Article

Catalytic Ozonation of the Secondary Effluents from the Largest Chinese Petrochemical Wastewater Treatment Plant—A Stability Assessment

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Abstract: Effluents discharged from petrochemical facilities are complex and composed of various types of highly toxic contaminants, which necessitates the development of sustainable treatment technologies. Stability is among the most important sustainability criteria of the wastewater treatment processes. In the present manuscript, the standard-reaching rate (η) index was used to evaluate the stability of the catalytic ozonation process for treating the secondary effluent from the petrochemical industry. A pilot-scale device was designed and implemented for catalytic ozonation. The effluents were taken from the secondary sedimentation tank of a petrochemical wastewater treatment plant in China. A commercially available γ - Al_2O_3 was used as the catalyst after a pre-treatment heating step. The catalyst was characterized using scanning electron microscopy. Three mathematical statistics indexes, discrete coefficient (V_σ), skewness coefficient (C_{so}), and range coefficient (V_R), were used to analyze the results achieved from the catalytic ozonation process. Continuous operation of the pilot-scale device was monitored for 9 months under an ozone concentration of 36 mg/L and the contact oxidation time of 1 h. The results demonstrated that the stability evaluation grades of chemical oxygen demand (COD) and suspended solids (SS) in the effluent of the catalytic ozonation system were both 3 and A, indicating that the process was relatively stable over a long period of application. The effluent COD compliance grade was also calculated as B, indicating that the effluent COD does not meet the standard and the process parameters need to be further optimized. When the reflux ratio is 150%, the removal rate of COD is the highest (38.2%) and the COD of effluent is 49.34 mg/L. Meanwhile, to enhance the efficiency and stability of the system, the ozone concentration and the two-stage aeration ratio are 40 mg/L and 4:1, respectively. Moreover, the presence of SS in the water of the catalytic ozonation system will result in the waste of ozone and reduce the utilization rate of ozone.

Keywords: catalytic ozonation; petrochemical industry; secondary effluent; stability evaluation

1. Introduction

The effluents from the petrochemical industry are characterized by a complex composition containing high concentrations of various types of pollutants with high concentrations and high toxicity [1]. These types of effluents normally contain a variety of bio-refractory organic compounds. In July 2015, the Ministry of Environmental Protection began to implement the “petrochemical industry pollutant emission standards” (GB 30571-2015) [2]. This standard has set limitations for the chemical oxygen demand (COD) of petrochemical wastewater drainage from 100 mg/L to 60 mg/L. Hence, there is a need for the industries to adopt effective approaches to meet these standards.

Catalytic ozonation is among the advanced oxidation processes (AOPs) developed in recent years to deal with highly polluted effluents containing non-biodegradable and recalcitrant organic compounds. This technique has the potential to degrade various refractory organic micro-pollutants (OMPs) in wastewater [3,4]. Furthermore, it has been used to reduce the chroma of wastewater, and further remove OMPs in secondary effluent. There are some reports in the literature for the efforts on the optimization of this process to be applicable for real applications [5,6]. Fu [7] efficiently used catalytic ozonation to treat petrochemical wastewater. Geng and Cui [8,9] indicated that catalytic ozonation is a feasible method for the treatment of secondary effluent from large-scale chemical wastewater treatment plants (WWTP). They demonstrated that, using this technology, the COD of effluent can reach the direct discharge limit stipulated in the GB31571-2015 standard, and the biodegradability of wastewater can be improved after photocatalytic oxidation by ozone.

