Characteristics of Dissolved Organic Matter in Tail Water of Wastewater Treatment Plant and its Influence on Receiving River

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Abstract. The dissolved organic matter (DOM) in the tail water of the municipal wastewater treatment plant (WWTP) are complex and changeable, and can react with the organic and metal ions in the receiving water, thus affecting their migration and transformation. In order to understand the characteristics of DOM in the tail water of WWTP, the Guozhen WWTP and Kui river in Xuzhou city were taken as the research objects. The spectral characteristics of DOM were analysed by three dimensional fluorescence spectroscopy (3D-EEM), and the water quality indexes such as pH, total nitrogen (TN), ammonia nitrogen (NH$_3$-N), nitrate nitrogen(NO$_3^-$-N), nitrite nitrogen(NO$_2^-$-N), TOC and UV$_{254}$ were measured. The changing rules of these indexes in sewage, tail water and receiving river were discussed. The results showed that DOM in the tail water was mainly composed of soluble microbial metabolites and humic acids. The TN, NH$_3$-N, NO$_3^-$-N, NO$_2^-$-N and TOC have been significantly reduced under the biological treatment process of the WWTP, but the large-scale drainage of the tail water will still have no negligible influence on the natural waterbody.

1. Introduction

Water is the source of human survival. At present, with the rapid increase of population and serious waste of water resources, the contradiction between supply and demand of water is increasingly prominent. As one of the most important ways of sewage reuse, urban sewage has attracted more and more attention [1]. In order to ensure the timely and effective treatment of sewage, the number of urban wastewater treatment plant (WWTP) is increasing gradually, and the amount of tail water discharge is increasing. If the first level A discharge standard in the “discharge standard of pollutants for municipal WWTP” (GB18918-2002) is taken as the judgment criterion for the discharge, the corresponding discharge limit values of NH$_3$-N and TN are 5.0 mg / L and 15.0 mg / L respectively, which are far beyond the class V water index (NH$_3$-N 2.0 mg / L and TN 2.0 mg / L) in the “environmental quality standard of surface water” (GB3838-2002) [2].

Although the sewage is discharged after the biochemical treatment of the sewage plant, there are still a lot of organic matters in the tail water, and the types and components are complex. Dissolved organic matter (DOM) in tail water can cause apparent water quality problems, affect the migration and transformation of pollutants in the water, and worsen the quality of effluent water. In recent years, DOM has become a research hotspot in the process of water treatment [3]. The study and analysis for the
characteristics of the organic matter in the tail water has important practical significance in improving the efficiency of sewage reuse and realizing the regional water circulation.

It is difficult to analyse all organic matters because of the complexity of the organic composition in urban WWTP. However, DOM in the tail water of WWTP mainly contains some organic compounds with fluorescent groups [4,5], which will emit fluorescence of different wavelengths after being excited by light of specific wavelengths. The three-dimensional fluorescence spectrum (3D-EEM) can clearly show the different fluorescence intensity of different organic compounds with fluorescence effect in the specified emission and excitation wavelength range. Therefore, this method is an effective method for investigating the characteristics of DOM in the tail water. It has the advantages of simple operation, good selectivity and high sensitivity, and is widely used in DOM research [5].

2. Materials and methods

2.1. Water sampling

Xuzhou Guozhen WWTP and Xuzhou Kui River were taken as research objects for collecting water samples. The main sewage sources of Xuzhou Guozhen WWTP include domestic sewage, industrial sewage and initial rainwater. Kui River is the river channel, where the tail water of Xuzhou Guozhen WWTP is discharged, that is, the receiving river channel. In Guozhen WWTP, the oxidation ditch is selected in the aerobic aeration stage, and A2/O is adopted in biological nitrogen and phosphorus removal process. The effluent is discharged to the Xuzhou Kui river after passing through the coagulation reactor and disinfection tank. The process flow of Xuzhou Guozhen WWTP is shown in Figure 1. The effluent meets the discharge requirements of first level A standard in the “discharge standard of pollutants for municipal WWTP” (GB18918-2002) (Table 1).

