Dean&Francis

ISSN 2959-6157

Comparison of the differences in photochemical degradation of dissolved organic matter in rivers, lakes, and ponds by adding nanoparticles TiO_2.

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Abstract:

This study examines the photolysis of Dissolved Organic Matter (DOM) in urban rivers, lakes, and ponds using photocatalysis experiments. Employing a photochemical reactor and UV spectrophotometer, we investigated the precise effects of TiO2 nanoparticles and illumination duration on the degradation efficiency, rate, and kinetics in water bodies. Simultaneously, an analysis was conducted on the photochemical degradation process of DOM from various sources. The results demonstrate that the photocatalyst TiO_2 can effectively improve DOM degradation and light absorption degradation efficiency, with longer illumination durations inversely correlating with DOM content. Both Dissolved Organic Carbon (DOC) and 254 nm absorbance degradation kinetics follow pseudo-first-order degradation kinetics. Notably, the pond exhibited the most significant change in degradation efficiency, reaching 96.7%. Our findings suggest that degradation efficiency in water bodies may be influenced by surrounding vegetation, population density, and rainfall conditions. This study contributes to a deeper understanding of DOM degradation processes by photocatalysts and provides a feasible method to effectively mitigate water pollution.

Keywords: Dissolved organic matter, Photodegradation, Photocatalyst, Titanium dioxide, UV spectrophotometer

1. Introduction

Agriculture, transportation, and irrigation worldwide heavily rely on water supplies. However, with increasing industrialization and population growth, water pollution, a condition in which the amount of contaminants in a body of water surpasses its ability to purify itself, has grown to be a serious issue. Much of this pollution is attributed to organic sources[1]. Dissolved Organic Matter (DOM) is a byproduct of various human activities, including land reclamation, over-cultivation of aquatic products, and excessive fertilizer use in agriculture. DOM can promote algae growth, causing eutrophication, forming “browning” of water[2], and leading to anaerobic fermentation[3]. Therefore, harmful by-products (such as DPBs) that have the potential to be carcinogenic and teratogenic, gravely jeopardizing human health[4].

DOM, a class of carbon-based organic compounds that are able to pass through a 0.1 μm to 0.7 μm filter membrane and a continuum of organic matter with different structures and molecular weights, accounts for 97.1% of the more than a trillion tons of natural organic matter in global aquatic ecosystems[5][6]. DOM originates from biological secretions and debris, but is an inanimate substance in the ecosystem. Therefore, researching a material that unites the inorganic and organic realms aids the exploration to assess the state of various water bodies[7].

However, DOM undergoes a variety of changes in the earth’s ecosystem cycle, including adsorption, aggregation, dissolution, degradation, and sedimentation, due to its diverse chemical composition and particle size. During these processes, DOM undergoes microbial and photochemical degradation, with a focus on the latter in this article [8][9]. Additionally, this article focuses on Chromophoric Dissolved Organic Matter (CDOM), a unique subset of DOM that strongly absrobs ultraviolet and visible light[10]. Recently, nanoparticles such as ZnS[11] and ZnO[12][13] have been widely used as photocatalysts to accelerate the photodegradation of DOM. However, they still face challenges such as low utilization and difficulty in removal. Consequently, a new photocatalyst TiO_2[14][15], was chosen for this experiment due to its small particle size (i.e., large surface area), availability of valence numbers, low cost, reactivity, and strong polarization effect[16]. TiO_2 is most commonly found in the anatase and rutile phases[17], with only 5% absorption of ultraviolet light in sunlight. Considering the characteristics of DOM in photochemistry and process efficiency, direct UV light was applied to the DOM-containing samples using a photochemical reactor and UV spectrometer, which have been widely used to characterize DOM since the 1920s[18].

Sources of DOM in natural waters are generally divided into two main types: endogenous emissions and external input, which include metabolic emissions of aquatic organisms, transformation of biological debris and terrestrial substances, and synthetic organic matter[19]. In this study, the river represents external input, while the lake and pond in Nanjing represent endogenous emissions.

