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Comparative Study of Colloidal Particles on Organic Matter Degradation in Environmental Water and Typical Urban Sewage

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Abstract

Water, as a critical natural resource in urban areas, faces severe pollution due to human production and living activities. Previous studies have shown that dissolved organic matter (DOM) significantly affects water quality. To deepen our understanding of the impact of colloidal particles on DOM, we conducted a comparative study on organic matter degradation by colloidal particles in environmental water and typical urban sewage. The experiments revealed that colloidal particles accelerate the photodegradation of DOM in all six experimental water bodies. This research is pivotal for solving the challenges of water pollution confronting society.

Keywords: DOM, Colloidal particles, Photodegradation

1. Introduction

China's water resources face significant challenges due to its dense population and uneven water distribution between its northern and southern regions. Additionally, another major issue people face is water pollution. It is observed that among the different kinds of reasons for water pollution, eutrophication is one of the biggest triggers. Eutrophication refers to the excessive enrichment of nutrients, primarily nitrogen, and phosphorus, in natural water bodies, leading to the overgrowth and proliferation of organisms such as algae and phytoplankton in the water[1], causing a significant consumption of dissolved oxygen in the water and resulting in fish mortality. Moreover, pollutants from water bodies can indirectly enter the human body through various ways, underscoring the urgency of water pollution prevention and control. Furthermore, Rapid urbanization in China has led to the proliferation of black and odorous urban rivers, further exacerbating water quality concerns. It was discovered that all previously mentioned problems are somehow linked to dissolved organic matter (DOM), an important part of aquatic ecosystems. DOM is a heterogeneous class of water-soluble compounds containing reduced (organic) carbon sourced from various biological and geographical origins, exhibiting a wide range of chemical reactivity. DOM plays a pivotal role in the biogeochemical cycling of carbon,[2] operationally defined as the fraction of organic matter in a water sample that passes through a 0.45 μm filter.[3] Urban DOM and natural DOM have relatively different compositions, with their unique chemistry emphasizing the potential impacts on aquatic ecosystem carbon and nutrient cycling due to rapid urbanization.[4] Based on this, our study aims to explore the differential impact of colloidal particles on the degradation of DOM in municipal sewage and natural water. By conducting comparative experiments, we seek to elucidate the effect of colloidal particles on the decomposition rate of DOM, thereby advancing research in water purification. A colloid is a mixture in which one substance consisting of microscopically dispersed insoluble particles is suspended throughout another substance. [5] In this experiment, TiO2 nanoparticles were used as colloidal particles to explore their effects on the photodecomposition of DOM in different water source samples. The study aims to deepen our understanding of the state of China's water bodies. This understanding will enable researchers to actively control the spread of polluted water, thereby contributing significantly to the restoration of water bodies and improving human living standards.

2. Materials and Methods

I. The materials of the experiment:

Photochemical reactor, syringe, filter membrane, vacuum filter, precision balance, pan paper, 250mL volumetric flask, channel pipette, U.V. spectrophotometer, and cuvette.

II. The steps of the experiment:

(1) Collecting and preparing water bodies

First, we sampled the water from NanJing Xuan Wu Lake, Zhen Zhu River, and the institute's pond. Second, the water sample was filtered using a vacuum filter to ensure that no particulate suspended solids in the liquid sample affected the experimental results, and they were subsequently placed into the 4-degree refrigerator. Third, the sewage was prepared in the laboratory according to the formula(Table 1):

Table 1. The physicochemical properties of the typical urban sewages

Water sample	Domestic sewage	Aquaculture sewage	Printing and dyeing sewage
Glucose	83.3mg	208.25mg	–
NH4Cl	33.4mg	23.1mg	–
KH2PO4	5.52mg	8.5mg	–
Methyl orange	–	–	50mg
Distilled water	250ml	250ml	250ml

A precision balance measured all the masses, and all the volumes of distilled water were measured using the 250mL volumetric flask.

