Performance of Multilevel Contact Oxidation in the Treatment of Wastewater from Automobile Painting Industry

Tong Zhu¹, Yufang Zhu¹, Udo Fienko², Xie Yuanhua¹ and Zhang Kuo¹

¹School of Mechanical Engineering & Automation, Northeastern University, Shenyang 110819, China.
²BMW Brilliance Automotive Ltd., Shenyang 100044, China

Prof. Zhu Tong, E-mail: tongzhu@mail.neu.edu.cn

Abstract: A multilevel contact oxidation system was applied in a pilot-scale experiment to treat the automobile painting wastewater, which had poor biodegradability and contained high concentration of Chemical Oxygen Demand (COD). The wastewater used for this experiment study was the actual painting wastewater which had been pre-treated by the physic-chemical process, and its Biological Oxygen Demand (BOD₅) /COD was less than 0.1, COD concentration was 800~1500mg/L. The results showed that the multilevel contact oxidation system could efficiently degrade the COD of the painting wastewater. When the experimental system kept stable operation, the total removal rate of COD and suspended solid (SS) were 84% and 82.5% respectively with the Hydraulic Retention Time (HRT) of 8 hours. Meanwhile, this system had a strong ability to resist the impact of COD concentration change. The COD concentration of final treated wastewater was less than 500 mg/L, which could reach the factory discharge requirement for the paint shop. Besides, this system with simple structure was able to reduce the excess sludge production greatly, which would reduce much cost for the treatment of painting wastewater.

1. Introduction
Before an automobile being painted in auto manufacturers, several technological procedures are needed. Such as, degreasing, activation, passivation, electrophoresis, acid cleaning, alkaline cleaning, etc. During these processes, much wastewater will be generated, which contains various and complicated organic substance, like surface active agent, electrophoretic paint and fossil oil, and also contains a certain amount of heavy metal [1-3]. Except the inorganic matter, the complicated organic substance is very hard to biodegrade. B/C stands for the biodegradability indicator of paint shop wastewater and it is less than 0.1 in general [4].

At present, the physicochemical and biochemical technology has become the main treatment process for domestic automobile painting wastewater. And classification pretreatment-hydrolysis acidification-aerobic treatment process is relatively common used in automobile painting wastewater treatment. The common treatment methods for domestic automobile painting wastewater are hydrolysis acidification-SBR (such as: Iveco car factory); hydrolysis acidification-biological aerated filter (such as: Jiangling
Group); hydrolysis acidification-single stage contact oxidation (such as: Changchun car factory); hydrolysis acidification-MBR (such as: Changchun car accessories factory).

The specific treatment process should be chose according to some factors, such as, the painting wastewater characteristics, discharge conditions, cover space, outlet requirements, etc.

In this paper, the car factory requires that the fossil oil, heavy metal and COD must be reduced and reach the internal targets before discharging this kind of painting wastewater into the general sewage treatment station inside the factory, which is aimed to reduce the influence on the subsequent wastewater treatment and outlet index in the general sewage station. All kinds of wastewater in paint shop are treated by a series of physic-chemical methods and the COD concentration of the mixed wastewater at the end of the system is 800~1500mg/L. However, the COD concentration discharge standard in paint shop is performed according to the level 3 standard of maximum allowable discharge concentration of the second type of pollutant in the integrated wastewater discharge standard (DB8978-1996), namely, COD should be less than 500mg/L.

For the above problem, comprehensively considering the treatment effect, cover space and running cost in practical engineering, a multilevel biological contact oxidation system is applied to retreat the wastewater which has been pre-treated by the physic-chemical process in paint shop. Figure 1 is the flowchart of the original physic-chemical process with new added biological process.

![Flowchart of the painting wastewater treatment process](image)

**Figure 1.** Flowchart of the painting wastewater treatment process.

2. **Experiment wastewater**

The water used for this experiment is from that interim storage tank, as shown in figure 1. Because of the process particularity in paint shop, the change of wastewater quality is not stable. So the COD concentration of wastewater used for the experiment is also changing randomly. Besides, the biodegradability of painting wastewater is poor and B/C is only about 0.1. The situation of the painting wastewater quality is shown in table 1.

| Main pollutant | pH | COD | BOD | TP | TN | NH3-N | SS |
|---------------|----|-----|-----|----|----|-------|----|
| Test value    | 6.5~8.5 | 800~1500 | 50~100 | 0.3~0.9 | 0~20 | 1~10 | 50~200 |

**Table 1.** Quality of wastewater used for experiment
3. Biological experiment device
The experiment system mainly includes inlet tank, multilevel contact oxidation reactor and outlet tank, as shown in figure 2.