However, the effluents from the petrochemical industry are of quite a complex nature, which can be affected by crude oil quality, production process, and production equipment. The quality and quantity of the petrochemical effluents can, hence, fluctuate greatly. It is reported that the average freshwater intake and wastewater discharge per ton of crude oil are about 0.55 t and 0.27 t, respectively [10]. The concentration of COD in petrochemical wastewater varies from 2500 mg/L to 15,000 mg/L [11]. Hence, different qualities for the final treated effluents can be expected [12]. On the other hand, the industries are looking for sustainable wastewater treatment technologies to satisfy the long-term needs for a reliable wastewater treatment method. As discussed in the literature [13,14], stability is among the most important sustainability parameters that define the degree of reliability of the developed wastewater treatment technology for real applications. This is of high importance, especially for industries such as the petrochemical industry, to ensure the quality of the discharged effluents and to prevent the secondary environmental issues resulting from the release of the effluents containing toxic and non-biodegradable organic pollutants [15,16].

According to the very recent literature, stability is among the most important sustainability criteria of industrial wastewater treatment technologies. However, there is currently a lack of such in-depth studies, especially in pilot and real scales, to evaluate the reliability of the already developed wastewater treatment technologies. Although there are several studies in the literature on the efficiency and cost analysis of AOPs, such as catalytic ozonation, to our best knowledge, the reports on the systematic stability analysis of such technologies are rare in the literature. Hence, the present manuscript tends to evaluate the stability of the ozonation process of the secondary effluents from the largest petrochemical wastewater treatment plant in China during a long-term period of operation using a pilot-scale catalytic ozonation system. Moreover, statistical analysis was employed to this end and the required modification in the process was identified and recommended using the obtained results.

2. Materials and Methods

2.1. The Petrochemical WWTP

The selected WWTP is the largest petrochemical WWTP in China (PetroChina), located in the northeast of China. The influent mainly comes from the petrochemical industries

from more than 60 sets of production equipment, such as refining, chemical, synthetic materials, and domestic sewage from nearby communities (Table 1).

Table 1. The wastewater type and volume entering the wastewater treatment plant.

No.	Effluent Source	Water Volume (m ³ /h)	COD (mg/L)	COD (g/h)
1	The wastewater of the dye factory	227.14	662.46	150,471.16
2	The wastewater of fertilizer plant	90.35	2179.39	196,907.89
3	The wastewater of acrylonitrile plant	370.79	394.03	146,102.38
4	The wastewater of calcium carbide plant	221.89	1485.1	329,528.84
5	Organic wastewater of calcium carbide plant	201.27	1223.79	246,312.21
6	Glycol wastewater of glycol plant	70.59	612.95	43,268.14
7	Ethylene oxide wastewater of glycol plant	31.09	376.52	11,706.01
8	The wastewater of the organic synthesis plant	545.66	374.56	204,382.41
9	The wastewater of refinery plant	1089.54	412.41	449,337.19
10	The wastewater of synthetic resin plant	176.77	409.11	72,318.37
11	The wastewater of fine chemicals factory	11.76	566.56	6662.75
12	Lusheng pesticide factory	11.06	1281.79	14,176.60
13	CITIC Chemical Co., Ltd. wastewater	5.44	2049.64	11,150.04
14	Yingtai Chemical Co., Ltd.	0.73	2049.64	1496.24
15	Fu Landa Chemical Co., Ltd.	0.35	26.91	9.42
16	Zongheng Plastic Packaging Co., Ltd.	5.27	4110	21,659.70
17	Northern cleaning	12.09	179.6	2171.36
18	Entering industry and trade	0.05	120.77	6.04
19	Bei Dagou municipal drainage	350.00	240	84,000.00
20	Industrial park drainage	84.44	225	18,999.00
21	Buried plant permeate	10.00	1300	13,000.00
22	805, 806 tank drainage	100.00	50	5000.00
23	Domestic waste heaping plant permeate	0.00	0	0.00
24	Domestic sewage	1412.28	224.57	317,155.72
25	Ash dam drainage	100.00	120	12,000.00
26	Fertilizer plant containing nitrogen water	100.00	150	15,000.00
	Subtotal	5228.56	453.84	2,372,921.47
	New wastewater volume (Standardization)	767.76	318.8	244,763.40
	Direct drainage water consumption	473	30	14,190
	Total displacement	6469.32	406.83	2,631,874.87

The influent flowrate is ~6500 m³/h. The WWTP utilizes a biochemical treatment method as the core and adopts anaerobic hydrolysis acidification-anoxic/aerobic (A/O) as the main process (Figure 1).