(2) Degrading DOM by photochemical reactor

We poured six types of water into 12 test tubes, each occupying two tubes. As the concentration of all the individual types of water was constant, there was no need to measure exactly how much of the water was poured into each tube. The only thing we needed to pay attention to was to ensure that the amount of water sample was sufficient to be separated into smaller portions to prepare our following experiment. After that, we took one of each pair of test tubes of the same type of water to add 2mL of pre-prepared titanium dioxide (TiO2) sol. TiO2, as colloidal particles and a photo semiconductor, played a role in the catalysis of photodegradation. The tubes that had not added TiO2 were labeled 1 to 6, respectively, representing different types of water samples without TiO2 particles, while those that had already added TiO2 particles were labeled 1-1 to 6-1 for each. To further investigate the effect of time on the decomposition of dissolved organic matter, we repeated the above steps eight times in total to record the values at periods of 0h, 10min, 20min, 30min, 1h, 2h, 3h, 4h, and 20h. Following that, the new samples were placed into the photochemical reactor, a device in which a photochemical reaction takes place. After a certain period, tubes were removed from the photochemical reactor, with 4ml of each sample collected. Since we needed to filter out the colloidal particles before transferring the solution into the centrifuge tubes to ensure that our subsequent detection was accurate, we used filter paper with a pore diameter of 0.45μm to filter out the nanoparticles of the samples to which TiO2 had been added and then transferred them into the centrifuge tubes. As for the samples containing only the original water, a channel pipette was used to transfer them into centrifuge tubes. Considering that the printing and dyeing wastewater concentration is too high and its color affects the absorbance, we decided to dilute groups 6 and 6-1. 4.5ml ultra-pure water was added into centrifuge tubes with a pipette, and then 0.5ml printing and dyeing wastewater was added separately into centrifuge tubes with a pipette at different times. Finally, each centrifuge tube carrying the sample was marked accordingly to facilitate identification in subsequent experiments.

(3) Detecting and calculating the absorbance by the U.V. spectrophotometer

After all the new samples had been prepared, they were detected by the UV spectrophotometer one by one to determine how much UV light was absorbed by each sample. According to the formula, absorbance equals the natural logarithm of the ratio of the incident light intensity before passing through a solution or substance to the transmitted light intensity after passing through the solution or substance (abs = ln(C0/C)), and the instrument calculated all the absorbance values at the wavelength of 254μm. To ensure the accuracy of the experiment, all the above experimental steps were repeated twice to obtain more accurate and precise data.

Detection procedure: Before detection, the device was calibrated. The cuvette was filled with distilled water and inserted into the machine. Auto-zero was clicked, and then the cuvette was removed. We poured the samples into the cuvette, ensuring that the volume of liquid occupied about 2/3-3/4 of the cuvette. The cuvette was held on a matte surface (avoid touching the glass surface with your hands because this may increase the dust on the surface and influence the final data). Then, the cuvette was placed into the U.V. spectrophotometer, ensuring that the matte surface faced the front, and the machine was started by clicking the measure key. The data obtained was recorded. After detecting each sample, the cuvette was rinsed with distilled water and dried with tissue. It was ensured that there was no water on the surface of the cuvette before placing it back into the spectrophotometer, as this could affect detection).

3. Results

(1) Changes in DOC concentration and degradation efficiency in different water bodies during the photodegradation process

The following four graphs clearly show the changes in the concentration of DOC and the degradation efficiency in different water bodies under the influence of colonial

particles TiO2 or not. What could be immediately concluded from them is that the concentrations of DOC in all water bodies decrease over time, regardless of whether the colloidal particles were added and whether the water bodies are environmental sewage or typical urban sewage. The DOC degradation rates of the three water bodies were presented on the right axis of each image. After adding colloidal particles TiO2, the DOC degradation rates of all six water bodies significantly increased.

(a) Environmental sewage:

According to the graphs(Fig.1), the initial DOC concentrations of the water samples from the lake, river, and pond without TiO_2 are 7.37±0.20, 10.48±0.28, and 7.81±0.37 mg/L, respectively. After photodegradation, the remaining DOC concentrations of lake, river, and pond samples are 2.60±0.12, 3.59±0.03, and 2.90±0.02 mg/L, respectively. Through calculation, the final DOC degradation rates are river sample (66.63%) > lake sample (64.72%) > pond sample (62.86%). The data of the experiment with-TiO_2 initially show similar with the DOC concentration of lake, river, and pond, respectively, being 7.62±0.27, 10.21±0.57, 7.47±0.11 mg/L, with the eventual data being 1.80±0.12, 1.90±0.13 and 0.49±0.13 mg/L. However, the DOC degradation rates differ somewhat from the final figure of the pond sample (93.41%) > river sample (81.37%) > lake sample (76.38%). It is speculated that one reason for the high DOC concentration in the river sample is the erosion of riverbanks by rainwater runoff, which brings a large amount of organic matter from the soil into the river water.