![Multilevel contact oxidation reactor diagram](image)

**Figure 2.** Experiment system of multilevel contact oxidation.

The multilevel contact oxidation reactor includes six biological tanks and its total effective volume for the experiment is 80L. The stuffing frame is placed in each biological tank and the special stuffing which can be used to cultivate microbial membrane efficiently is placed on the stuffing frame. The aeration system with different intensities is placed on the bottom of each biological tank, which can bring air into the biochemical tank through the air blower, providing enough oxygen to the microbial. Besides, the aeration intensity and dissolved oxygen concentration can be adjusted according to the changes of water quality and the growth state of biofilm [5].

4. Experimental start-up and process
The inoculation sludge used for the experiment is the sludge from the secondary sedimentation tank of the general sewage treatment plant in the car factory. The MLSS (Mixed Liquid Suspended Solids) of the initial dosing sludge is about 3000 mg/L. 25L active sludge, 30L painting wastewater and 25L clean water is evenly mixed and then it’s fed to the biological tank where is placed with special biological stuffing. Two days later, the whole surface of biological stuffing in each tank is covered evenly by active sludge and a layer of mud-yellow biofilm is growing, which can prove that the biofilm formation is successful.

Later, the experiment water begins to flow into the biological tank constantly from the inlet tank through the water pump. The flowrate starts with 80L/d and gradually increases to 240L/d, which is controlled by the flowmeter. That’s to say, the HRT starts with 24 hours and gradually reduces to 8 hours. It has taken about 30 days totally during the experiment commissioning and running.

The biofilm in each biological tank is keeping growing and getting thicker over time until reaching a stable state. Besides, the biofilm in the first biological tank is the thickest and the biofilm texture is the closest. The biofilm thickness and texture in the later biological tanks are decreasing in turn. The appearance color of stuffing in each biological tank is also changing constantly, as shown in figure 3. The appearance color of stuffing in the start stage is mud-yellow at the beginning, then slowly turns into deep tan, and finally becomes black. The appearance color of stuffing in the middle stage is mud-yellow at the beginning, then slowly turns into tan. The appearance color of stuffing in the final stage is mud-yellow.
5. Experiment results and analysis

5.1 Organic matter removal

During the experiment, every day take water sample regularly and test the COD value. Take samples at three special points during the whole biological system: the start stage, the middle stage and the last stage.

As shown in figure 4, under the conditions of different COD loads and different HRT, the COD concentration in the last stage is less than 500mg/L and can reach the discharge standard stably.

It can also be seen that an obvious COD concentration difference has formed between every biological tank. This is because that the wastewater flows through each biological tank in turn, the difference of pollutant composition and concentration in each biological tank will result in a different kind of microbial generating accordingly and forming a biologic chain. The microbial with different species and structures in each tank can efficiently decompose the refractory organic matters step by step, and finally the COD concentration is able to reach the discharge standard stably [6-7].
As shown in figure 5, under the condition of different HRT, the COD removal rate in each stage of the multilevel contact oxidation system decreases step by step. Besides, the change of inlet flowrate has the greatest influence on the COD removal rate in the first stage and the least influence on the COD removal rate in the last stage.

This is because that the microbial in the first biological tank plays a main role in degrading the COD. Since the COD concentration of wastewater entering the first biological tank is the highest, the microbial in the first biological tank can grow fastest and degrade the COD most quickly under the suitable dissolved oxygen (2.0-4.0mg/L) and water temperature (25-30°C). When the inlet flowrate is changed, the wastewater with high COD concentration will first enter the first biological tank. So the microbial in the first biological tank will be most greatly affected by the concentration impact and the degradation efficiency will also appear a larger fluctuation accordingly [8].

5.2 Impact resistant properties
During the experiment, the COD concentration range of influent is 800~1500mg/L. When the HRT is set as 24h, 16h, 12h and 8h successively, the experimental test results show that the COD concentration of the final effluent can still stay in 300~500 mg/L stably.

When the HRT is shortened every time, the COD removal rate in each stage decreases first, then increases, finally tends to be stable. That’s because when the HRT is shortened, the inlet flowrate will be increased, the microbial in each biological tank needs time to adapt to the changed environmental conditions. The experiment results can show that this multilevel contact oxidation system can adjust to the changed HRT in shorter time and quickly achieve the stable operation. After the biological system achieving stable operation, the total COD removal rate can reach 84% with HRT of 8 hours.

