

Fabrication and Evaluation of a Total Organic Carbon Analyzer Using Photocatalysis

Do Yeon Lee¹, Jeong Hee Shin¹, and Jong-Hoo Paik^{1,*}

Abstract

Water quality is crucial for human health and the environment. Accurate measurement of the quantity of organic carbon in water is essential for water quality evaluation, identification of water pollution sources, and appropriate implementation of water treatment measures. Total organic carbon (TOC) analysis is an important tool for this purpose. Although other methods, such as chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are also used to measure organic carbon in water, they have limitations that make TOC analysis a more favorable option in certain situations. For example, COD requires the use of toxic chemicals, and BOD is time-consuming and can produce inconsistent and unreliable results. In contrast, TOC analysis is rapid and reliable, providing accurate measurements of organic carbon content in water. However, common methods for TOC analysis can be complex and energy-intensive because of the use of high-temperature heaters for liquid-to-gas phase transitions and the use of acid, which present safety risks. This study focuses on a TOC analysis method using TiO₂ photocatalysis, which has several advantages over conventional TOC analysis methods, including its low cost and easy maintenance. For TiO₂, rutile and anatase powders are mixed with an inorganic binder and spray-coated onto a glass fiber substrate. The TiO₂ powder and inorganic binder solutions are adjusted to optimize the photocatalytic reaction performance. The TiO₂ photocatalysis method is a simple and low-power approach to TOC analysis, making it a promising alternative to commonly used TOC analysis methods. This study aims to contribute to the development of more efficient and cost-effective approaches for water quality analysis and management by exploring the effectiveness and reliability of the developed equipment.

Keywords: Total organic carbon, Titanium dioxide, Photocatalyst, Inorganic binder, Water quality analysis

1. INTRODUCTION

Organic compounds in water are a major cause of water pollution, and there has been a shift from biodegradable to non-biodegradable substances with industrialization. With industrial advancements, the nature of organic compounds in water has changed from those that can be naturally broken down to those that cannot. Owing to this shift, conventional approaches to water quality evaluation, which previously relied on indirect assessments of organic compounds using biochemical oxygen demand (BOD) and chemical oxygen demand (COD), have given way to more direct methods, such as total organic carbon (TOC) analysis [1,2].

BOD quantifies organic compounds by calculating the amount

of oxygen used by heterotrophic microorganisms to decompose organic matter in water, whereas COD quantifies organic compounds by oxidizing water with an oxidant and converting the amount of oxidant consumed [3]. Technically, BOD is an indirect method that is not suitable to measure non-biodegradable substances. It requires complex preconditions and has problems, such as secondary pollution caused by the use of oxidants and time-consuming analysis. Additionally, COD cannot measure the total amount of organic matter, including non-biodegradable organic matter, owing to its low oxidation rate, which limits its usefulness in organic matter management [4,5]. Therefore, the direct measurement of organic compounds in water using TOC analysis is most suitable for the rapid measurement of non-biodegradable substances. The conventional high-temperature oxidation method used for TOC analysis is shown in Fig. 1. Conventional TOC analysis methods can be classified into non-purgeable organic carbon (NPOC) measurement, which removes inorganic carbon before measuring organic carbon, and the addition-subtraction method (Total carbon - Inorganic carbon, TC - IC), which measures total carbon and subtracts inorganic carbon to determine the TOC. Particularly, the NPOC measurement method requires the use of acids to remove inorganic carbon,

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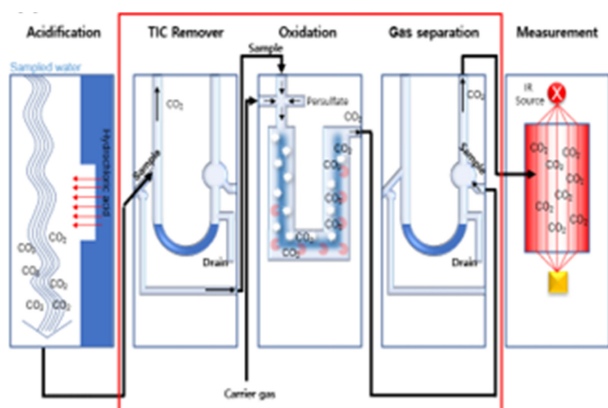


Fig. 1. Conventional TOC analysis process.

posing safety risks. As shown in Fig. 1, the entire process and analysis method are complex and are power-consuming owing to high temperatures. Additionally, commercial TOC analyzers are not ideal for real-time water quality analysis in remote monitoring systems, such as TMS (tele-monitoring system) because of their large size and high cost [6-8].

Thus, a novel method to analyze TOC using the photocatalytic reaction of TiO_2 was proposed [9].

