Comparison of Degradation Differences in Typical Urban Wastewater Dissolved Organic Matter

Abstract:

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Dissolved organic matter (DOM) is a class of organic mixtures commonly found in natural water bodies with complex structures and diverse sources, which are closely related to the structure and function of the water body environment. Given the declining quality and quantity of lake waters in China, studying the dynamic degradation/change processes of DOM in lakes is essential to understand and manage the ecological health of these water bodies. In this experiment, by conducting photocatalytic experiments of DOM, we analyzed and compared the changes of absorbance and DOC concentration of different kinds of urban wastewater water samples with time, and the results showed that the degradation efficiencies of DOC were in the order of domestic wastewater>farming wastewater>industrial wastewater from the largest to the smallest, and the degradation efficiencies of the light-absorbable substances at the wavelength of 254 nm were farming wastewater>industrial wastewater>domestic wastewater. This study not only explored the photo-degradation process of DOM in urban wastewater, but also provided a scientific basis for wastewater treatment and management, with a view to optimizing the wastewater treatment process, improving the level of water quality management and reducing the impact of harmful pollutants on the environment.

Keywords: dissolved organic matter; urban wastewater; photo-degradation

1.1 Research Background

The regulation and optimization of various water bodies in the ecosystem can't be ignored. Besides providing drinking water resources, they play an important role in the supervision in ecology, agriculture and fishery. Nevertheless, our country's lake rate is only 1.4%, far behind the 3% of world's average rate. Up to 2020, the amount of lakes greater than 1 square kilometer is 2670, which is minimizing in spite of both quantity and area comparing to past investigations. Moreover, the quality of water bodies is decreasing year by year, threatening the aquatic ecosystem. The exposure of organic pollutants and heavy metal waste and etc all causes water to stink. Redundant nitrogen, phosphorus and other nutrients discharged into the lake, but also lead to water eutrophication, resulting in serious algal bloom phenomenon. Among the 110 major-monitoring lakes and reservoir, 90.9% of lakes and reservoir have reached or beyond moderate eutrophication. It stands to reason that all kinds of water bodies in our country are facing increasingly serious problems of eutrophication and pollution.

Dissolved organic matter (DOM) is a kind of organic mixture that commonly exists in natural water, which can pass through 0.45µm aperture filter membrane. Due to its complicated construction and diverse sources, its significant influence to the structure and function of aquatic ecosystem has made it the focus of recent water management study. DOM in aquatic environment effectuate the pH, the effectiveness of nutrients and the environmental behavioral characteristics of pollutants. At the same time, DOM can synergistically affect the migration and degradation behavior of pollutants in water environment through complexation, light attenuation and acid-base buffering. The sources of DOM in nature are mainly divided into exogenous and endogenous sources. Exogenous refers to organic substances that penetrate into the water body through rainfall and surface flow in the natural environment, while endogenous refers to the products of a series of metabolic activities carried out by organisms in the water body. In recent years, DOM has become a hot topic of discussion among ecologists. Its presence and behavior in the environment not only affect the physical and chemical properties of urban water bodies but are also directly related to pollution levels and ecosystem service functions. Studying the dynamic degradation/variation process of DOM in urban water bodies is crucial for understanding and managing the ecological health of these waters.

1.2 Research Purpose

This research is designated to contrast the degradation rate of DOM through photo-degradation in typical municipal sewage. The research will analyze the efficiency and velocity of DOM photo-degradation from different types of municipal sewage, and thus reveal the distinction of DOM degradation rate and its potential factors.

2. Methods and Materials

2.1 Instruments

Precision balance, medicine spoon, glass fibre filter membrane, extraction device, glass reagent bottle, quartz tube, pipette gun, photochemical reactor, UV-visible spectrophotometer (SH-6600 type), cuvette.

2.2 Water Sample Pretreatment Experiment

2.2.1 Stock Solution Configuration

Wastewater Types	Configuration Methods
Farming Wastewater	Measure 5.0 mg of xanthate, 2.0 mg of bovine serum protein and 5.0 mg of glucose, NH_4Cl and KNO_3 with a precision balance in a glass reagent bottle, add 500 mL of ultrapure water, cover and shake to mix.
Domestic Wastewater	Measure 2.5 mg humic acid and 5.0 mg glucose, NH_4Cl and KNO_3 with a precision balance into a glass reagent bottle, add 500 mL of ultrapure water, cover and shake to mix.
Industrial Wastewater	Use filter paper with a pore size of $0.22 \mu\text{m}$ to construct a filtration unit, and filter raw industrial waste- water samples collected in the laboratory. The portion filtered through the membrane was the dissolved organic matter sample.

