Process Parameters Optimization of Multilevel Bio-Contact Oxidation System Treating Automobile Painting Wastewater

Y F Zhu¹, T Zhu¹, M Groetzbach², Y G Ma³ and B Ma⁴

1 School of Mechanical Engineering & Automation, Northeastern University, Shenyang, China
2 BMW Brilliance Automotive Ltd., Shenyang, China
3 Liaoning Provincial Machinery Research Institute Co., Ltd., Shenyang, China
4 SNF China FLOERGER, Taixing, China
E-mail: tongzhu@mail.neu.edu.cn

Abstract. A laboratory experiment of biological treatment has been performed with multilevel bio-contact oxidation system to treat the actual automobile painting wastewater pre-treated by physicochemical processes. The influence of three important process operating parameters (namely, hydraulic retention time, dissolved oxygen concentration, organic loading) on treating efficiency of multilevel bio-contact oxidation system has been investigated, and the optimum process operating parameters have been determined.

1. Introduction
With rapid development of automobile industry, automobile painting wastewater has become a difficulty and key point in the process of industrial pollution treatment. Painting wastewater is a kind of typical degradation-resistant industrial wastewater and has such features as great variation in discharge, high concentration of organic pollutants, complex compositions, and low biodegradability[1]. For automobile painting wastewater with pollutants of complex compositions and high concentration, different pretreatment in physicochemical method is commonly required for various kinds of painting wastewater, and biological method is then applied for further treatment after balanced water quality and quantity[2]-[3]. Currently, physicochemical and biological method are becoming main method for treatment of automobile painting wastewater by replacing pure physicochemical method, which not only delivers good treatment effect, saves operation cost, but also ensures stability of the entire process operation[4].

At present, there are few researches on Multilevel Bio-contact Oxidation (MBCO) system treating automobile painting wastewater at home and abroad, and the technical data is not complete[5]-[6]. The MBCO technique is based on the traditional contact oxidation method, and the reactor is designed into multilevel form, so that the microorganisms in original unipolar reactor could create natural differentiation of dominant bacteria in the multilevel reactor, and it could realize selection and allocation in space of microorganisms at different growing stages and with different functions spatially, promote biophase separation, enhance the synergistic effect in the same microbial population, and overcome antagonism among different microbial populations, thus treatment efficiency of the entire reactor is improved[7]-[8].

A joint venture automobile factory in Liaoning Province requires that the final effluent of painting wastewater receiving independent treatment in paint shop should reach more rigorous internal control standard; existing painting wastewater treatment process in paint shop uses a series of
physicochemical methods, and organic matter concentration of effluent is still high and fails to meet internal control standard. This research adopts the MBCO system to perform biological treatment on actual automobile painting wastewater receiving pre-treatment of physicochemical process and optimize process operating parameters.

2. Methods

2.1. Experiment Device
The experiment device system mainly includes MBCO reactor, biological carrier, adjust tank, discharge tank, peristaltic pump and aerating system, as shown in Figure 1.

![Figure 1. Experiment system of multilevel contact oxidation](image)

The MBCO reactor is the core apparatus of experiment system, materials of which are transparent organic glass, with length, width and height of 90cm, 25cm and 45cm respectively, and total effective volume of 80L. The whole biological reactor is separated internally into 6 tanks with the same size spatially, and left upper corner or right bottom corner of each tank partition is reserved with an overflowing port in 8cm × 8cm, so that wastewater can flow in the upper and at bottom to pass through the whole biological reactor and fully contact and react with microorganism on the biological carrier. Biological carrier is made of polypropylene fiber, and each piece of carrier is fixed at carrier holder at certain interval to form a carrier unit, which can directly be put in each segment of biological tank, with carrier amount of 2.5 kg/m³. Such biological carrier has super large specific surface area of 1200 m²/m³, and with density of 25 kg/m³ and porosity of 97%; Each segment of biological tank is configured with aeration pipeline and aeration disk; air enters each segment of biological tank through aeration pump to provide sufficient oxygen to microorganism. The air pressure flow of aeration pump is 120 L/min. Aeration intensity can be adjusted via the flow valve.