Overall, this experiment aimed to explore the differences that the photocatalyst TiO_2 would have on the degradation of DOM in natural water bodies, including the river, the lake, and the pond. Following sample collection and the establishment of the control group by adding or removing TiO_2, a photochemical reactor and a spectrometer were utilized for photodegradation and UV absorbance measurement at 254 nm. This study predicts that the addition of colloidal particles TiO_2 will enhance the effectiveness of DOM degradation in water by supplying more free radicals to attack the macromolecule groups in DOM, thereby releasing small molecules and facilitating efficient breakdown. The aforementioned techniques were employed in this study to examine variations in the TiO_2 degradation efficiency of sewage in various natural water bodies, as well as to compare the kinetics of DOM degradation and the water quality conditions of various water bodies.

2. Materials and methods

2.1 Overview of the studied area

Nanjing is located in East China and is situated along the Yangtze River, spanning over 200 kilometers of shoreline. Due to the presence of highways, bridges, and lake embankments, the lake's water system is entirely artificially controlled. The lake, which is freshwater and shallow, measures 2.4 km in length from north to south and 2.0 km in width from east to west. The average depth of the lake bed is 70 cm, consisting of mostly clay with fine grains. Zhenzu River, approximately 21 km long, runs from Xianlin University Town to the Yangtze River. The river characterized by its calm and clean water, with both banks being home to a diverse range of aquatic and terrestrial flora. In this case, three samples containing DOM were collected on January 29, 2024, from the Zhenzhu River, Xuanwu Lake, and pond in the Institute of Limnology, Chinese Academy of Sciences, Nanjing. These three surface water bodies are the focus of research in this article.

2.2 Sample collection and pretreatment

Before collection, the researchers rinsed the sampling vials three times with the original solution at the places mentioned. Sterilized sampling bottles were then used to collect 1L of surface water samples at each sampling point. After collection, the sample vials was kept out of direct sunlight and placed in an incubator set at 4 °C. Later, a 0.45 μm polyethersulfone PES filter membrane (PALL, U.S.), a diaphragm air pump (Shengaohua, China, SH-6600), and a suction filter bottle were used to separate large particles of sediment and to eliminate microbial interference. Lastly, 500 mL of each sample was filtered and preserved.

2.3 Photodegradation experiment

The 3 samples of the lake (S_1), the river (S_2), and the pond (S_3) were each divided into 6 tubes (Table 1). Since the reaction rate is only related to the concentration of reactant and the rate constant, the exact volume of each sample is not considered. The 6 tubes of samples were divided into 2 groups, with each group containing samples from three different sampling sites. Group 1 (G_1) had 2 mL of TiO_2 suspension added to each tube, while Group 2 (G_2) did not, thus serving as the control group. The suspension ratio was 0.05 g of TiO_2 added to 100 mL of distilled water.

Table 1 The setting of the degradation of experiment in Nanjing

Sampling location	Photocatalyst	Abbreviation	Experimental objective
Xuanwu Lake 32°04’23”N 118°47’54”E	TiO_2	S_1-G_1	Test the difference in the degradation of DOM according to the addition of TiO_2 by the use of UV light
	No addition	S_1-G_2	
Zhenzhu River 32°03’17.7”N 118°47’50.3”E	TiO_2	S_2-G_1	
	No addition	S_2-G_2	
Pond 32°03’27.9”N 118°48’15.1”E	TiO_2	S_3-G_1	
	No addition	S_3-G_2	

The 6 samples were then set into the photochemical reactor and exposed to the UV light irradiation. In order to summarize a formula for the rate of degradation by forming a line chart, 4 mL of the 6 samples were taken after the instrument had operated for 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 4 h, and 20 h. There were 8 sampling times in total, including the sample at 0 h. When extracting the liquid from G_1, the TiO_2 photocatalyst needs to be separated with a 0.4 µm filter membrane. All samples were tested twice to ensure the precision of the final data and to control errors.