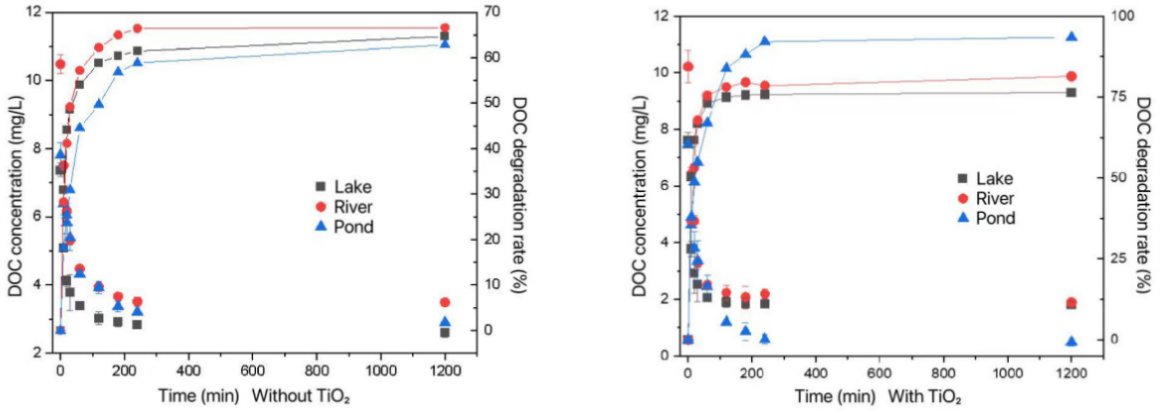
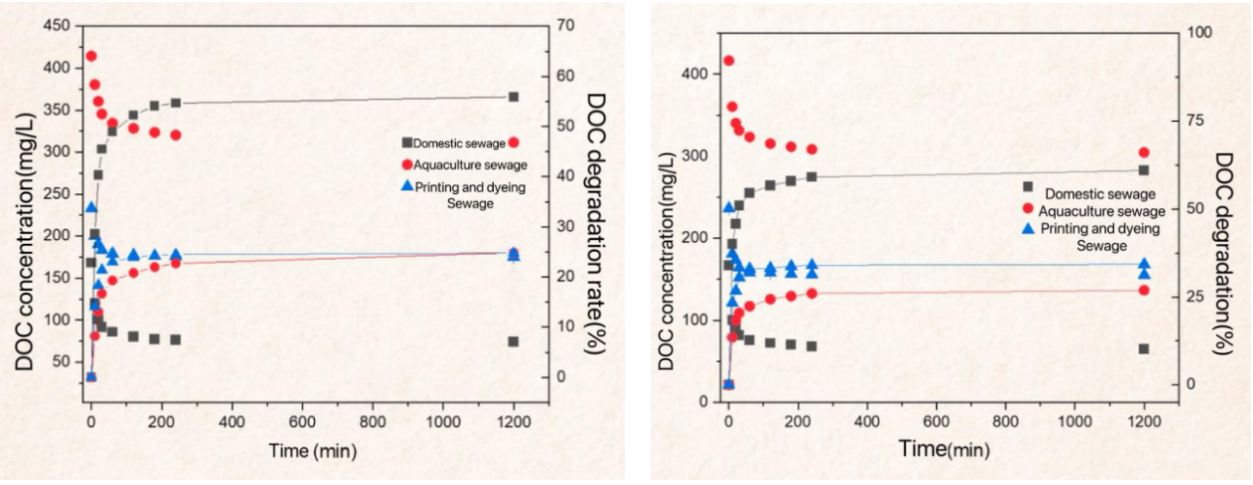


Fig.1. Effects of TiO_2 addition on the DOC degradation for the environmental waters

(b) Typical urban sewage:

Overall, the influence of TiO2 on typical urban sewage is not as evident as on environmental sewage. However, colloidal particles still speed up the degradation of DOC in the water samples, acting as a catalyst. The initial DOC concentrations of domestic sewage, aquaculture sewage, and printing and dyeing sewage are respectively 168.32±5.56, 414.43±13.83 and 233.12±7.67 mg/L, and the final concentration are respectively 74.21±2.45, 311.5±10.48 and 175.34±5.76 mg/L. Through calculation, the DOC degradation rates are obtained, with the final data being domestic sewage (55.90%) > aquaculture sewage (24.83%) > printing and dyeing sewage (24.79%). The experiment with the addition of TiO2 obtained similar DOM concentration data, but the colloidal particles accelerated the decomposition of DOM. As for DOM degradation rate, domestic sewage (60.95%) > printing and dyeing sewage (34.27%) > aquaculture sewage (26.89%). Aquaculture sewage contains the greatest amount of DOC. It is predicted that the reason for this is respiration, excretion, microbial decomposition, and other processes in biological aquaculture. (Fig.2)