2.2. Experimental Set-Up

The pilot-scale device in this study is shown in Figure 2. Ozone production was calculated by detecting the flow rate of the gas and the concentration of ozone. A quantitative relationship was established between intake air volume of oxidation tower, generation power of ozone generator, and ozone production. The process of the pilot-scale device is shown in Figure 3. The pilot-scale device was continuously operated for 9 months under an ozone concentration of 36 mg/L and the contact oxidation time of 1 h.

2.3. Wastewater Treatment Process

The test water was taken from the secondary sedimentation tank of the petrochemical WWTP. The wastewater samples were taken once a day from the bench-scale and pilot-scale experimental reactors during the operation period. The wastewater characteristics of influent and effluent are given in Table 2.

Figure 1. A schematic of the wastewater origin and the treatment process of the WWTP.

Figure 2. Pilot-scale experimental set-up used for the stability assessments.

Figure 3. The schematic of the catalytic ozonation process implemented in the present study.

Table 2. Characteristics of the effluents (1-year average).

Items	COD (mg/L)	TOD (mg/L)	BOD ₅ (mg/L)	NH ₄ ⁺ -N (mg/L)	TN (mg/L)	TP (mg/L)	SS (mg/L)
Secondary effluent before catalytic ozonation	84.7 ± 20.9	26.0 ± 8.90	5.22 ± 0.62	1.22 ± 2.85	13.6 ± 2.11	0.90 ± 0.25	26.6 ± 12.4
GB 8978-1996 *	100	-	30	15	-	0.5	70
GB 31571-2015 **	60 (50)	20 (15)	20 (10)	5	30	0.5	50

* The Level A limited concentration; ** the values in parentheses are special limited concentration.

The catalyst in this pilot-scale study was commercially bought from a Chinese company (Cathay Chemical, Co., Ltd., Dalian, China). This is a catalyst that supports heavy metals (Table 3) with γ -Al₂O₃ as a carrier (Figure 4). The catalysts were washed several times with milli-Q water (18.2 MΩ·cm, Millipore Corporation, Burlington, MA, USA) before use and then burned in the muffle furnace for 2 h at 600 °C to remove the impurities from the surface.

Table 3. The energy-dispersive X-ray spectroscopy (EDS) of the catalyst element composition.

Element	App Conc.	Intensity Corr.	Weight %	Weight % Sigma	Atomic %
O	29.06	0.8443	43.46	0.48	59.19
Mg	0.15	0.7629	0.25	0.06	0.23
Al	29.55	0.8466	44.06	0.43	35.59
S	0.76	0.7236	1.32	0.13	0.90
Cl	0.91	0.6791	1.70	0.15	1.04
K	1.02	0.9749	1.32	0.15	0.73
Ca	2.11	0.9466	2.82	0.16	1.53
Ce	3.25	0.8101	5.07	0.48	0.79

Figure 4. SEM images of the catalyst used in the catalytic ozonation treatment of the effluents (**up**), and the X-ray energy spectrum analysis of catalyst composition (SEM-EDS) (**down**).

The basic characteristics of the commercial catalyst are listed in Table 4.

Table 4. The characteristics of the commercial catalyst used in the present study for the catalytic ozonation process.

Item	Unit	Value
Particle size	mm	2~4
Density	g/mL	0.66
Specific surface area	m ² /g	206.9
Void volume	cm ³ /g	0.47
Compressive strength	N/particle	137
Wear rate	%	0.31
Water absorption	%	47
Qualified size	%	94
Major catalytic component	-	Activated alumina as a carrier; the ingredients are a trade secret
Years of use	year	≥6

The catalyst was spherical with an average size of 2–4 mm. It possessed a mesoporous surface with a packed lamellar structure. SEM (scanning electron microscope) images of catalyst are presented in Figure 4.