![Figure 1. The process flow of Xuzhou Guozhen WWTP](image)

| Table 1. Discharge standard of pollutants for municipal WWTP (mg/L) |
|---|---|---|---|---|---|---|---|
| Index | COD | BOD | SS | NH₃-N | TN | TP | LAS |
| Level 1 B | 60 | 20 | 20 | 8 | 20 | 1 | 1 |
| Level 1 A | 50 | 10 | 10 | 5 | 15 | 0.5 | 0.5 |

2.2. Water sample pretreatment

The containers were plugged with stopper and made partitions by using foam plastic to avoid collision damage. A certain amount of collected water sample was taken to filter through filter paper for removing the sludge and other sediment. Most of them were removed by 0.45 μm microporous membrane filtration.
2.3. Analysis methods
The water sample analysis methods are listed in Table 2. pH was measured by portable pH meter (pH / DO HQ40), TN and TOC by multi N/C 3100, NO$_2^-$-N by N-(1-naphthyl)-ethylenediamine spectrophotometry (GB 7493-87, China), NO$_3^-$-N by ultraviolet spectrophotometry (HJ/T 346-2007, China), NH$_3$-N by Nessler’s reagent spectrophotometry (HJ 535-2009, China), UV$_{254}$ by ultraviolet spectrophotometry (Lambda 36).

| Indexes  | Methods and instruments                        |
|----------|-----------------------------------------------|
| pH       | pH / DO HQ40                                  |
| NH$_3$-N | Nessler’s reagent spectrophotometry            |
| NO$_2^-$-N | N-(1-naphthyl)-ethylenediamine spectrophotometry |
| NO$_3^-$-N | Ultraviolet spectrophotometry            |
| TN       | Multi N/C3100                                 |
| TOC      | Multi N/C3100                                 |
| UV$_{254}$ | Ultraviolet spectrophotometry            |
| DON      | Fluorescence spectroscopy                     |

The three-dimensional fluorescence spectrum was determined by F-4600 fluorescence spectrophotometer (Hitachi, Japan). The pH of the water samples was adjusted to 7-8, and the samples were put into 1 cm quartz fluorescence sample pool. Set the excitation wavelength scanning range of 280-420 nm, the interval of 5 nm, the emission wavelength scanning range of 300-500 nm, the interval of 1 nm, the excitation and emission slit width of 5 nm, and the scanning speed of 1200 nm/min.

3. Results and discussion

3.1. TOC
TOC can be used to characterize the content of various carbon compounds and oxidation state substances. Compared with BOD$_5$, COD$_{cr}$ and COD$_{Mn}$, TOC reflects a more comprehensive, accurate and clear content of total organic matter, which is considered to be one of the most important indicators in water evaluation of the degree of organic pollution.

The TOC of inlet and outlet in the WWTP and receiving river is shown in the figure 2. It can be seen that under the biological treatment process of the WWTP, from the initial 28.9mg/L to the effluent 8.4mg/L, the concentration of TOC decreases step by step, so the content of organic matter is significantly reduced. The TOC concentration in the river is 8.7 mg/L, which is slightly different from that in the tailwater of WWTP 8.4 mg/L.

3.2. UV$_{254}$
Due to the complexity of organic compounds in water, their chemical formula is difficult to be determined [6]. UV$_{254}$ reflects a kind of organic matter with similar properties, which can show the content of humus macromolecular organic matter and aromatic compounds with carbon oxygen double bond and carbon double bond in water.

UV$_{254}$ is used as the indicator to characterize the organic matter, and the test results of each water sample are shown in figure 3. UV$_{254}$ is 0.334 in the sewage and 0.085 in the tail water. After the WWTP, the organic content is reduced. When the tail water flows to the river, it is measured that the UV$_{254}$ of the river water is 0.095, and the content of organic matter is slightly increased. The river water may be affected by other sewage outlets around.
Previous studies have shown that the main matter of UV absorption in water is organic matter with molecular weight greater than 3000, and the UV absorption of organic matter with molecular weight less than 500 is relatively weak[6]. The higher UV254 is, the higher the molecular weight is. It can be seen that UV254 is absorbed at low concentration in the tail water, so the DOM in the water samples of the WWTP and receiving river is mainly small molecular weight organic matter. The reason may be that the water quality of the wastewater treatment plant is mainly domestic wastewater, industrial wastewater and initial rainwater, which leads to the poor removal effect of organic matters with relatively small molecular weight, such as humic acid in industrial wastewater. Therefore, for the WWTP, it is necessary to select a reasonable treatment process and control the process conditions properly to increase the removal of small molecular organics represented by humic acids, reduce the pollutant load of the receiving water to the maximum extent, and improve the effluent quality.

3.3. Nitrogen contaminant

When excessive nitrogen contaminant are discharged into the natural water body, the nitrogen cycle balance of the water will be broken, resulting in a significant increase in the concentration of nitrogen nutrients as the primary pollutant, and then the water quality continues to deteriorate [7]. Therefore, the WWTP needs to focus on it.