Compared with conventional TOC analyzers, this method has a simpler structure and shorter measurement time, making it more efficient for analysis and is expected to be effectively applied to TMS in the future. To prevent the organic carbon from influencing the measurement of TOC in the photocatalytic reaction, an inorganic binder system without organic carbon components was used, and the efficiency of the photocatalytic reaction was analyzed as a function of the amount of TiO_2 photocatalyst coated onto the glass fiber.

This study introduces a self-designed and manufactured photocatalytic TOC analyzer and proposes its development potential into a more accurate water-quality analysis device.

2. EXPERIMENTAL

2.1 TOC analysis method using the photocatalytic reaction

A schematic of the new TOC analysis method for the photocatalytic reaction conducted in this experiment is shown in Fig. 2.

As shown in Fig. 2, 2-12 wt% of TiO_2 powder was added to a coating solution containing an inorganic binder to prepare a coating solution. When this solution was coated on a glass fiber

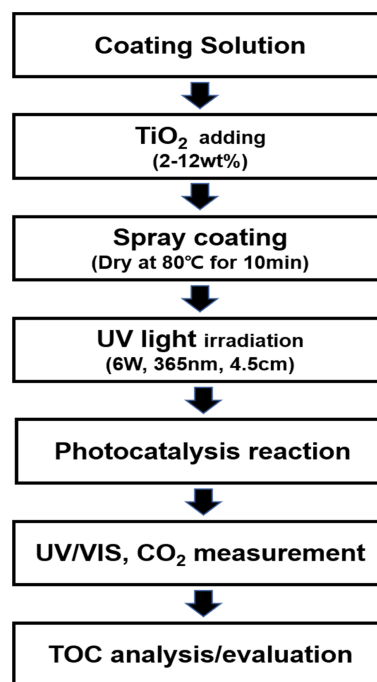


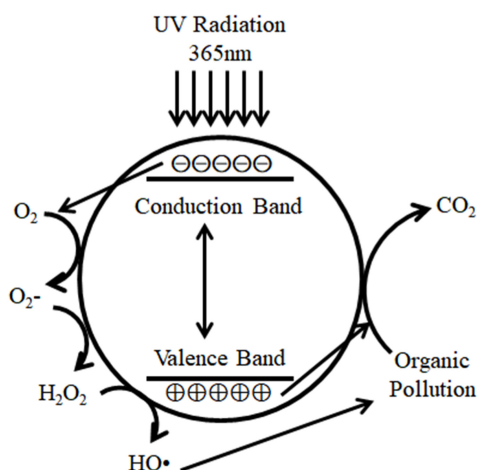
Fig. 2. TOC water quality analysis process with photocatalytic reaction.

substrate using a spray coating method and UV irradiation, water was oxidized owing to a photocatalytic reaction and converted into CO_2 . The CO_2 produced was measured using a CO_2 sensor (SENSIRION, SCD30, Gascard NG, EDINBURGH SENSORS). Additionally, the photocatalytic reaction efficiency at each concentration was analyzed by comparing the absorbance at a specific wavelength (500 nm) using a UV/VIS/NIR spectrophotometer (V-570, JAS.CO).

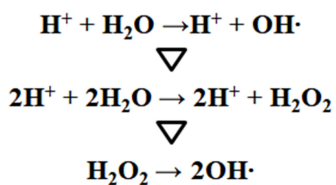
A schematic of the principle of CO_2 generation through the photocatalytic reaction of TiO_2 is shown in Fig. 3. When the energy corresponding to the bandgap is received, electron-hole pairs are formed by electron excitation, forming hydroxyl radicals (OH) and superoxide radicals (O_2^-), which oxidize and decompose the organic compounds into H_2O and CO_2 , respectively [10,11].

Photocatalytic reactions occur only on the surface of the material and can be terminated when light is blocked, making it easy to control the reaction. As a photocatalyst, TiO_2 is chemically stable, does not react with hydrogen fluoride or chlorine, and exhibits excellent durability.

Using this photocatalytic reaction, the structure can be simplified and the volume of the equipment can be considerably reduced. Non-biodegradable samples that are difficult to measure using the existing indirect measurement method can be accurately analyzed; the number of samples required is also small, thus reducing the measurement time and the possibility of secondary



Reaction by Hole



Reaction by Electron

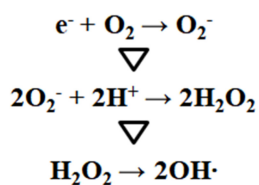


Fig. 3. CO₂ generation through the photocatalytic reaction of TiO₂.

pollution caused by the measurement sample [12,13].