Table 1 Methods of Stock Solution Configuration

2.3 Photocatalysis Experiment

2.3.1 Photo-catalyze using photochemical reactor

Take 6 quartz tubes and divide them into three groups, labeled 1, 2, 3, and 1-1, 2-1, 3-1, respectively. Add 50 mL aquaculture wastewater to test tubes 1 and 1-1, 50 mL domestic sewage to test tubes 2 and 2-1, and 50 mL industrial wastewater to test tubes 3 and 3-1, respectively.

A total of 48 centrifuge tubes were divided into eight groups according to the reaction time of 0 min, 10 min, 20 min, 30 min, 60 min, 120 min, 180 min and 240 min. Each group contained three kinds of water samples (numbered 1, 2, 3) and their repeat samples (numbered 1-1, 2-1,

3-1).

Put 6 quartz tubes into the special turntable of the photo-photochemical reaction meter in sequence, and connect the tap water cooling circulation device before the device is opened to ensure that the water sample is at room temperature. Lamp power Select 300W Mercury lamp. According to the experimental setting, when the timer sounded, shut down the machine, take out the test tube, use the pipette to absorb 4 mL of liquid each, and move it into the centrifuge tube with the corresponding number. After the sampling is finished, put the test tube back into the instrument, and continue the timing after starting. Each sample was repeated twice until 8 sets of experiments were com-

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ISSN 2959-6157

pleted.

2.3.2 Determination of Absorbance

Measurement of absorbance using a UV spectrophotometer, which is an analytical method that uses molecules of a substance to absorb radiation in the UV-visible spectral region, is based on the basic principle of Lambert's Beer's law, i.e., the proportion of light absorbed by a transparent medium is independent of the intensity of the incident light, and the absorbance is directly proportional to the thickness of the absorbing layer, the concentration of the solution, and the light absorption rate.

Absorbance is calculated using the following formula: Eq:

A is the absorbance;

k is the molar absorbance coefficient, $L/(g \cdot cm)$;

b is the optical range, i.e., the transmittance thickness (cm) of the tank holding the solution;

c is the concentration of the solution;

Warm up the instrument 30 min in advance and make sure there is no light shield in the sample chamber. After switching on the power, the tungsten lamp will light up, input the wavelength of 254 nm into the computer, and the device will be automatically calibrated when it is switched on. Press the START button to start the measurement. After adjusting the zero with the absorption cell filled with ultra-pure water, put the samples into the test sequentially and record the test results. Wash the cuvette with ultra-pure water several times during the measurement, and dry the water stains on the optical surface with paper towel in time. Repeat the above operation to complete the measurement of three water samples in eight different time periods, and then plot the absorbance standard curve. Remove the absorption cell after measurement, clean and dry it, and store it in the box. Switch off the power, unplug the power supply, put desiccant in the sample chamber, cover the sample chamber lid and put on the dust cover.

3. outcomes and discussions

3.1 Comparison of Absorbance Changes of

DOM in Different Environmental Waters





Figure 1 shows the absorbance of the three water samples at different time intervals under UV at 254 nm. From the figure, it can be seen that the absorbance at the initial 254 nm for domestic wastewater, farming wastewater, and industrial wastewater are 0.061, 0.179, and 1.054, respectively. Among them, domestic wastewater contains higher values of initial absorbance compared with the other two samples due to the higher amount of organic matter in domestic wastewater. From the photolysis process, it can be found that the absorbance at 254 nm of the three water samples increase with the increase of time. The remaining absorbance values at 254 nm at the end of photolysis for domestic wastewater, farming wastewater and industrial wastewater are 0.014, 0.005 and 0.112, respectively. The degradation efficiencies of the three water bodies are found to be 77.05%, 97.21% and 89.37%, respectively, which indicates that the degradation efficiency of the three water bodies in terms of the absorbable substances is the largest for farming wastewater, followed by industrial wastewater, and the last for domestic wastewater.