2.4. Analytic Items and Methods

2.4.1. Water Sample Test Methods

All the chemicals (purity > 99%) used in this study were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The concentration of gas ozone was determined by the iodometric method [17], and the ozone in water was determined by the

indigo method [18]. UV absorption at 254 nm is frequently used to monitor water quality for dissolved organic matter (DOM) removal since aromatic structures in DOM absorb UV light at 240–260 nm [19]. UV_{254} was measured with a UV spectrometer (Shimadzu Co. Ltd., UV-1700, Kyoto, Japan). Chemical oxygen demand (COD) and suspended solids (SS) were assayed according to the Chinese State Environmental Protection Administration of China (SEPA) Standard Methods [20]. All experiments were conducted in triplicate, and the presented results are an average of replications.

2.4.2. Stability Assessment Indicators and Evaluation Criteria

In the present study, the fluctuations of the wastewater quality indicators were monitored during a specific period to evaluate the stability of the wastewater treatment system. The characteristics of time series dispersion composed of historical data of monitoring indicators are analyzed. The long-term operation stability of catalytic ozonation technology for treating petrochemical secondary effluent was evaluated [21], as a main sustainability criterion of the applied process. For this, standard-reaching rate (η) was utilized; η is an important index to evaluate the operation stability of the technical processes. In addition, according to the statistical principle, three mathematical statistics indexes, discrete coefficient (V_σ), skewness coefficient (C_{so}), and range coefficient (V_R), are selected to evaluate the operation stability of the technology. To describe the merits and demerits of the monitoring data with time series, the four evaluation indexes are divided into different grades. Achievement rate was strictly controlled, so the other three indicators are divided into three grades: A, B, and C [22]. Among them, A means the best; B means the abnormal situation, but the degree is not high; C means the worst and unacceptable. The critical values of the three grades are determined by the discussion of several water treatment experts and the mathematical and physical characteristics of the three statistics. The classification of COD and SS of secondary effluent from the petrochemical industry by catalytic ozonation is shown in Table 5.

Table 5. Criteria for evaluation of the COD and SS stability of catalytic ozonation process.

Degree	η	V_σ	C_{so}	V_R
A	$\eta = 100\%$	$V_\sigma \leq 0.5$	$ C_{so} \leq 0.5$	$V_R \leq 1$
B	$\eta < 100\%$	$0.5 < V_\sigma \leq 1$	$0.5 < C_{so} \leq 3$	$1 < V_R \leq 1.5$
C	-	$V_\sigma > 1$	$ C_{so} > 3$	$V_R > 1.5$

The definition and basic connotation of the four evaluation indicators are as follows: (1) standard-reaching rate (η) refers to the ratio of days (N_s) to total monitoring days (N_t) according to the emission concentration of pollutants specified in GB 31571-2015 for 9 months of continuous monitoring data (Equation (1)). (2) Discrete coefficient (V_σ) indicates the degree of concentration of the values monitored by each indicator in the monitoring time series around its center position (average value) (Equation (2)). (3) Skewness coefficient (C_{so}) refers to the deviation degree of the monitoring sample data in the monitoring time series (Equation (3)). (4) The range coefficient (V_R) refers to the relative range of the maximum fluctuation value of each monitoring index in the monitoring time series (Equation (4)).

$$\eta = \frac{N_s}{N_t} \times 100\% \quad (1)$$

In Equation (2), X_i is the monitoring value in the effluent water quality data sample, which is the average value of the monitoring value of the index, and N is the total monitoring data sample number.