2.2. Seeding Sludge and Experimental Wastewater
The return sludge from secondary sedimentation tank of the automobile factory wastewater treatment station is obtained as seeding sludge, which appears to be yellowish-brown, has abundant microorganism and great activity. The MLSS of seeding sludge added initially is about 3600 mg/L. The quality of experimental wastewater has been shown in Table 1.

| Pollutants | PH | COD (mg/L) | BOD (mg/L) | TP (mg/L) | TN (mg/L) | NH₄⁺-N (mg/L) | SS (mg/L) |
|------------|----|------------|------------|-----------|-----------|---------------|----------|
| Actual value | 7±0.5 | 1200±50 | 180±10 | 0.5±0.1 | 30±5 | 10±2 | 150±10 |
| Standards | 6.5-8.5 | 500 | 250 | 5.0 | 50 | 40 | 300 |

2.3. Start-up and Acclimation
Starting process takes place under condition of room temperature of 20-25°C; DO concentration is controlled at 2.0-4.0 mg/L or so, and pH at 6.5-8.5. After two days of aeration only, the suspended
MLSS in biological tank is 200 mg/L or so; the majority of activated sludge in biological tank has covered on the surface of the entire biological carrier evenly, generating a layer of sludge-yellow biological film, and sludge floc has a good growing condition. After successful biofilm formation, start inject water to the biological reactor and gradually cultivate and domesticate activated sludge slowly, which enables the microorganism which can effectively treat painting wastewater to further breed and grow through survival of the fittest, and to adapt to the biological environment gradually.

3. Results and Discussion

3.1. Effect of Hydraulic Retention Time
Set the hydraulic retention time (HRT) to be 24h, 16h, 12h and 8h respectively, and the system operates constantly for 10 days under conditions of each HRT. As Figure 2 shows, COD value of influent has a great fluctuation range, with maximum value of 1480 mg/L, minimum value of 869 mg/L, and average value of 1214 mg/L. After biological treatment with MBCO system, COD fluctuation range of final effluent of painting wastewater is 187-490 mg/L, which reaches internal control discharge standard of COD<500mg/L stably. After shortening the HRT each time, the variation tendency of COD removal rate in each segment is basically the same, namely reducing firstly, rising subsequently, and tending to stability at last. When HRT is 24h, 16h and 12h, total removal rate of biological system rapidly rises and keeps stable state. However, when HRT is reduced to 8h, the system requires longer period to adapt to the influent load, and total removal rate rises slowly and needs a longer period to achieve stable state.

![Figure 2. Remove efficiency of COD in MBCO system on condition of different HRT](image)

In Figure 3, the fluctuation range of influent total nitrogen (TN) value is 25.7-35.8mg/L, and as HRT decreases gradually, average TN value of final effluent rises little by little. Extension of HRT is conducive to the removal of TN in wastewater, which may because that the longer HRT is, and the less influent is, the slower water flow is, resulting in less washing force on biological film on carrier and lower oxygen transmission efficiency. This is also beneficial for the formation of anaerobic environment in the internal three-dimensional space of carrier or inside biological film, which could facilitate the denitrifying bacteria performing denitrifying reaction [9]-[11]. Under different HRT conditions, the removal situation of ammonia nitrogen (NH$_4^+$-N) by the biological system is similar with variation tendency of TN. Small fluctuation occurs to both TN and NH$_4^+$-N concentration of final effluent and can be kept in a range of low concentration stably; average of TN and NH$_4^+$-N concentration of final effluent is 7.9 mg/L and 0.7 mg/L respectively, which is much less than discharge standard of internal requirement. When biological system reaches stable state under conditions of HRT being 24h, 16h, 12h and 8h respectively, average removal rate of TN is 77%,
76%, 76% and 65% separately; average removal rate of NH$_4^+$-N is 97%, 96%, 94% and 86% separately.

When HRT is 12h, the MBCO system has a high removal rate on COD, TN and NH$_4^+$-N, and the values of COD, TN and NH$_4^+$-N of final effluent all could satisfy the discharge standards of internal requirement. If HRT is extended continuously, carbon and nitrogen removal efficiency of biological system increases slowly. Given operation cost, occupying area and removal effect comprehensively, the optimum HRT is determined to be 12h.

![Figure 3](image)

**Figure 3.** Remove efficiency of total nitrogen in multilevel contact oxidation system on condition of different HRT

### 3.2. Effect of Dissolved Oxygen Concentration

To explore efficient process treatment efficiency and further energy saving and consumption reduction, orthogonal experiment is employed to analyze the dissolved oxygen (DO) concentration in each segment of the MBCO system, as shown in Table 2. The optimum DO concentration in each segment is determined via evaluating the influence of DO concentration in each segment of biological tank on carbon and nitrogen removal.