2.4 . The measurement of absorbance by UV spectrophotometer

The absorption of UV light by the residual macromolecules following the breakdown of DOM into smaller molecules is the test object in this experiment. Therefore, samples exposed to UV light for different periods of time were added to one-half to two-thirds of the way into the 5 cm quartz cuvette, respectively. Distilled water was used as a blank reference, samples were scanned, and the absorbance (Abs) value was tested at a wavelength of 254 nm in a UV spectrophotometer. According to this study's conjectures, the absorption rate of UV light may be inversely proportional to time, indicating that as exposure duration rises, the Abs value would drop. Because extended UV exposure causes more DOM to break down into smaller molecules, the absorbance ought to fall overall. As a result, throughout this experiment, the projected trend was also utilized to gauge the validity of the actual absorption rate data.

2.5 . Analytical methods

2.5.1 . Degradation efficiency of DOC

Since DOM is mainly composed of DOC, the total carbon contained in DOM, the absorption of DOC, measured in A.U (AU/cm), at a certain wavelength of light, 254 nm (UV), can indirectly represent the amount of DOM present. The study predicted that the A.U will gradually decrease with the rise in the time the samples are exposed to UV light. This is because large compounds in DOM will decompose into inorganic substances, water, and carbon dioxide, which cannot absorb 254 nm due to the increase in the presence of free radicals and the decrease in the concentration of DOC. Consequently, the degradation efficiency of DOC can be deduced from the variation in A.U.

2.5.2 . SUV254

The primary organic contaminants found in natural water bodies and secondary treatment effluents from sewage facilities include lignin, tannin, humus, and different organic compounds comprising aromatic hydrocarbons and conjugated systems of double bonds or hydroxyl groups. At 254 nm, these organic contaminants absorb heavily. The environment can be severely contaminated by aromatic compounds, which are stable organic substances with several benzene rings and double bonds that are difficult to break down. Consequently, based on the Specific Ultraviolet Absorbance at 254 nm (SUV254 (mg/L)), this study compared the variation in aromaticity of samples using their structural and compositional features.