$$V_\sigma = \frac{\sqrt{\sum (X_i - \bar{X})^2 / N}}{\bar{X}} \quad (2)$$

$$\beta_3 = \frac{\sum (X_i - \bar{X})^3}{N} / \left[\sqrt{\frac{\sum (X_i - \bar{X})^2}{N}} \right]^3 \quad (3)$$

$$V_R = \frac{(X_{max} - X_{min})}{\bar{X}} \quad (4)$$

Stability is mainly determined by the size of discrete coefficients; skewness coefficients and range coefficients are complementary to describing the stability of data over time series. When the value of discrete coefficients is large, it can be found that skewness coefficients and range coefficients will increase correspondingly according to the statistical relationship among them. Therefore, the grade evaluation results of skewness coefficient and range coefficient will not be better than those of skewness coefficient. Based on this, the possible comparison of evaluation results is shown in Table 6.

Table 6. The outcome of the stability assessments of the implemented catalytic ozonation process.

No.	η	V_σ	C_{so}	V_R	Evaluation Result
1	A	A	A	A	1
2	A	A	A	B	1
3	A	A	A	C	2
4	A	A	B	A	1
5	A	A	B	B	2
6	A	A	B	C	2
7	A	A	C	A	2
8	A	A	C	B	3
9	A	A	C	C	3
10	A	B	B	B	3
11	A	B	B	C	4
12	A	B	C	B	3
13	A	B	C	C	4
14	A	C	C	C	4
15	B	A	A	A	3
16	B	A	A	B	3
17	B	A	A	C	3
18	B	A	B	A	3
19	B	A	B	B	3
20	B	A	B	C	3
21	B	A	C	A	3
22	B	A	C	B	4
23	B	A	C	C	4
24	B	B	B	B	4
25	B	B	B	C	4
26	B	B	C	B	4
27	B	B	C	C	4
28	B	C	C	C	4
Remarks	<p>(1) Evaluation result 1 means the water quality of long-term running effluent meets the standard and has good stability. The time series are concentrated near the average value, and there is no abnormal value.</p> <p>(2) Evaluation result 2 means the water quality of long-term operation effluent meets the standard and has good stability. Most of the values are relatively concentrated, some values are abnormal, or the values are evenly dispersed</p> <p>(3) Evaluation result 3 means, in the long-term operation process, the effluent quality may not meet the standard, the operation stability may be general, the time series is scattered, and there are many abnormal values.</p> <p>(4) Evaluation result 4 means, in the long-term operation process, there must be a situation that the effluent quality cannot meet the standard. The operation stability is poor and the time series dispersion is high.</p>				

3. Results and Discussion

3.1. Stability Assessment

The stability of the 9-month operation of the pilot-scale device was monitored and the parameters, including the COD and SS, were measured daily. The variations in COD and SS are shown in Figure 5.

Figure 5. Variation of the COD (a) and the SS (b) of the effluent after treatment with the catalytic ozonation process.

Most of the final COD values of the effluent after catalytic ozonation reached the COD limit specified in the new standard. Furthermore, the SS of the effluents during the operating period met the straight-line SS limits specified in the new standard. The evaluation results of the stability for the system are shown in Tables 7 and 8.

Table 7. Evaluation results of stability of the catalytic ozonation of the effluents.

Contaminants	η	V_σ	$ \beta_3 $	V_R
COD	92.6%	0.37	3.00	3.14
SS	100%	0.46	3.75	4.82

Table 8. Stability evaluation results of catalytic ozonation process used for the treatment of the effluents in the present study.

Contaminants	η	V_σ	$ \beta_3 $	V_R	Evaluation Result
COD	B	A	B	C	3
SS	A	A	C	C	3

In the process of catalytic ozonation treatment on secondary effluent from the petrochemical industry (Table 8), it can be seen that the stability evaluation grades of effluent COD and SS are 3, and there are similarities and differences among the four sub-indicators. The discrete coefficients of these two parameters are A, which indicates that the process is relatively stable. This treatment process can keep the values of COD and SS in a relatively stable range. The skewness coefficient of SS is C, which indicates that the average value of effluent SS is different from most SS monitoring values. Moreover, the skewness coefficient of COD is B, indicating a relatively low degree of abnormality. However, the standard-reaching rate of SS is A, which indicates that SS can meet the standard in the long-term operation process, so this index will not affect the effectiveness of this process.