**Table 2.** Factor and level table of orthogonal experiment

| Factor | A DO$_{F}$ (mg/L) | B DO$_{M}$ (mg/L) | C DO$_{L}$ (mg/L) |
|--------|-------------------|-------------------|-------------------|
| Level  | 0.5~1             | 1~2               | 1~2               |
| 2      | 1~1.5             | 2~3               | 2~3               |
| 3      | 1.5~2             | 3~4               | 3~4               |

$^a$ DO concentration in the front segments.

$^b$ DO concentration in the middle segments.

$^c$ DO concentration in the back segments.

Choose comprehensive removal rate as the evaluation index of orthogonal experiment; comprehensive removal rate is the sum of COD removal rate and TN removal rate, and a higher comprehensive removal rate indicates that the corresponding DO concentration condition is more in favor of efficient operation of biological system. It is available to clearly judge primary and secondary sequence of influence of three experiment factors on treatment efficiency of biological system with visual analysis and calculation table of orthogonal experiment, and to analyze optimum experiment level corresponding to each experiment factor as well, thus optimum level combination of three experiment factors is confirmed. The orthogonal experiment results is shown in Table 3.
Wherein, $T_{xy}$ refers to total of three experiment results corresponding to factor in column $x$ with $y$ level ($x$ referring to factor, i.e. A, B, C respectively; $y$ referring to level, i.e. 1, 2, 3 respectively ;) $K_{xy}$ refers to average of three experiment results corresponding to factor in column $x$ with $y$ level; $R$ refers to range, namely difference between maximum value and minimum value of $K_{xy}$. A greater $K_{xy}$ means a better treatment effect. A less range value ($R$) means factor corresponding to range has less influence on experiment result. It can be indicated via comparison range corresponding to various factors that DO concentration of each segment has the greatest influence on middle segment of decarbonization and denitrification effect of multilevel contact oxidation system, then back segment, and front segment with the least.

Table 3. Intuitive analysis and calculation of orthogonal experiment results

| Factor | A | B | C | COD removal rate (%) | TN removal rate (%) | General removal rate (%) |
|--------|---|---|---|----------------------|---------------------|-------------------------|
| Level  | DO$_f$ | DO$_M$ | DO$_L$ | KO | TN | K |
| 1      | 0.5-1 | 1-2 | 1-2 | 76.4 | 58.6 | 135.0 |
| 2      | 0.5-1 | 2-3 | 2-3 | 89.3 | 69.5 | 158.8 |
| 3      | 0.5-1 | 3-4 | 3-4 | 91.7 | 58.6 | 150.3 |
| 4      | 1-1.5 | 1-2 | 2-3 | 78.1 | 60.9 | 139.0 |
| 5      | 1-1.5 | 2-3 | 3-4 | 84.6 | 58.2 | 142.0 |
| 6      | 1-1.5 | 3-4 | 1-2 | 81.7 | 62.6 | 144.3 |
| 7      | 1.5-2 | 1-2 | 3-4 | 80.1 | 57.5 | 137.6 |
| 8      | 1.5-2 | 2-3 | 1-2 | 83.8 | 61.8 | 145.6 |
| 9      | 1.5-2 | 3-4 | 2-3 | 88.2 | 62.1 | 150.3 |

As shown in Figure 4, when DO concentration is in range of 0.5-1 mg/L, COD and TN have the greatest average comprehensive removal rate, so the optimum DO concentration in front segment should be controlled in 0.5-1 mg/L. When DO concentration of middle segment and back segment is in range of 2-3 mg/L, the greatest average comprehensive removal rate occurs. Given full consideration of energy consumption and carbon and nitrogen removal efficiency, it can be determined that the optimum combination of DO concentration in each segment of MBCO system is: DO concentration in the front segments is 0.5-1 mg/L, with that in the middle segments of 2-3 mg/L, and that in the back segments of 2-3 mg/L. Under the optimum DO concentration, the average removal rate on COD and TN of MBCO system is 89.3% and 69.5% respectively.