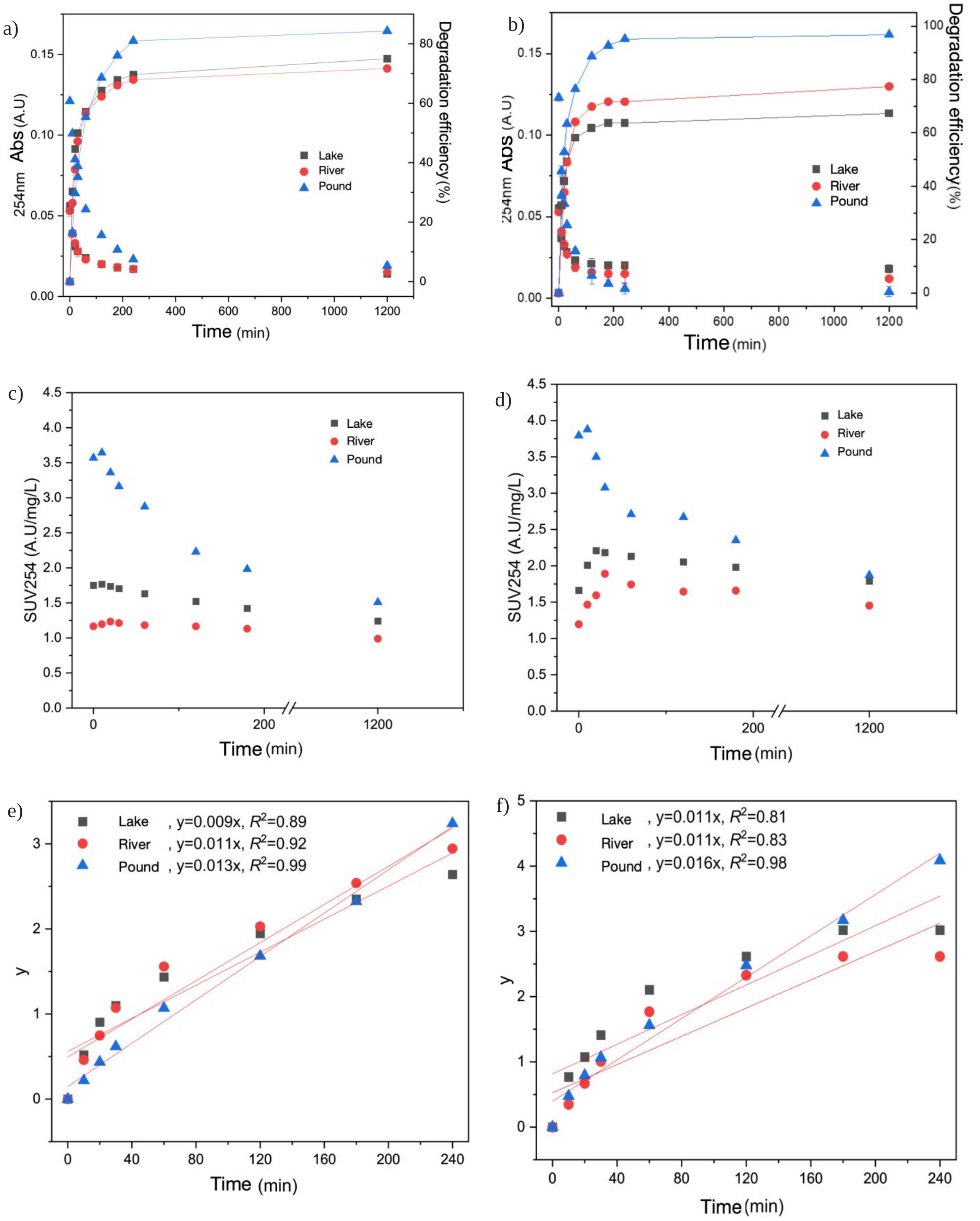
2.5.3 . Degradation kinetics with UV-Vis spectroscopy

Samples exposed to UV light for 0 h, 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 4 h, and 20 h from the river, the pond, and the lake were scanned at 245 nm (the wavelength of UV light) in a spectrophotometer (Xujiang, China, XPA-7). The spectral slope k at 254 nm was obtained by fitting the absorbance coefficient to a single exponential decay function—the logarithmic function. The kinetic model was verified by the following formula:

$[C]_t = [C]_0 \times e^{-kt}$

where t is the length of time the sample exposed under UV irradiation while C_0 and C each represents the Abs of samples experienced 0 h and t h of UV irradiation, respectively.

