The Correlation Analysis of TOC and COD\textsubscript{Cr} in Urban Sewage Treatment

Xi Tian\textsuperscript{1,2}, Chunling Zhao\textsuperscript{1,2}, Xiaona Ji\textsuperscript{1,2}, Tiezhu Feng\textsuperscript{3}, Ying Liu\textsuperscript{1,2} and Dejun Bian\textsuperscript{1,2*}

\textsuperscript{1} Changchun Institute of Technology, Changchun, Jilin, 130012, China
\textsuperscript{2} Jilin Provincial Key Laboratory of Municipal Wastewater Treatment, Changchun, Jilin, 130012, China
\textsuperscript{3} Jilin Provincial Zhongshi Engineering Design Company Limited, Changchun, Jilin, 130000, China

Abstract. Total organic carbon (TOC) and chemical oxygen demand (COD\textsubscript{Cr}) are indicators of the degree of organic pollution in water. At present, COD\textsubscript{Cr} is mainly used as an evaluation index in China, and the detection method of COD\textsubscript{Cr} is more complicated and time-consuming than TOC. In this paper, it uses the Micro-Pressure Inner-Loop Bioreactor (MPR) to treat urban sewage, studies the treatment effect of MPR on organic pollutants, and further analyzes the correlation between TOC and COD\textsubscript{Cr}. TOC and COD\textsubscript{Cr} of municipal wastewater and MPR treated effluent were measured by total organic carbon analyzer and dichromate method respectively, and the degree of organic pollution of water samples was analyzed. The results showed that the average removal rates of TOC and COD\textsubscript{Cr} in municipal wastewater were 83.54% and 90.81%, respectively. The theoretical correlation coefficient between TOC and COD\textsubscript{Cr} in experimental raw water was only 0.732. After MPR treatment, the correlation coefficient increased to 0.9534. For water samples with fixed contaminants and stable contents, TOC can be used to calculate water COD\textsubscript{Cr} by linear fitting relationship.

1 Introduction

The most common and harmful of environmental pollution is organic pollutants. With the implementation of China's total pollutant discharge control system, online automatic monitoring of organic pollutants is particularly important. TOC and COD\textsubscript{Cr} are two comprehensive indicators for evaluating organic pollutants in water environment, and have theoretical correlation. The research on the correlation is more at home and abroad[1-4]. At present, the United States mainly monitors the content of organic matter in water bodies by TOC indicators. Japan also included TOC indicators in Japanese industrial standards in the early 1970s. However, most of China's current environmental quality standards, pollutant discharge standards, etc. mainly use COD\textsubscript{Cr} as a water quality evaluation index to characterize the content of organic pollutants.

Chemical oxygen demand (COD\textsubscript{Cr}) refers to the amount of oxygen consumed in chemical oxidation of substances that can be oxidized in water. It is a comprehensive indicator of the degree of contamination of water by organic matter, expressed in milligrams of oxygen consumed per liter of water. The higher the COD\textsubscript{Cr} value, the more serious the water is contaminated (usually considered to be caused by organic pollution). The COD\textsubscript{Cr} value can reflect the degree of contamination of the water body by reducing substances[5]. Total organic carbon (TOC) reflects the absolute amount of organic matter containing carbon in water. It is a comprehensive indicator of the total organic matter content in water, expressed as the number of milligrams of carbon per liter of water. All carbon-containing substances, including benzene-based compounds, aromatic hydrocarbons such as pyridine, and other toxic and harmful organic substances can be reflected in the TOC index, so that the content of organic matter can be more directly and comprehensively expressed[6]; the larger the TOC value, the more serious the organic pollution of water quality is reflected. At the same time, the measurement of TOC has the advantages of fast, accurate, high sensitivity, easy to realize on-line detection, and no secondary pollution[7]. Therefore, studying the correlation between TOC and COD\textsubscript{Cr} under specific conditions is of great significance for broadening the scope of TOC application, realizing rapid and accurate monitoring of wastewater and revision of water quality standards[8].