The evaluation grade of the range coefficient for the two parameters is C, which indicates that the maximum and minimum values of effluent differ greatly. It may be due to this fact that there are some moments when the COD and SS values of effluent are too low. The standard-reaching rate of COD is B, which indicates that the effluent COD does not meet the standard all the time and does not meet the standard of A.

3.2. Influencing Parameters

3.2.1. Reflux Ratios

Effect of Different Reflux Ratio on COD Removal by Catalytic Ozonation

The reflux ratios of 0%, 50%, 100%, 150%, 200%, 300%, and 400% were set, respectively. Under different reflux ratios, the change in influent and effluent COD is shown in Figure 6. It can be seen that, when the reflux ratio increased, the COD removal rate increased first and then decreased. When the reflux ratio was 150%, the removal rate of COD was the highest (38.2%) and the effluent COD was 49.34 mg/L. When the reflux ratio was more than 150%, the lowest COD removal per unit of ozone was 1.19 gO₃/gCOD, and then it showed a decreasing trend.

Figure 6. The variation in influent and effluent COD values under different reflux ratios.

The reason may be that increasing the reflux ratio makes the wastewater and catalyst mix evenly, and the ozonation effect is enhanced, thus improving the removal of COD [23]. However, when the reflux ratio continued to increase, the rapid flow rate affected the contact between the organic substances in the water and the catalyst surface, resulting in a decrease in the COD removal rate [24].

Effect of Different Reflux Ratio on UV₂₅₄ by Catalytic Ozonation

UV₂₅₄ is an indicator of the content of aromatic compounds in water and compounds with a conjugated double bond structure [25,26]. The indicator has the advantages of simple operation, low cost, and good reproducibility [27]. The results of UV₂₅₄ variation in different reflux ratios of the sequencing batch oxidation test were shown in Figure 7. The influent UV₂₅₄ fluctuation range is 0.567–0.855 cm^{−1}. From the experimental results, ozone has a significant effect on UV₂₅₄ reduction in wastewater, which is consistent with the results of Zheng et. al. [28]. Ozone and hydroxyl radical (•OH) can act on active sites, such as aromatic rings or double bonds, and oxidize and decompose refractory macromolecular substances into small molecular substances by ring-opening or breaking bonds, thereby reducing UV₂₅₄.

As shown in Figure 7, increasing the reflux ratio resulted in the reduction in UV₂₅₄, in which the UV₂₅₄ removal without reflux was the worst. The removal efficiency of 150% reflux ratio is the best. The average UV₂₅₄ of the effluent of this reflux ratio was 0.203 cm^{−1}, and 0.547 cm^{−1} was removed compared with the influent.

Figure 7. UV₂₅₄ values of influent and effluent at different reflux ratios.

3.2.2. Ozone Concentration

The removal of total organic carbon (TOC) under different ozone concentrations was shown in Figure 8. The experiment results showed that the removal rate of TOC shows an increasing trend with the increase in ozone concentration. When the ozone dosage was increased from 10 to 40 mg/L, the average removal rate of TOC was 55.92% and 66.27%, respectively.

Figure 8. TOC removal using the implemented set-up under different ozone dosages.

3.2.3. Effect of Different SS Concentrations

The changes in influent and effluent SS concentrations are shown in Figure 5. The presence of SS results in the waste of ozone and the reduction in the ozone utilization rate, which may also lead to the COD value of effluent above the limits set in the standards [29–31].