Figure 4. Efficiency variation of comprehensive removal rate
3.3. Effect of influent organic loading
To explore organic loading of influent influence on treatment efficiency of MBCO system, adjust the organic loading of influent with other process parameters unchanged to analyze the variation tendency of COD, $\text{NH}_4^+$-N and TN when COD value of influent is 1000 mg/L, 2000 mg/L, 3000 mg/L, 4000 mg/L and 5000 mg/L.

Figure 5. COD removal efficiency under different organic loading conditions

Figure 5 shows that as organic loading of influent increases, the variation tendency of total COD removal rate in biological system is not obvious and maintains at 90% or so basically. COD value of final effluent rises little by little as the COD value of influent increases; when the COD value of influent is 5000mg/L, the COD value of final effluent exceeds 500mg/L and fails to reach internal control discharge standard of the enterprise. It shows that the increase of influent organic loading has little influence on the COD removal efficiency of biological system, and the biological system has a strong ability to resist the impact of high organic matter concentration. To better meet the discharge standard, the influent COD value of biological system had better remain 5000 mg/L below.

Figure 6 shows that the total removal rate of ammonia nitrogen has a small variation range under five different organic loading conditions, and maintains in range of 86.4%-92.5%, and the ammonia nitrogen of final effluent is low and almost maintains in range of 0.7-1.3 mg/L. It is clear that with the impact of influent organic loading variation, the nitrification effect of nitrifier in biological system still could occur normally and is subject to little influence of organic loading variation, and the ammonia nitrogen concentration of effluent is stable and completely could meet the discharge standard.

Figure 6. Removal efficiency of ammonia nitrogen under different organic loading conditions
Figure 7 shows that as organic loading of influent increases, the TN removal rate of biological system presents rising trend, and the average TN removal rate is 70.1%, 71.8%, 75.7%, 80.7% and 85.6% successively, and the average TN value of final effluent is 9.4 mg/L, 9.0 mg/L, 7.4 mg/L, 5.9 mg/L and 4.7 mg/L successively. It results from that the nitration in biological system could remain in normal process, the increase of influent organic loading could provide more carbon source for denitrification, which could make for denitrification of denitrifying bacteria and further improve the denitrification effect of biological system.

![Figure 7. Removal efficiency of total nitrogen under different organic loading conditions](image)

4. Conclusions
Three influence factors are investigated in the process of biological treatment of automobile painting wastewater by multilevel bio-contact oxidation system via a laboratory experiment and the optimum process operating parameters are determined. When HRT is 12 h, DO concentration in the front segments, the middle segments and the back segment of biological system is in range of 0.5-1 mg/L, 2-3 mg/L and 2-3 mg/L respectively; when the organic matter concentration of influent remains under 5,000 mg/L, the total COD removal rate in the biological system is 90% or so; the total removal rate of NH$_4^+$-N maintains in range of 86.4%-92.5%, and the total removal rate of TN maintains in range of 70.1%-85.6%. Relevant results and analysis may provide important theoretical basis and technical reference for the promotion and application of multilevel bio-contact oxidation system in future.

5. References
[1] El-Gohary F A, Abo-ElEla S I and Ali H I 1989 Water Sci. Technol. 21 255-63
[2] Wahaab R A 2001 Bull. Environ. Contam. Toxicol 66 770-6
[3] Aboulhassan M A, Souabi S, Yaacoubi A and Baudu M 2005 Environ. Technol. 26 705-11
[4] Krithika D and Philip L 2016 Int. Biodeter. Biodegr. 107 31-41
[5] Li P, Zheng T, Wang Q, Yang S, Liu S, Li L and Huang P 2015 Environ. Prog. Sustain. 34 339-45
[6] Zheng T L, Li P, Wang Q H, Li X S, Ai H Y, Gan K M and Sharavsambuu A 2015 Desalin. Water Treat. 55 1142-51
[7] Yang Q X, Wang J and Wang H T 2012 Bioresource Technol. 117 155-163
[8] Zheng T, Li P and Wu C Int. J. Environ. Technol. Manage. 18 3-12
[9] Hu Z, Zhang J, Xie H, Liang S and Li S 2013 J. Biosci. Bioeng. 115 272
[10] Zhang Y, Wang X, Hu M and Li P 2015 Appl. Microbiol. Biot. 99 1977-87
[11] Kargi F and Uygur A 2004 Enzyme Microb. Tech. 35 167-172