2 Materials and methods

2.1 Experimental device and operating conditions

The experimental device is made of plexiglass and consists of the Micro-Pressure Inner-Loop Bioreactor (MPR) and a secondary settling tank. The entire reactor has an effective volume of 54 L. It consists of upper and lower parts, and the upper part is open, and the structural size is 500 mm × 80mm × 60mm, the main role is to raise

*Corresponding author’s e-mail: ccgxxybdjyjs@163.com
the water level, so that the lower part of the reaction zone is subjected to micro-pressure, thereby improving the efficiency of oxygen transfer in the reactor. The lower part is the main reaction zone, and the structure size is 800mm×600mm×110mm. The main reaction zone is provided with a baffle plate at an appropriate position, which is favorable for the mixed liquid to form a circulating flow inside the reactor. A perforated aeration tube is installed at the bottom of the main reaction zone at an angular position on the open side. The outer diameter of the aeration tube is 10 mm, the inner diameter is 7 mm, and the perforation hole diameter is 0.3 mm. The mixed liquid inside the reactor forms a circulating flow in the main reaction zone under aeration. The secondary sedimentation tank is a vertical flow sedimentation tank with a diameter of 200 mm and a height of 850 mm, and its effective volume is 27 L.

The experimentally inoculated activated sludge was derived from the aeration tank of a sewage treatment plant in Changchun. The wastewater was taken from the domestic sewage of a municipal sewage treatment plant in southern Changchun. After cultivation and domestication, the system reached a stable operation state. The specific operation of the experiment is shown in table 1.

| Serial number | Project            | Parameter          |
|---------------|--------------------|--------------------|
| 1             | Temperature (°C)   | 15                 |
| 2             | HRT (h)            | 12                 |
| 3             | Influent flow (L/d)| 108                |
| 4             | Reflux ratio (%)   | 100%               |
| 5             | Aeration (L/min)   | 3                  |
| 6             | MLSS (mg/L)        | 8000               |
| 7             | SRT (d)            | 60                 |

Table 1. Experimental operating conditions

2.2 Analysis projects and detection methods

2.2.1 Detection method of TOC. In this experiment, TOC-5000A of Shimadzu Corporation of Japan was used for the determination of TOC.

2.2.2 Detection method of CODCr. The method for detecting CODCr is the dichromate method (HJ 828-2017).

3 Results and discussion

3.1 Analysis of MPR removal efficiency

3.1.1 TOC removal. Figure 1 shows the processing of the TOC by the MPR system. The raw water in this experiment is mainly urban sewage, and the TOC concentration in raw water during the experimental operation is generally 20 ~ 40 mg·L⁻¹. It can be analyzed from figure 1 that the TOC concentration in the effluent of MPR treatment is about 3.20 ~ 5.80 mg·L⁻¹, and the removal rate fluctuates between 74% and 89%, with an average of 83.54%. The reactor has a better removal effect on the TOC.

![Figure 1. MPR removal effect of TOC](image1)

3.1.2 CODCr removal. Figure 2 shows the removal of CODCr by the MPR system. In order to ensure the stability of the raw water quality during the experiment,
the appropriate amount of starch, sodium acetate and other drugs were added to the urban sewage used in the experiment to maintain the CODCr concentration at 350~550 mg·L⁻¹. After the raw water is biochemically treated by the MPR system, the purpose of simultaneous nitrogen and phosphorus removal and removal of organic matter can be achieved. The concentration of CODCr in the effluent is 30~48 mg·L⁻¹. The removal rate is in the range of 85% to 95%, and the average removal rate is 90.81%, which meets the first-class A standard for pollutant discharge standards of urban sewage treatment plants (GB 18918 - 2002). The reactor has a good removal effect on CODCr.

3.2 Correlation analysis between TOC and CODCr

3.2.1 Correlation between TOC and CODCr in wastewater. Figure 3 shows the linear relationship between TOC and CODCr in wastewater from municipal wastewater treatment systems. It can be seen from figure 3 that there is a certain correlation between TOC and CODCr in wastewater, but the correlation is poor. The fitting equation is CODCr = 12.7930 TOC + 86.343, and the correlation coefficient is only 0.7322. Combined with figure 1 and figure 2, the TOC concentration of the sewage fluctuated greatly during the first 25 days of the test, and then stabilized. The average concentration was 28.48 mg·L⁻¹. The CODCr concentration is always controlled to maintain it around 450 mg·L⁻¹, fluctuating between 350 and 550 mg·L⁻¹. The experimental raw water is derived from urban domestic sewage, and the types and contents of pollutants are relatively stable. The reason may be due to the fact that there are more inorganic suspended solids in the raw water sample and the sample content is not uniform, which has adversely affected the accuracy and repeatability of the instrument. At the same time, due to the wide area of the sewage treatment plant, or a small amount of industrial wastewater, there are dynamic changes in the type and content of sewage. Among them, the TOC and CODCr contents are uncontrollable, resulting in poor correlation between TOC and CODCr. 