Without TiO2 With TiO2

Fig.2. Effects of TiO_2 addition on the DOC degradation for the typical urban sewages

(2) Changes in absorbance and degradation efficiency at 254nm in different water bodies during the photodegradation process

The colored DOM in water can absorb the light passing through the water sample. When colored DOMs degrade, the absorbance of the water samples also decreases. Therefore, detecting 254nm absorbance of the water bodies indirectly indicates the change in the amount of DOM in each water sample. According to the graphs, it is evident that as time elapses, the 254nm absorbance of all samples decreases, suggesting that the concentration of DOM in all the samples is decreasing, which is consistent with the conclusion drawn in the previous section. The absorption degradation rate is calculated and presented on the right axis. After adding TiO2 colloidal particles, all absorption degradation rates show remarkable growth, once again proving the catalytic effect of colloidal particles on the photodegradation of DOM.

(a) Environmental sewage:

According to the graph(Fig.3), the 254nm absorbance of the three water samples, lake, river, and pond without TiO2 are respectively 0.056±0.0011, 0.053±0.0003, and 0.121±0.0037 A.U. The pond has the highest absorbance, which could be attributed to the large amount of humic acid in the falling leaves around the pond. Due to numerous light-absorbing groups in humic acid, the pond sample absorbs more light, exhibiting a high absorbance phenomenon. After the reaction, the 254nm absorbance of lake, river, and pond are respectively 0.014±0.0040, 0.015±0.0001 and 0.842±0.00014 A.U. Upon calculation; it is shown that the absorption degradation rates are highest for the pond sample (84.30%), followed by lake sample (75.00%), and then the river sample (71.70%). Overall, the data on absorption degradation rate compared to the data on DOM degradation rate is higher, showcasing that colored DOM can be photochemically degraded more efficiently than colorless DOM particles. After adding colloidal particles, the initial data do not show much difference. In contrast, the data at the end decrease except for the lake sample, with the figure of lake, river, and pond respectively being 0.014±0.0006, 0.012±0.0004 and 0.004±0.0007 A.U. Especially for the pond sample, the colloidal particles have the greatest impact on its photodegradation process. The absorption degradation rates are highest for the pond sample (96.75%), followed by the river sample (77.36%), and then the lake sample (74.55%), which maintains the same rank as the one without TiO2.

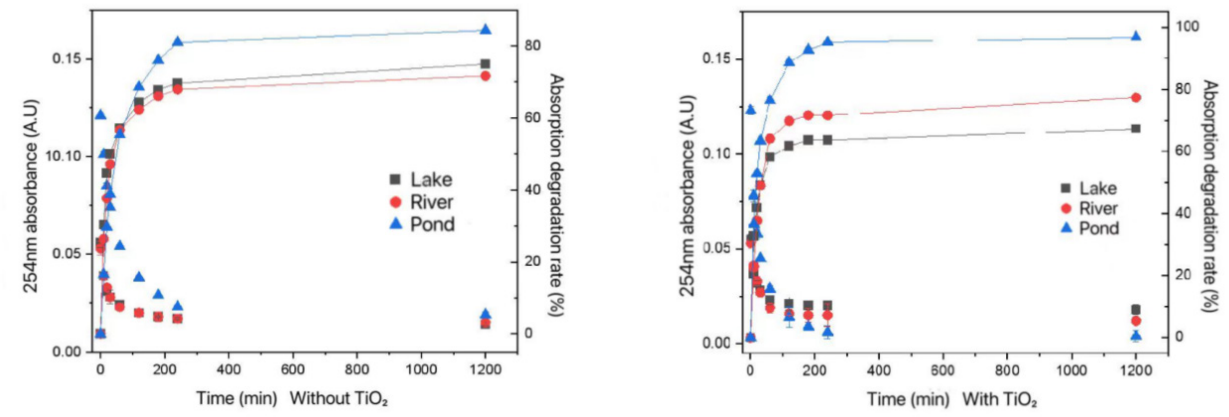
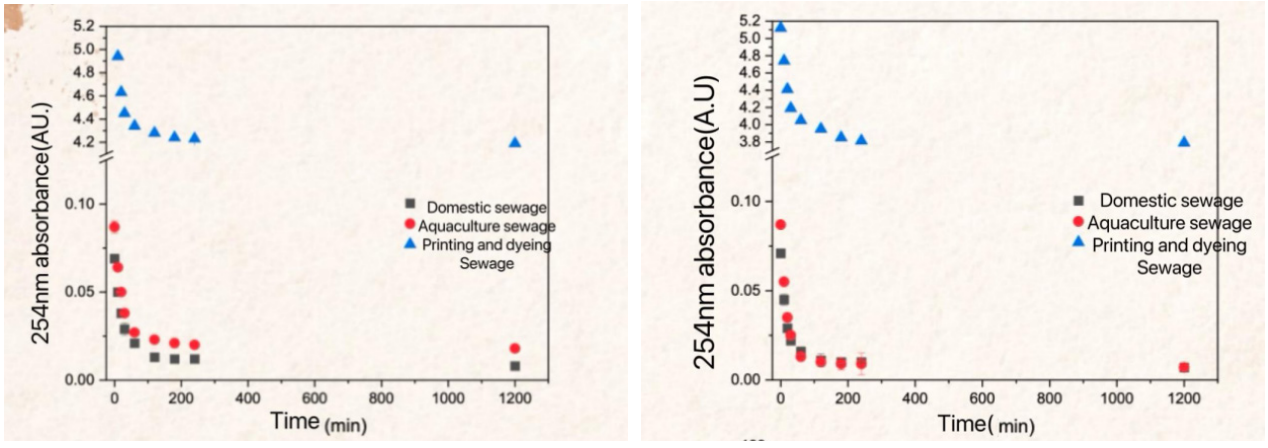