3. Results and discussion



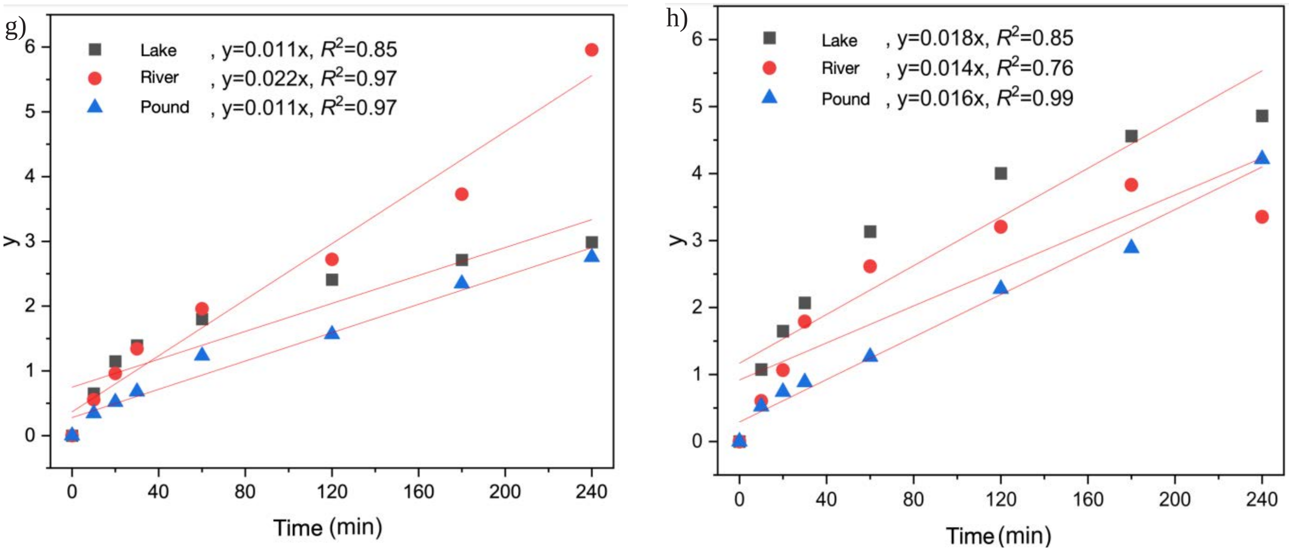


Fig. 1. Variations of the absorption value A.U of DOC in different samples at 254 nm without (a) and with (b) the addition of TiO_2. Comparison of aromatic changes of DOM in water bodies in different environments without (c) and with (d) TiO_2 during photodegradation. Comparison of photodegradation kinetics of DOM in three samples without (e) and with (f) TiO_2. Photodegradation kinetics of DOC in DOM in different water bodies.

3.1 . Degradation efficiency of DOC

Figures (a) and (b) illustrate the comparison of absorbance changes at 254 nm and degradation rates in the lake, river, and pond with and without the addition of TiO_2 during the photodegradation process. It can be seen from the figure that the initial absorbance at 254 nm of water bodies in the lake, the river, and the pond without TiO_2 is 0.129 ± 0.001 A.U, 0.122 ± 0.0003 A.U, and 0.279 ± 0.0003 A.U, while with TiO_2 it is 0.127 ± 0.0005 A.U, 0.122 ± 0.0005 A.U, and 0.283 ± 0.0006 A.U. The changes in absorbance values at 254 nm in water bodies in different environments correspond to the order of DOC. During the photodegradation process, the absorbance at 254 nm of the three water bodies gradually decreased with increasing degradation time, indicating effective degradation of light-absorbing substances in the three water bodies. After photodegradation, the remaining absorbance values at 254nm after 1200 min in the lake, the river, and the pond without TiO_2 are 0.032 ± 0.0004 A.U, 0.035 ± 0.00005 A.U, and 0.044 ± 0.0001 A.U, respectively, while with TiO_2 they are 0.032 ± 0.0006 A.U, 0.028 ± 0.0004 A.U, and 0.0092 ± 0.0007 A.U. The presence of sycamore trees around the pond used for this experiment may contribute to the discharge a large amount of organic waste containing humic acid and other compounds into the water body when their leaves fall. So, the pond water has high absorption values because these compounds contain a lot of light-absorbing groups. Also, the river may have a high rate of UV absorption because of the large concentration of organic materials carried by precipitation runoff throughout its length. Through calculation, before the addition of TiO_2, the degradation efficiency of the lake, the river, and the pond was 75% ± 0.04%, 71.7% ± 0.005%, and 84.3% ± 0.01%, respectively. With the addition of TiO2, the degradation efficiency values were as follows: the pond (96.7% ± 0.07%) > the river (77.4% ± 0.04%) > the lake (74.5% ± 0.06%). The absorbance of samples with TiO_2 nanoparticles added at 254 nm is generally lower than that without TiO_2, and the absorption degradation rate is higher than that without TiO_2. As a result, the degradation efficiency of DOC could be improved by adding the photocatalyst TiO_2 during photodegradation.