![Figure 3. Correlation between TOC and CODCr in wastewater](image)

![Figure 4. Correlation between TOC and CODCr of MPR effluent](image)

3.2.2 Correlation between TOC and CODCr of MPR effluent. Figure 4 shows the correlation between TOC and CODCr in the treatment of municipal wastewater effluent by the MPR system. After the sewage has been biochemically treated, the inorganic suspended matter and a small amount of inorganic reducing substances which cannot be represented by TOC are deeply removed, and the correlation between TOC and CODCr is improved. It can be seen from figure 4 that the linear relationship between TOC and CODCr in the effluent is good, the fitting equation is CODCr = 7.7197 TOC + 5.1194, and the correlation coefficient is 0.9534, which is significantly higher than that of the original water. Since the organic component in the effluent is relatively fixed, the accuracy of the sample detection is ensured, so the TOC can be used to derive the water CODCr by a linear fitting relationship.

4 Conclusion

During the operation of MPR at 15 °C, the treatment effect of TOC and CODCr in municipal wastewater was good, and the average removal rates were 83.54% and 90.81%, respectively. The theoretical correlation coefficient between TOC and CODCr in experimental raw water is only 0.7322. After MPR treatment, the correlation is significantly improved, and the correlation coefficient is increased to 0.9534. When the inorganic suspended matter in the water sample and a small amount of inorganic reducing substances which cannot be represented by TOC are contained, the correlation between TOC and CODCr is significantly reduced. For water samples with fixed pollutant content and stable content, the accuracy of sample detection is guaranteed. TOC can be used to calculate water CODCr by linear fitting relationship.

Acknowledgments

This work was supported by the National Key Science and Technology Program of China (Granted No. 2014ZX07201-011), the National Natural Science Foundation of China (Granted No. 51878067) and the Jilin Provincial Science and Technology Development Project (Granted No. 20170101082JC and 20190303091SF), the
Funding for Capital Construction in the Budget of Jilin Province in 2019 (Innovative Capacity Building - High-tech Industry Part) (Granted No. 2019C056-4), and Changchun Institute of Technology Innovation Team Project (Granted No. 320180007) for their financial support.

References

1. Liu, S.C., Xue, G.F., Zhou, J.X. (2013) Study on Correlation between COD and TOC of Industrial Wastewater. J. Characterization of Minerals, Metals, and Materials, 2013: 217-223.
2. Yuan, M., Dong, D.M., Hua, X.Y., Zhang, L.H. (2008) Comparison of Correlations between COD and TOC, PV and TOC, COD and PV of Different River Systems in Jilin Province. J. Scientia Geographica Sinica, Vol.28(No.2): 286-290.
3. Zhang, L.H., Yuan, M., Liu, B.L., Hua, X.Y., Dong, D.M. (2007) Correlation between COD and TOC of river waters in Jilin province. J. Journal of Jilin University (Science Edition), Vol.45(No.3): 501-505.
4. Christian, E., Batista, J.R., Gerrity, D. (2017) Use of COD, TOC, and Fluorescence Spectroscopy to Estimate BOD in Wastewater. J. Water Environment Research, Vol.89(No.2): 168-177.
5. Dong, D.M., Song, X., Hua, X.Y., Yuan M., Liang, J.H., Guo, Z.Y., Liang, D.P. (2012) Relationship Between COD and TOC of Typical Wastewaters in Jilin Province and Mechanism and Main Influencing Factors. J. Journal of Jilin University. Earth Science Edition, Vol.42(No.5): 1446-1455.
6. Hua, X.Y., Song, X., Yuan, M., Dong, D.M. (2011) The Factors Affecting Relationship between COD and TOC of Typical Papermaking Wastewater. J. Advances in Computer Science, Intelligent System and Environment. 2011: 239-244.
7. Canals, A. (2002) Ultrasound-assisted method for determination of chemical oxygen demand. J. Analytical and Bioanalytical Chemistry, Vol.374(No.6): 1132-1140.
8. Dubber, D., Gray, N.F. (2010) Replacement of chemical oxygen demand (COD) with total organic carbon (TOC) for monitoring wastewater treatment performance to minimize disposal of toxic analytical waste. J. Journal of Environmental Science and Health, Part A, Vol.45(No.12): 1595-1600.