2.2 Manufacturing an inorganic binder TiO₂ coating solution

The manufacturing process of an inorganic binder coating solution is shown in Fig. 4; an inorganic binder system that does not contain organic carbon and does not decompose in the photocatalytic reaction was used to increase the adhesion of the TiO₂ powder without affecting the measured value of organic carbon in the photocatalytic reaction.

The binders used were tetraethyl orthosilicate (TEOS, 99.5%, Daejung, Korea), phenyltrimethoxysilane (PTMS, 99.5%, Sigma-Aldrich, USA), isopropanol (2-propanol) anhydrous (IPA, 99.5%, Sigma-Aldrich, USA), and nitric acid (60%, Daejung, Korea). To prepare the solution, the starting material was synthesized in a molar ratio of TEOS: EtOH: H₂O: HNO₃ = 0.35:16:1 of 0.005. To facilitate the synthesis, IPA, TEOS, and PTMS were added in order of the heaviest materials, and the mixture was continuously stirred when the materials were added. The coated binder solution was synthesized by adding nitric acid to the produced solution and stirring it at room temperature for 24 h. Subsequently, it was heated at 60 °C and stirred for 24 h to evaporate ethanol. TiO₂ powder (Degussa, p25) was added to the coated binder solution to

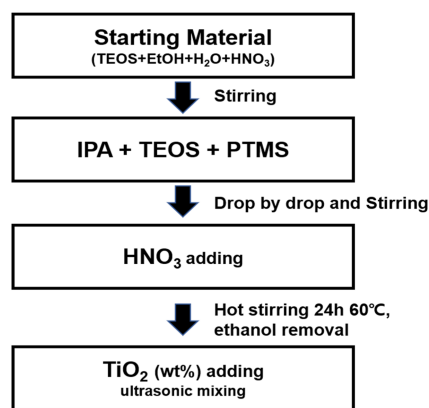


Fig. 4. Coating solution manufacturing process.

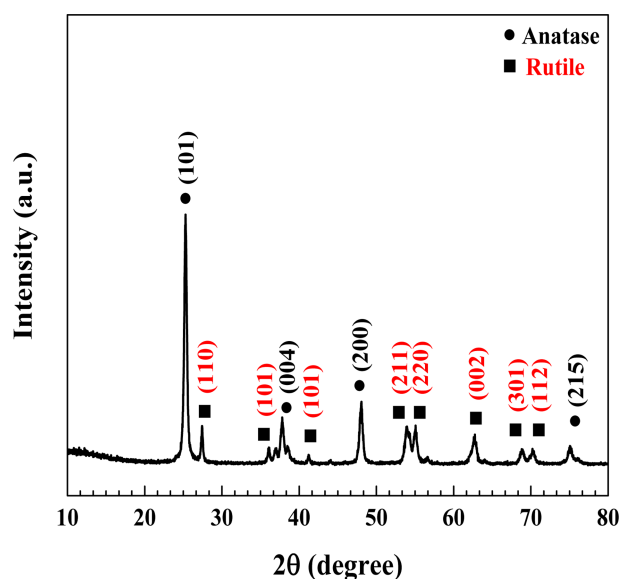


Fig. 5. X-ray diffraction patterns of the TiO₂ powder.

obtain a coating solution. The produced coating solution was diluted in ethanol and ultrasonically mixed for 1 h. The optimal concentration of the coating solution was adjusted to 2-12 wt% at a ratio of 2 wt% to analyze the photocatalytic properties according to the change in TiO₂ concentration.

The results of the X-ray diffraction (XRD, RIGAKUDMAX2500, Japan) analysis of the TiO₂ (Degussa P25, Germany) powder used as a material for the photocatalytic reaction is shown in Fig. 5. XRD analysis revealed the coexistence of rutile and anatase phases in the TiO₂ powder. The photocatalytic performance of TiO₂ was improved when anatase and rutile phases coexisted compared with that of a single phase. Therefore, as shown in Fig. 5, we conducted an experiment using a powder in which the rutile and anatase phases coexisted [14].

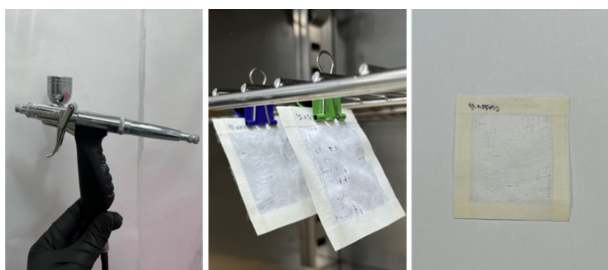


Fig. 6. Spray coating using the TiO₂ coating solution.