Fig.3. Effects of TiO_2 addition on the degradation of aromatic substances in the environmental waters

(b) Typical urban sewage:

Looking at the graphs without TiO2 first, the initial data of domestic sewage, aquaculture sewage, and printing and dyeing sewage are respectively 0.069±0.0002, 0.087±0.0007, and 0.564±0.0119 A.U., while the eventual data are 0.008±0.0004, 0.018±0.0009 and 4.19±0.0080 A.U. The high absorbance of printing and dyeing sewage is due to its many colored substances that absorb light. The calculated absorption degradation rates are highest for domestic sewage (88.41%), followed by aquaculture sewage (79.31%), and then printing and dyeing sewage (25.71%). The huge gap between the absorption degradation rate of aquaculture sewage and printing and dyeing sewage could also result from the colored substances not degraded by the photochemical reactor in the latter water sample. After adding colloidal particles, the data of domestic sewage and printing and dyeing sewage are similar. Still, the absorbance of aquaculture sewage decreases significantly, and its absorption degradation rate ascends as well, indicating that the TiO2 particles have the biggest influence on it. Therefore, the conclusion that the aquaculture sewage contains the greatest concentration of DOM is suggested, which is the same as the one obtained from the research on the DOC concentration. (Fig.4)



Without TiO2 With TiO2

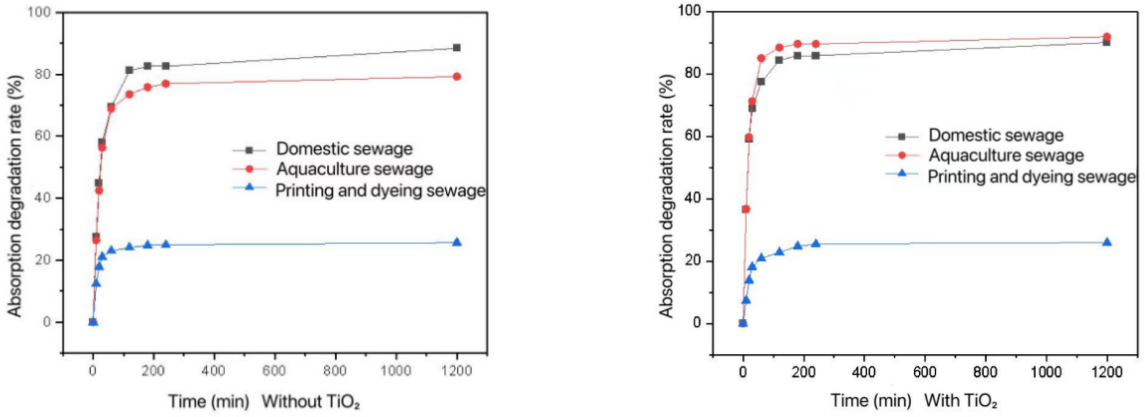
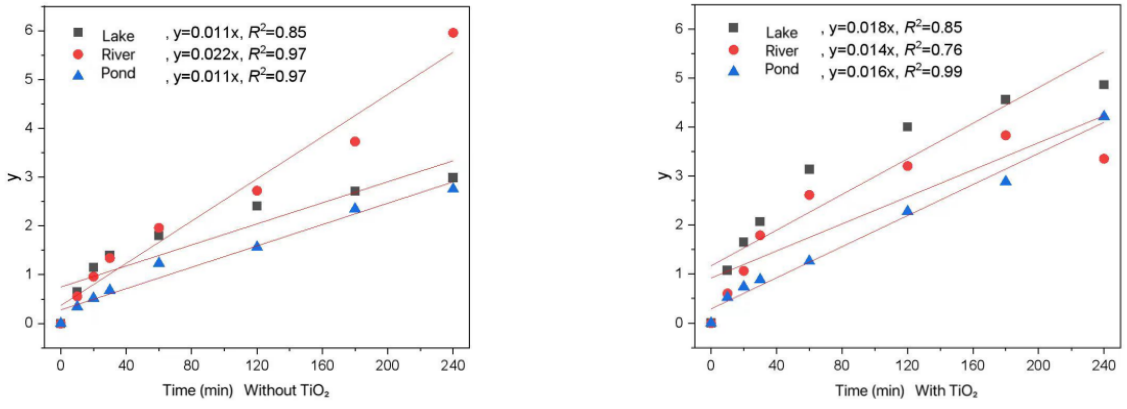