The effect of influent SS on ozone depletion for the removal of per unit COD is shown in Figure 9. As the influent concentration increased, the amount of ozone depletion for the removal of per unit COD was gradually increased. When the influent SS concentration ranged from 0 to 10 mg/L, the average ozone depletion for the removal of per unit COD was 1.17 g. When the influent SS concentration became 30 to 35 mg/L, the average

ozone depletion rate for the removal of per unit COD was 2.31 g. Hence, the influent SS concentration has a significant effect on catalytic ozonation. On the other hand, SS increases ozone consumption. Therefore, without increasing ozone dosage, the increase in influent SS concentration can enhance the performance of the catalytic ozonation to meet the applicable standards for the final COD.

Figure 9. Ozone consumption per g COD removal under different influent suspended solid concentrations.

3.2.4. Effect of Different Aeration Ratios

The ozone transfer rate and utilization rate of the two-stage aeration experiment are shown in Table 9. Among them, when the two-stage aeration ratio is 4:1, the ozone transfer rate and utilization rate are maximized. When the two-stage aeration ratio is 1:1, the primary and secondary oxidation tower have the same amount of ozone, but organic compounds are mainly removed in the primary oxidation tower. This is consistent with the removal of COD, so the ozone dosage of the secondary oxidation tower is too high and is not fully utilized. Further increasing the ozone dosage of the primary oxidation tower is beneficial to remove OMPs in the effluents. It is obvious that, under a high concentration of ozone, the decomposition of the refractory organic matter in the content of effluents is facilitated. In addition, a higher ozone dosage may lead to mineralization of the OMPs, leading to high TOC removal efficiencies.

Table 9. Ozone transfer and utilization rates of the implemented two-stage process.

Aeration Ratio	Ozone in Water (mg/L)	Ozone in the Exhaust Gas (>mg/L)	Ozone Concentration (mg/L)	Transfer Rate (%)	Utilization Rate (%)
1:1	0.21	0.82	36	96.59	98.50
2:1	0.12	0.60	36	97.49	99.37
3:1	0.19	0.55	36	97.69	99.12
4:1	0.19	0.50	36	97.90	98.72
5:1	0.34	0.60	36	97.41	98.52

4. Conclusions

Currently, several industries consume large amounts of raw water and produce highly polluted effluents. In this situation, industries are looking for sustainable treatment technologies to deal with the produced effluents. Stability is among the most important sustainability criteria, which can not only determine the degree of the reliability of the method but can also decrease the costs of the periodical maintenance. In the present study, the long-term operational stability of a pilot-scale catalytic ozonation system was evaluated

for the treatment of secondary effluents coming from the petrochemical industry. It was found that the stability evaluation grade of COD and SS of the effluent of the system is 3, and their discrete coefficient grade is A. It was indicated that the catalytic ozonation process is feasible to treat secondary effluent from the petrochemical industry, but the process parameters need to be optimized to improve the COD standard-reaching rate of effluent. The evaluation results of COD and SS stability of the effluent coincide with the actual operation effect, which shows that the selection of evaluation index and evaluation criteria is reasonable. In the catalytic ozonation process, different reflux ratios will affect the removal rate of COD and UV₂₅₄. With the increase in the reflux ratio, the COD removal rate increased first and then decreased. When the reflux ratio was 150%, the COD removal rate was the highest (38.2%) and the effluent COD was 49.34 mg/L. With the increase in ozone concentration, the removal effect of TOC improves. A low concentration of TOC is beneficial for system stability. SS exists in the water of the catalytic ozonation system, which will cause ozone waste and reduce the ozone utilization rate. The excessive SS concentration in the influent will also result in the system effluent COD not meeting the standard. Moreover, the ozone transfer rate and utilization rate are different when the two-stage aeration ratio changes. The two-stage aeration ratio for the best experimental effect is 4:1. Finally, it is suggested for future studies to use the filtration system before the catalytic ozonation to reduce the influence of SS on the catalytic ozonation system. Moreover, it is recommended for future studies to implement the analytical methods developed in this study to evaluate the stability of the catalytic ozonation process and other AOPs in real and large-scale wastewater treatment plants.

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