COD ratio of efficiency in different modes of oxidation system

Experiment mode	BOD, mg/L	COD, mg/L	BOD/COD
UV/H_2O_2 system			
sample	779	3626	0.22
H_2O_2(1.5 times)	878	2132	0.41
UV/H_2O_2(0.8 times)	603	1160	0.51
UV/H_2O_2(1.5 times)	568	1087	0.52
UV/H_2O_2(2.5 times)	509	979	0.52
UV/O_3 and systems sample	779	3626	0.22
O_3(1.0 g/L)	824	2501	0.33
UV/O_3(0.8)	654	1667	0.40
UV/O_3(0.6)	648	1631	0.40
UV/H_2O_2(0.8 times)/O_3(0.6 g/L)	472	906	0.52

Fig. 7 and Fig. 8 show the chromatograms of spent caustic after solvent extraction, which shows clearly the reduction of organic compounds in spent caustic after the treatment of $UV/H_2O_2/O_3$ process, peaks observed at retention time 5.7 min and 19.7 min in Fig.7 were attributed to tetradecane($C_{14}H_{30}$) and 2, 6, 10, 14-methyl hexadecane($C_{20}H_{42}$), respectively.

3   Conclusions

The use of H_2O_2 in combination with UV showed better results than the use of H_2O_2 alone. COD removal and BOD/COD ratio was improved with the increase of hydrogen peroxide dosage up to an optimum limit.
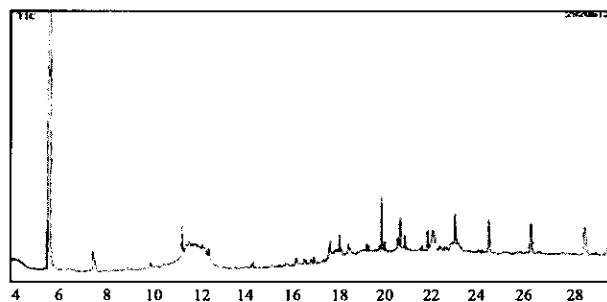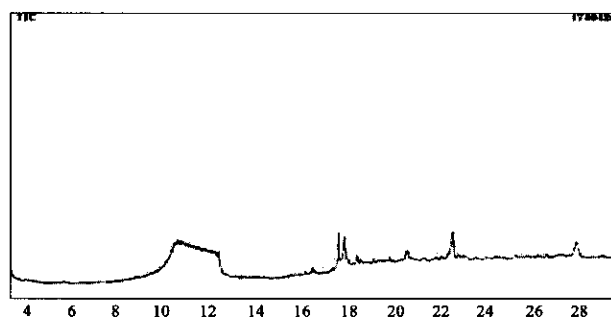

Fig.7   Chromatogram of spent caustic before $UV/H_2O_2/O_3$

Fig.8   Chromatogram of spent caustic after $UV/H_2O_2/O_3$ treatment

The highest COD removal per gram of H_2O_2(850 mg/g) in UV/H_2O_2 system was observed at low dosage of hydrogen peroxide(0.8). This is due to the scavenging of OH' with the increase of hydrogen peroxide concentration in the reaction mixture.

In UV/O_3 oxidation experiments, COD removal was increased and BOD/COD ratio was improved with the increase of ozone dosage up to an optimum limit. Ozone in combination with UV showed good oxidation potential than ozone alone.

The highest COD removal per gram of O_3(3.3 g/g) in UV/O_3 system was observed at low dosage of ozone (0.6 g/ L).

Combination of H_2O_2 with UV/O_3 system could further increase the COD removal and also improve the BOD/COD ratio(from 0.22 to 0.52). In $UV/H_2O_2/O_3$ oxidation system, the optimum loadings of H_2O_2 and O_3 is 0.8 and 0.6 g/L respectively, and its COD removal reaches up to 76% accordingly.

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