Fig.4. Effects of TiO_2 addition on the degradation of aromatic substances for typical urban sewages

(3) Study on photodegradation kinetics of dissolved organic matter in typical sewage of different cities

Here are the differences between three urban sewage samples(Fig.5). The samples' DOC and 254nm photodegradation are by first-order degradation kinetics. The R-squares are larger than 0.82, which shows that our data is almost accurate. According to 254nm photodegradation, for samples without TiO2, the rate of degradation is aquaculture sewage (k=0.014) > printing and dyeing sewage (k=0.013) > domestic sewage (k=0.011). According to DOC degradation rate, printing and dyeing sewage (k=0.017) > domestic sewage (k=0.014) > aquaculture sewage (k=0.009). For samples with TiO2, the rate of 254nm photodegradation is printing and dyeing sewage (k=0.015) = aquaculture sewage (k=0.015) > domestic sewage (k=0.012). The rate of DOC degradation is printing and dyeing sewage (k=0.017) > aquaculture sewage (k=0.012) = domestic sewage (k=0.012). The results show that printing and dyeing sewage has the highest degradation rate.



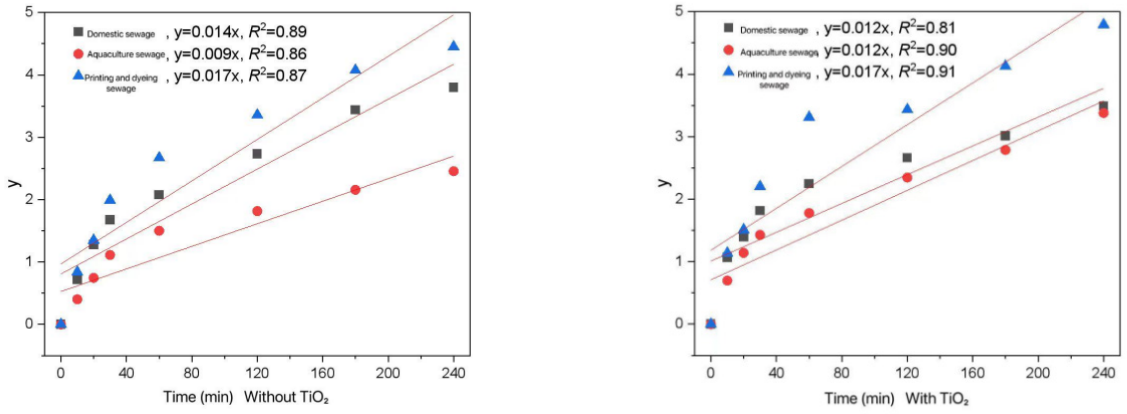


Fig.5. Comparison in degradation kinetics of DOC in terms of TiO_2 addition and water types