3.2 Comparison of Photo-degradation Characteristics of Dissolved Organic Carbon in Differ-

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Figure 2. Changes in Dissolved Organic Carbon (DOC) Concentration and Degradation Efficiency in Different Water Bodies During Photo-degradation

Figure 2 compares the changes in dissolved organic carbon (DOC) concentration over time during the photo-degradation process. The initial DOC concentrations in domestic sewage, aquaculture wastewater, and industrial wastewater were 118.37, 213.78, and 334.64 mg/L, respectively. Among them, aquaculture wastewater had the highest initial DOC concentration, primarily due to the large amount of organic matter from terrestrial plant debris and human production and living activities entering the wastewater. During photo-degradation, the DOC concentration in all three types of water bodies decreased rapidly in the first 0–30 minutes and then slowly declined and stabilized from 30–240 minutes, indicating that UV

light has a significant effect on DOC degradation. After photo-degradation, the remaining DOC concentrations were 26.63 mg/L for domestic wastewater, 156.48 mg/L for aquaculture wastewater, and 240.59 mg/L for industrial wastewater. Calculations reveal that the degradation efficiencies for domestic wastewater, aquaculture wastewater, and industrial wastewater were 77.50%, 28.11%, and 26.80%, respectively, indicating that DOC in domestic wastewater is most significantly affected by photo-degradation, followed by aquaculture wastewater, with industrial wastewater showing the least degradation.

3.3 Comparison of Photo-degradation Kinetics of DOM in Different Environmental Waters



Fig. 3 Comparison of photodegradation kinetics of dissolved organic matter in three water samples

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(A) 254 nm absorbance degradation kinetics; (B) DOC degradation kinetics

Figure 3 shows the kinetic rates of degradation at 254 nm absorbance and DOC degradation for the three water samples. The figure shows that the fitted lines of absorbance at 254 nm and DOC concentration are consistent with the first order reaction kinetics. The R2 values of the kinetic rates of absorbance at 254 nm are 0.97, 0.99 and 0.90 for domestic wastewater, farming wastewater and industrial wastewater, respectively. The R2 values of the DOC degradation kinetics are 0.92, 0.95 and 0.94 for domestic wastewater, farming wastewater and industrial wastewater, respectively. The degradation rate constants of DOM at absorbance at 254 nm are 0.02, 0.02 and 0.94. 0.94. The degradation rate constants for DOM with absorbance at 254 nm were 0.026 > 0.018 > 0.015; for DOC concentration, the degradation rate constants are 0.026 > 0.023> 0.017. The above results indicate that the degradation rate of light-absorbable DOM and DOC is faster for the industrial wastewater under UV irradiation, followed by domestic wastewater, and slowest for the farming wastewater.

3.4 Experimental Discussion

Photochemical reaction is one of the major principals DOM degrade in water. The reaction mineralize DOM to active micro-molecular organic matters that can be degraded by organisms. A portion of light activated DOMs can otherwise produce CO2 and CO directly. CDOM, as the dominant photo-reactive component, absorbs substantial amount of ultraviolet, which provokes photo-degradation.

There are two ways of the photo-degradation of DOM. Due to the rich carboxyl group, benzene ring, hydroxyl group and other functional groups, DOM can directly absorb sunlight, change its structure, physical properties and chemical composition, and produce photochemical intermediates, such as singlet oxygen and three-state excited states of hydroxyl radicals. Additionally, DOM can also participate in re-dox reaction with soluble oxygen in water under illumination. The strength of illumination, the concentration of soluble oxygen, and heavy metal ions and etc can all effect DOM degradation rate.

4.0 Conclusions

In this experiment, the 254 nm absorbance, DOC concentration and DOC degradation efficiency, and photo degradation kinetic rate constants of different types of urban wastewater after photo-degradation were systematically compared to show the variability of the degradation characteristics and degradation efficiencies of DOM in the three types of water bodies. The results showed that although the degradation efficiency of DOC was domestic wastewater>farming wastewater>industrial wastewater, the degradation efficiency of the absorbable substances in it was farming wastewater>industrial wastewater>domestic wastewater. The degradation of DOM in water bodies from other sources can be further investigated in future work, with a view to proposing more comprehensive solutions for the management of urban wastewater.

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