3.2 . SUV254

Figure (c) and (d) depict the comparison of the aromatic changes of DOM in different water bodies during photodegradation. The initial values of SUV254 for the lake, the river, and the pond without TiO_2 were 1.75 A.U, 1.17 A.U, and 3.57 A.U, respectively, while the ones with TiO_2 were 1.66 A.U, 1.19 A.U, and 3.8 A.U, indicating higher aromatic and benzene ring substance levels in pond water. The residual values of SUV254 after 1200 min in the lake, the river, and the pond without TiO_2 all showed a slight decline, with values of 1.24 A.U, 0.99 A.U, and 1.51 A.U, respectively. However, only pond water demonstrated a noticeable decrease in SUV254 value in samples with TiO_2, indicating that the pond (1.87 A.U) > the lake (1.79 A.U) > the river (1.45 A.U) at 1200 min. The SUVA254 value of each water sample increased to varing extents during the first 30 min of photodegradation, suggesting that this phase of the process might elevate the aromaticity of DOM. This is because environmental water contains a significant number of non-light-absorbing compounds in addition to light-absorbing ones. The early stage of photodegradation is characterized by a rise in the aromaticity of DOM due to the faster degradation rate of non-light-absorbing chemicals compared to light-absorbing substances. Subsequently, SUVA254 in the lake, river, and pond steadily declined as photodegradation progressed. After photodegradation, the SUVA254 values of DOM in each sample were lower than those of the initial samples, indicating that the photodegradation process effectively reduced the aromaticity of DOM in the lake, river, and pond.

Nevertheless, TiO_2 did not accelerate the decline in aromaticity in water, which could have been caused by the low amount of macromolecular organic matter in the sample. this can be attributed to two potential reasons: 1. The enhancement of the system's photochemical activity upon the addition of nanoparticles mainly stems from the photosensitivity of titanium dioxide (TiO_2). When TiO_2 is exposed to ultraviolet (UV) light, photocatalytic reactions occur on its surface, generating reactive oxygen species (such as hydroxyl radicals and superoxide anions), which can oxidize organic pollutants and break them down into smaller molecules or harmless products. However, the reactive species produced, like hydroxyl radicals, indiscriminately degrade dissolved organic matter, while the chromophoric portion of dissolved organic matter (indicated by SUVA254) constitutes only a small fraction of the total dissolved organic matter. It is possible that the degradation rate of non-absorbing substances is enhanced in the sensitized photolysis process promoted by TiO_2, leading to a relatively higher SUVA254 value in samples with TiO_2 added compared to those without. 2. The introduction of nanoparticles results in the suspension of TiO_2 particles within the system, which absorbs the UV irradiation. This process may act similarly to a photonic shielding effect, causing a reduction in the overall irradiation intensity received by the dissolved organic matter in the system. Consequently, the degradation rate of light-absorbing substances in dissolved organic matter may relatively decrease, ultimately resulting in a higher SUVA254 value in samples with TiO_2 particles added.

3.3 . Degradation rate and kinetics

Table 2 The kinetic constant k and R^2 of the samples from the lake, the river, and the pond with or without TiO_2 during photodegradation.

Samples	DOC			254 nm Abs	
	k (min^{-1})	R^2		k (min^{-1})	R^2
S_1-G_1	0.011	0.85		0.009	0.89
S_1-G_2	0.018	0.85		0.011	0.81
S_2-G_1	0.022	0.97		0.011	0.92
S_2-G_2	0.014	0.76		0.011	0.83
S_3-G_1	0.011	0.97		0.013	0.99
S_3-G_2	0.016	0.99		0.016	0.98