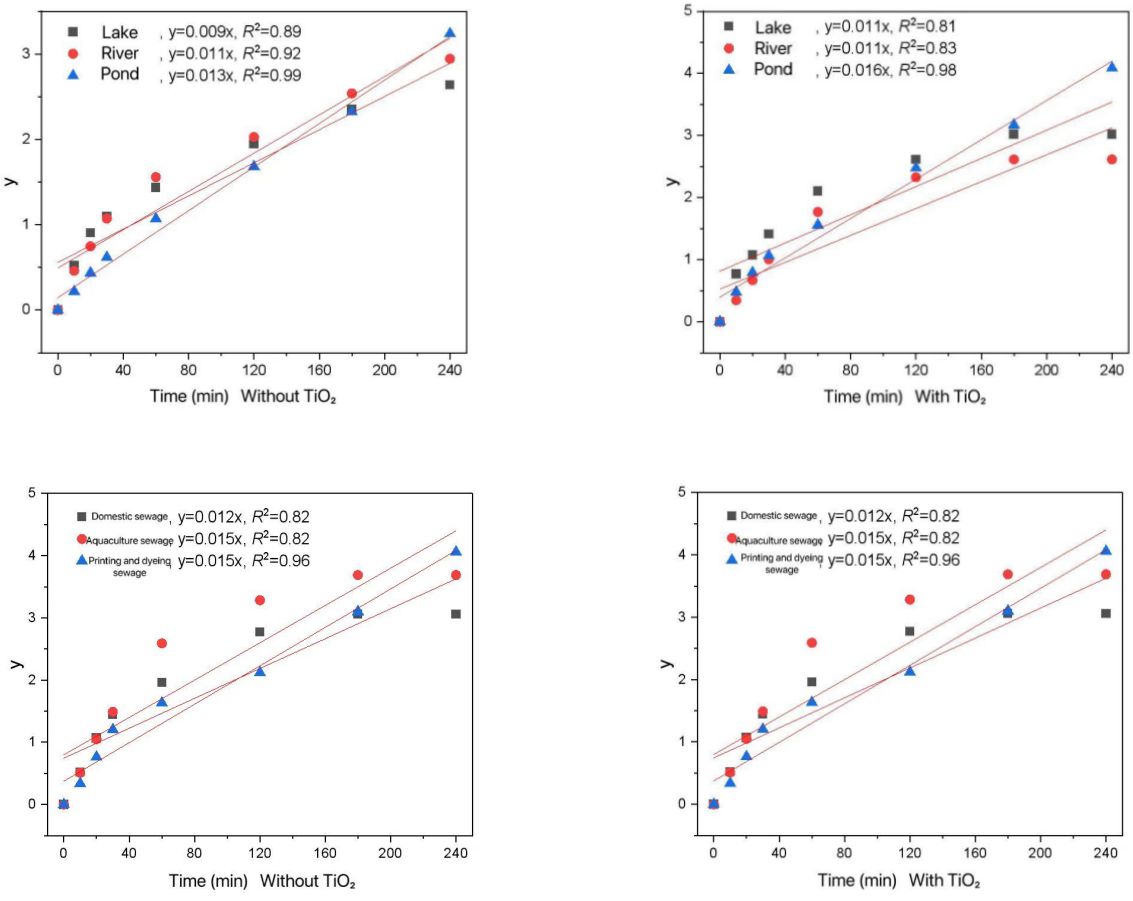


Fig.6. Comparison in degradation kinetics of aromatic substances in terms of TiO_2 addition and water types

(4) Comparison of aromaticity changes of DOM during photodegradation

The following figures(Fig.6) depict the comparison of DOM aromaticity among six types of water bodies during photodegradation. It is evident from the figures that the initial SUV254 data of lakes, rivers, ponds, printing and dyeing wastewater, aquaculture wastewater, and domestic wastewater indicate that pond water bodies and printing

and dyeing wastewater contain more benzene ring substances and exhibit higher aromaticity. In the initial stage of photodegradation (less than 30 minutes), the aromaticity of environmental water and domestic wastewater generally increased, suggesting that the aromaticity of these waterbodies could be improved during the initial stage of photodegradation. This is likely because these water bodies also contain a large number of non-absorbent substances, and the degradation efficiency of non-absorbent substances is greater than that of absorbent substances at the initial stage of photodegradation, resulting in an overall improvement of DOM aromaticity. However, only when TiO2 is not added for domestic wastewater will the data show that the initial aromaticity will be improved. It is speculated that TiO2 accelerates the photodegradation reaction, causing the process of improving and reducing the aromaticity of domestic wastewater to be completed before the second test. After that, in the six water bodies without TiO2 added, SUV254 decreased with further photodegradation, and each sample was also lower than its initial SUV254 value at the end of the process, demonstrating that the photodegradation process can effectively reduce the aromaticity of these six water bodies without colloidal particles. However, in the samples with TiO2, SUV254 of river water, lake water, and printing and dyeing wastewater were all higher than their initial values at the end. The reason may be that TiO2 catalyzed the degradation of light-absorbing and non-light-absorbing substances, resulting in increased aromaticity in the final samples. The difference in the final aromaticity may be attributed to the varying proportions of light-absorbing and non-light-absorbing substances in different samples.