5.3 Excess sludge production
This experiment has been running for 30 days and treated 5000L painting wastewater, but the excess sludge production is only less than 0.5kg.

When the biological system reach stable operation with the HRT of 8 hours, the suspended solid (SS) of influent and effluent has been tested, as shown in figure 6. The average remove rate of SS is about 82.8%.
The reasons why this multilevel biological contact oxidation system can efficiently reduce the excess sludge production are as follows:

Firstly, the difference of pollutant composition and concentration in each biological tank will result in a different kind of microbial generating accordingly, and the microbial in each biological tank is changing and evolving continually, thereby forming a food chain. Higher trophic level microbial can prey on the low trophic level microbial, such as the bacteria and the dead microbial, thus decreasing the sludge yield.

Secondly, energy was lost at every transition in a natural food chain because part of the organic material is converted into carbon dioxide and water \[9\]. So, the yield coefficient of microbial will be reduced. Accordingly, the sludge yield will also be reduced.

Thirdly, Higher microbial is easy to survive and can keep endogenous metabolism \[10\], which can decrease the yield of dead microbial, namely, decrease the sludge yield.

6. Conclusions
The experiment results show that the multilevel contact oxidation system is able to reduce the COD concentration of painting wastewater by cultivating activated sludge and controlling process conditions. During the whole experiment commissioning and running, the painting wastewater after pretreatment by physicochemical method is retreated by the multilevel biological contact oxidation system, and the COD concentration of outlet water can reach the internal discharge standard.

When the HRT is shorten every time, the system can quickly achieve stable operation again, so the system has strong impact resistance. Besides, the system can effectively reduce the excess sludge production.

Comparing the traditional biological methods for treating automobile painting wastewater, the multilevel contact oxidation system has obvious advantages. Firstly, it can efficiently reduce the excess sludge production and greatly reduce the sludge treatment cost. Secondly, the reactor structure is simple, the cover space is small, the operation is easy and the running is stable. Thirdly, it has high treatment efficiency and can decompose the refractory organic matters in painting wastewater.

This multilevel contact oxidation method can greatly reduce the treatment cost of automobile painting wastewater, and it has good economic and social benefits. The experiment results have important reference value for the automobile painting wastewater treatment.

References
[1] Tian Y P, Kong S S. Study on automobile painting-wastewater treatment with the process technology of pretreatment-air flotation-SBR[J]. Advanced Materials Research, 2012,550-553:2237-2240.
[2] Huang C, Liu Y Y, Luo Y. Research status of dyeing wastewater treatment [J]. Chongqing University, 2001, 24 (6), 139-142.
[3] Chen C L, Zhang J A, Li X P, et al. Treatment of wastewater coming from painting processes: application of conventional and advanced oxidation technologies [J]. Ozone Science & Engineering, 2005, 27(27):279-286.
[4] Shaw C B, Carliell C M, Wheatley A D. Anaerobic/aerobic treatment of colored textile effluents using sequencing batch reactors [J]. Water Research, 2002, 36(8):1993-2001.
[5] Li X D, Wang Q H, Li Q F. Study on treatment of simulant dairy processing wastewater using FCR multilevel contact oxidation system [J]. Environmental science, 2007, 28(9):2020-2024.
[6] Du T X, Fei Q Z, Xu Z. Study of soybean wastewater treatment with eight-series biological contact oxidation system [J]. Journal of Dalian Jiao tong university, 2008, 29(3):67-69.
[7] Qiu G L, Cheng J G, Xiang L C. Pilot-Scale Test of Biological Contact Oxidation Process for Decentralized Wastewater Treatment [J], China Water &Wastewater, 2007, 23(5):78-81.
[8] Rocher M, Goma G, Begue A P. Towards a reduction in excess sludge production in activated sludge process: biomass physicochemical treatment and biodegradation [J]. Appl Microbio Biotechnol, 1999, 6(51):883-890.
[9] Ghyoot W, Verstraete W. Reduced sludge production in a two-stage membrane-assisted bioreactor [J]. Wat Res, 1999, 34(1):205-215.
[10] Divyalakshmi P, Murugan D, Sivarajan M. In situ disruption approach on aerobic sludge biomass for excess sludge reduction in tannery effluent treatment plant [J]. Chemical Engineering Journal, 2015, 276:130-136.