According to figure 5, the TN in the sewage is 47.1 mg/L. After the A2/O biological nitrogen and phosphorus removal process, the TN in the tail water is reduced to 14.2 mg/L, which meets the discharge requirements of first level A in the discharge standard (TN≤15 mg/L). When the tail water flows through the transportation network to the receiving river, the TN decreases from 14.2 mg/L to 11.9 mg/L. On the one hand, the dilution effect of the upstream river makes the TN decrease. On the other hand, the tailwater transportation pipe network between the urban sewage plant and the receiving water plays a certain role. The biofilm in the water transportation pipe network removes some nitrogen pollutants from the water. The microorganisms attached to the biofilm of the pipe network use the ammonia nitrogen and protein in the sewage to synthesize amino acids, which provide energy for the life metabolism activities. Part of the ammonia nitrogen in the water is consumed, and the TN is reduced. However, the nitrogen content of river water still exceeds the class V water (TN 2.0 mg/L) in the “environmental quality standard for surface water” (GB3838-2002).
In the water not affected by human activities, dissolved organic nitrogen accounts for a large proportion of total nitrogen in the water [7]. Therefore, the decrease of TN content is partly due to the decrease of dissolved organic nitrogen content. Some studies have shown that microorganisms will preferentially use protein organic nitrogen sources for life metabolism, and the content of dissolved organic nitrogen will be reduced. At the same time, the metabolites of microorganisms will release humic acid substances into the water, and increase the content of refractory organic nitrogen, which will cause water pollution in the tailwater transport channel, and the tailwater will become the main pollution source of the channel.

3.4. Three dimensional fluorescence properties of DOM

Three dimensional fluorescence spectrum technology shows the fluorescence intensity of organic matter with fluorescence effect under different excitation and emission wavelengths in the form of three-dimensional projection diagram. Three dimensions correspond to excitation wavelength, emission wavelength and fluorescence intensity respectively, so that the contour map of fluorescent matter can be displayed intuitively and accurately [8]. In order to further understand the change of organic matter in each component, by measuring the three-dimensional fluorescence spectrum of organic matter and observing the change of fluorescence peak position, we can qualitatively determine the change characteristics of organic matter in water after treatment by WWTP. The three-dimensional fluorescence spectrum characteristics of each organic component inlet and tailwater of sewage plant and river water are shown in figure 5, figure 6 and figure 7.

![Figure 4](image1.png)

**Figure 4.** The concentration of total nitrogen at each sampling point

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![Figure 5](image2.png)

**Figure 5.** DOM three-dimensional fluorescence spectrogram of sewage

![Figure 6](image3.png)

**Figure 6.** DOM three-dimensional fluorescence spectrogram of the tail water
Table 3. Correspondence between peak area of fluorescence spectrum and properties of organic matter

| Regions | \( \lambda_{Ex} \) (nm) | \( \lambda_{Em} \) (nm) | Category                  |
|---------|----------------|----------------|-------------------------|
| I       | 220~250        | 280~330        | Aromatic protein I      |
| II      | 220~250        | 330~380        | Aromatic protein II     |
| III     | 220~250        | 380~480        | Fulvic acid             |
| IV      | 250~370        | 290~380        | Soluble microbial metabolites |
| V       | 250~360        | 380~480        | Humic acid substance    |

Generally, the positions of the fluorescence centres of DOM components in the tailwater are mainly divided into three categories: humus (\( \lambda_{Ex}/\lambda_{Em} = 237~260 \text{ nm}/400~500 \text{ nm} \) and 300~370 nm/400~500 nm), tryptophan (\( \lambda_{Ex}/\lambda_{Em} = 275 \text{ nm}/340 \text{ nm} \) and 225~237 nm/340~381 nm) and complex ammonia (\( \lambda_{Ex}/\lambda_{Em} = 275 \text{ nm}/310 \text{ nm} \) and 225~237 nm/309~321 nm)[9-11]. The three-dimensional fluorescence spectrogram can be roughly divided into five regions [12, 13]. The corresponding relationship between the fluorescence peak areas of the fluorescence spectrum and the organic matter is shown in figure 8 and table 3.

According to the above classification method, the fluorescence peaks in the sewage are mainly concentrated in two places: \( \lambda_{Ex}/\lambda_{Em} = 280~300 \text{ nm}/350~379 \text{ nm} \) and \( \lambda_{Ex}/\lambda_{Em} = 340~360 \text{ nm}/420~450 \text{ nm} \). There are many soluble microbial metabolites and humic acid substances in the water. The fluorescence spectra of tailwater and river water are similar. The main fluorescence peaks are concentrated in \( \lambda_{Ex}/\lambda_{Em} = 280~300 \text{ nm}/310~330 \text{ nm} \) and \( \lambda_{Ex}/\lambda_{Em} = 330~360 \text{ nm}/410~430 \text{ nm} \). There are many soluble microbial metabolites, proteins and humic acid substances.