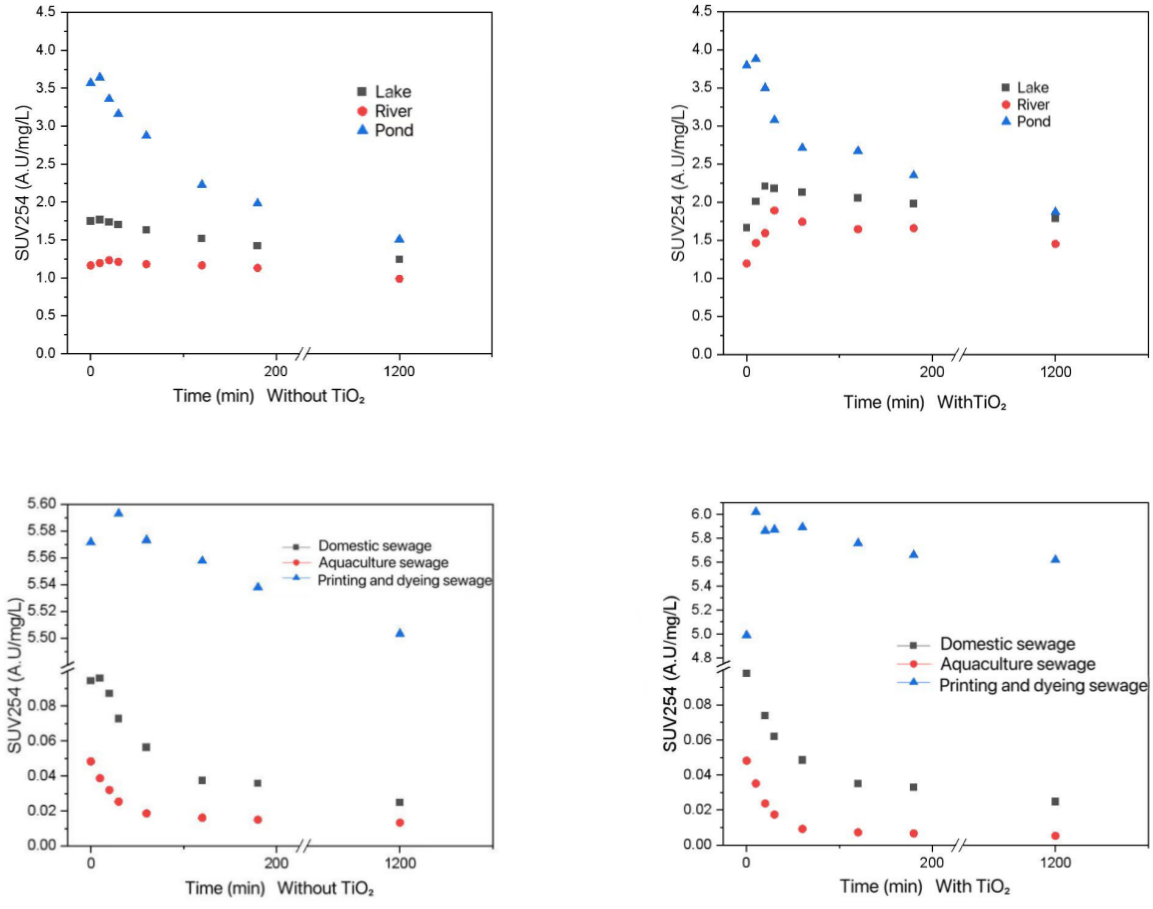


Fig.6. Comparison in the changes of irradiation-induced aromaticity in terms of TiO_2 addition and water types

4. Conclusion

After comparing the characteristics of DOC, absorbance, and aromatic changes in environmental and urban water bodies, it can be concluded that in environmental bodies, the pond has a relatively high concentration of DOC and a high value of 254nm absorbance. In urban water bodies,

aquaculture sewage has the highest concentration of DOC due to biological actions, while printing and dyeing sewage has the highest 254nm absorbance due to the colored substances it contains. They all follow first-order degradation kinetics. It is also evident that the properties of typical urban water bodies are completely different from those of environmental water bodies, indicating the need for separate studies in the future. The photodegradation process decreases the concentration of organic particles in water bodies and affects the aromatic characteristics of DOM in water. Overall, colloidal particles always significantly impact them, but to varying extents depending on the specific water bodies. In the future, the research direction could focus on the mechanism and efficiency of photodegradation of DOM in water to better apply this technology to real life and increase the rate of water treatment.

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