Figures (e) to (h) illustrate the comparison of photodegradation kinetics of DOM in water bodies in different environments. It can be observed from table 2 that regardless of whether the photocatalyst TiO_2 is added to the lake, the river, and the pond, the degradation of DOC and absorbance value at 254 nm follow pseudo-first-order degradation kinetics. The R^2 values of COD and 254 nm absorbance degradation kinetics were both 0.93 when there was no addition of any nanoparticles and were 0.867 and 0.87, respectively, after adding the nanoparticles. Regarding DOC, the degradation rate constants of the three water bodies with the addition of TiO_2 are lake ($k = 0.018$) > pond ($k = 0.016$) > river ($k = 0.014$). For the absorbance at 254nm, the degradation rate constants of the pond show the highest value at 0.016. These research findings indicate that the photodegradation rate of DOM in the pond is generally higher, followed by the river, and finally the lake.

3.4 . Further discussion

Firstly, both direct and indirect photochemical degradation of DOM can be achieved by UV light included in sunlight[20]. For the former, macromolecular structures that are not stable enough will directly decompose into multiple small molecules. For the latter, when exposed to light, molecules in the water gain energy and undergo electronic transitions, changing from valence bonds to conduction bonds. The water then release hydroxyl and oxygen free radicals[21][22]. These active oxygen species may break down organic materials into inorganic matter, carbon dioxide, and water by attacking the double bonds on the benzene ring and other amino acids.

Secondly, the reason why the addition of TiO_2 was chosen as the photocatalyst to accelerate the photodegradation of DOM in this experiment instead of others, such as ZnO, has been deduced as follows:

(1) Higher ionization energy: Zn ions have an 18-shell structure, while Ti ions have an 8-electron structure, resulting in the latter havine a higher ionization energy. Consequently, Ti ions have a stronger binding ability when forming hydroxyl radicals and reacting with DOM.

(2) More available valence numbers: When a water molecule is photolyzed, it will directly steal an electron from the water molecule, and the last four hydroxyl groups will recombine to produce oxygen molecules and water. Zn ions have no available valence, while Ti ions have the valence numbers of +4 and +3. Thus, Ti ions are more flexible during photodegradation.

(3) Lower reactivity: Zn ions are more active than Ti ions, and their oxides tend to form hydroxide precipitates, $Zn(OH)_2$, when exposed to water.

4. Conclusion

This study systematically compared the photochemical degradation characteristics of DOM in typical urban lakes, rivers, and ponds. Based on the results of this study, high-efficiency photodegradation technology will be an effective way to remove pollutants from urban water bodies, especially pond water bodies, in the future.

(1) Pond water has a relatively high DOC concentration, a high aromaticity index, and is mainly composed of humic acid-like substances.

(2) When the absorbance at 254 nm is used as the indicator, the photodegradation efficiencies of the three water bodies are: pond water > river water > lake water. However, the photodegradation rate of lake water is generally higher than that of pond and river water.

(3) The photodegradation process can not only reduce the concentration of DOM in urban water bodies but also change the physical and chemical properties of water bodies, such as reducing the aromaticity of water bodies. Additionally, the addition of TiO_2 could effectively improve the degradation efficiency of DOM.

(4) Factors such as the sources of the sample, population density, and vegetation distribution around the sampling site may cause distinct sample components, leading to differences in the photodegradation efficiency and kinetics of Xuanwu Lake, Zhenzhu River, and the pond.

5. Future outlook

The UV spectrophotometer was the only instrument used for analysis in this experiment. It allows samples to be reused, further processed, or analyzed, and enables measurements within a short time period. However, it faces the issue of stray light and light scattering due to suspended solids in liquid samples. Therefore, combining a UV spectrophotometer with parallel factor analysis and three-dimensional fluorescence spectroscopy may provide more precise information on the composition and sources of DOM. From this, subsequent research can utilize different photocatalysts to achieve more efficient degradation of water containing specific components. Lastly, since other photocatalysts such as ZnO also present advantages in the removal of metals, the combined photocatalyst ZnO-TiO_2 may enhance physicochemical and photocatalytic properties while ensuring better light harvesting capabilities[23].

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