In general, the fluorescence peaks of dissolved microorganisms in the influent water, tailwater and river water of the WWTP are obvious, and they all contain more metabolites of dissolved microorganisms. This is due to the discharge of domestic sewage and industrial wastewater, as well as the biochemical treatment process of WWTP, which will produce microbial metabolites. The microorganisms in the water body are active and the metabolism is vigorous. Too many dissolved microbial metabolites will have a certain impact on the life activities of aquatic plants and zooplankton in the natural water body. Therefore, in order to reduce the reduction of river self-purification capacity caused by tailwater discharge, further deep treatment can be carried out for the tailwater and strict discharge requirements can be strictly enforced.

4. Conclusion
After a series of process treatment, WWTP has been able to meet the discharge standard. Although the impact of sewage on the surrounding water environment has been greatly reduced, the tail water will
still have a great impact on the surrounding water environment quality. The drainage tailwater of WWTP is the main source of nitrogen pollutants in the water body. In the biological treatment process of the WWTP, the concentration of TOC decreases step by step, and the content of total organic matter is significantly reduced, among which the organic matter is mainly small molecular weight organic matter. The DOM in the tail water is mainly the metabolite of dissolved microorganism and humic acid like substance. The tail water can meet the integrated wastewater discharge standard, but it has not yet reached the surface water environmental quality standard. In order to improve the quality of water and the quality of water environment, the discharge standard of pollutants in the WWTP should be improved.

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References
[1] Wang X D, Liu P, Wang L, et al. (2014)Analysis characteristics of dissolved organic matters in the secondary effluent of municipal wastewater. Chinese Journal of Environmental Engineering, 8(6):2186-2190.
[2] Lei Y F, Jiang B B, Chen H.(2018) Impact of tail water from wastewater treatment plant on quality of tidal reach. Environmental Science and Management, 43(1):58-62.
[3] He A H, Bi X J, Chen L H.(2012) Research on characterization of dissolved organic matters in sewage after biological treatment. Journal of Qingdao Technological University, 33(2):62-67.
[4] Wu J, Cui S, Xie C B, et al.(2011) Fluorescence fingerprint transformation of municipal wastewater caused by aerobic treatment. Spectroscopy and Spectral Analysis, 31(12):3302-3306.
[5] Zhang H, Tian J Y, Huang J, et al.(2017) Analysis of dissolved organic matter transformation in wastewater treatment process by three dimensional fluorescence spectra technology. Environmental Pollution and Control, 39(4):375-378.
[6] Jiang S J, Liu Z Y.(2002) The meaning of UV254 as an organic matter monitoring parameter in water supply and wastewater treatment. Journal of Chongqing Jianzhu University, 24(2):61-65.
[7] Lewis W M. (2002) Yield of nitrogen from minimally disturbed watersheds of the United States. Biogeochemistry, 57-58(1):375-385.
[8] Vanderbilt K L, Lajtha K, Swanson F J. (2003) Biogeochemistry of unpolluted forested watersheds in the Oregon Cascades: temporal patterns of precipitation and stream nitrogen fluxes. Biogeochemistry, 62(1): 87-117.
[9] Chen S Y, Li Y, Li A M.(2015) Application of three-dimensional fluorescence spectroscopy in the study of dissolved organic matter. Environmental Science & Technology, 38(5):64-68.
[10] Shi J, Wang Z G, Feng K.(2011) Characterization techniques of dissolved organic pollutants in wastewater by three-dimensional fluorescent spectroscopy and its application in environmental analysis. Journal of atmospheric and environmental optics, 6(4):243-251.
[11] Zhong R S, Zhang X H, Guan Y T, et al.(2008) Three-dimensional fluorescence fingerprint for source determination of dissolved organic matters in polluted river. Spectroscopy and Spectral Analysis, 26(2):13-18.
[12] Chen W, Westerhoff P, Leenheer J A, et al. (2003) Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Environmental Science and Technology, 37(24):5701-5710.
[13] Jin W G, Xue S, Wang Z, et al. (2014) Changes of dissolved organic matter and fluorescent materials in municipal sewage treatment processes. Acta Scientiae Circumstantiae, 34(9):2298-2305.