2.3 Glass fiber substrate coating process and evaluation

The spray coating of a glass fiber substrate using a previously prepared coating solution is shown in Fig. 6. The spray coating method can be applied for low-cost mass production because the coating area can be adjusted and the coating thickness can be easily controlled. An airbrush (BEETLEBUG, GP-70) was connected to an air conditioner presser (COMPWORLD, CW35) and sprayed at a pressure of 0.1 MPa at a distance of 25 cm. The coating was performed on one side with 1 mL, dried in an oven at 80 °C for 10 min, and proceeded similarly on the other side to coat each side with 3 mL.

The substrate to be coated was obtained by cutting a glass fiber substrate with a mesh size of 100 μm into 45 × 50 mm. The concentration of the inorganic binder was fixed at 60% and TiO₂ was added at a rate of 2 wt% from 2 to 12 wt% and coated. The coating state of the fiber substrate was validated using an optical microscope (BX51, OLYMPUS).

The manufactured TiO₂-coated substrate was irradiated with a 6 W, 365 nm UV light (VL-4. L, VILBER) at a distance of 4.5 cm to compare photocatalytic reaction efficiencies. Methyl red (MR), a pH indicator, was used to compare the reaction efficiency. MR was used after the solution was diluted to 0.1 mM and the photocatalytic reaction efficiency was analyzed by comparing the absorbance at a specific wavelength (500 nm) through a UV/VIS/NIR spectrophotometer (V-570, JAS.CO) [15].

3. RESULTS AND DISCUSSIONS

3.1 Photocatalyst characteristics according to TiO₂ addition amount and reaction time

Fig. 7 shows the surface of a glass fiber coated with TiO₂ (a) before (b) and after (c) the photocatalytic reaction. The photographs of the photocatalytic reactions using MR

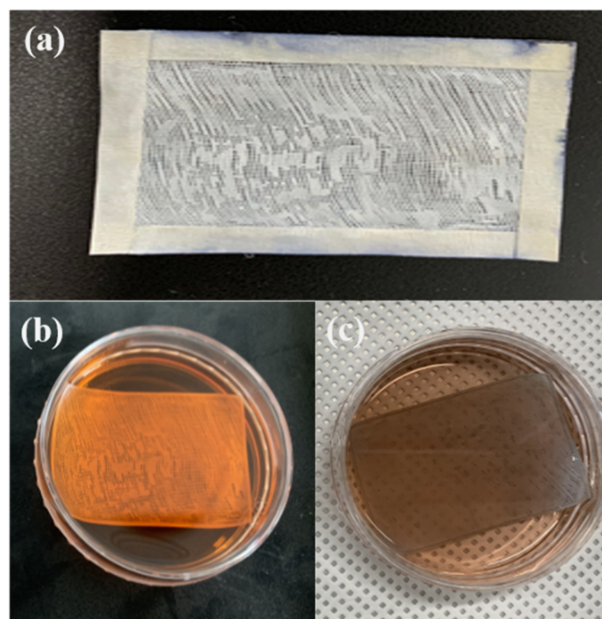


Fig. 7. UV Reaction of MR with coated substrates (a) coated substrate, (b) before reaction, and (c) after reaction.

(C₁₅H₁₅N₃O₂) reagents are shown in Fig. (b) and (c). To compare the photocatalytic reactions, the change in absorbance owing to the decomposition of organic MR was measured. MR was decomposed by a photocatalyst reaction, such as $2C_{15}H_{15}N_3O_2 + 43O_2 \rightarrow 30CO_2 + 6NO_3^- + 6H^+ + 12H_2O$. The coated substrate was immersed in 10 mL of MR; 365 nm UV light with a 6 W output was irradiated at a distance of 4.5 cm to analyze the photocatalytic reaction state. The organic carbon of MR was decomposed by the photocatalytic reaction and the MR became transparent. [16]

The change in absorbance when TiO₂ was coated with a concentration of 2-12 wt% and decomposed by the photocatalytic reaction according to the reaction time is shown in Fig. 8. A coating solution containing an inorganic binder was prepared and spray-coated on glass fibers with a mesh size of 100 μm and was then reacted for 0, 0.5, 1.0, 1.5, 2.0, and 2.5 h, showing absorbance change when the MR solution was decomposed by a photocatalytic reaction over time.

When the photocatalyst efficiencies were compared, the photocatalytic performance increased as the amount of TiO₂ increased up to 6wt%; however, it decreased again at higher concentrations. Regarding the total photocatalyst efficiency until 2.5 h of reaction time, the best efficiency was observed when 6 wt% of TiO₂ was added. Most of the MR was decomposed within 1 h, compared with conventional water quality analysis methods.

Fig. 9 shows the scanning electron microscopy (SEM) images

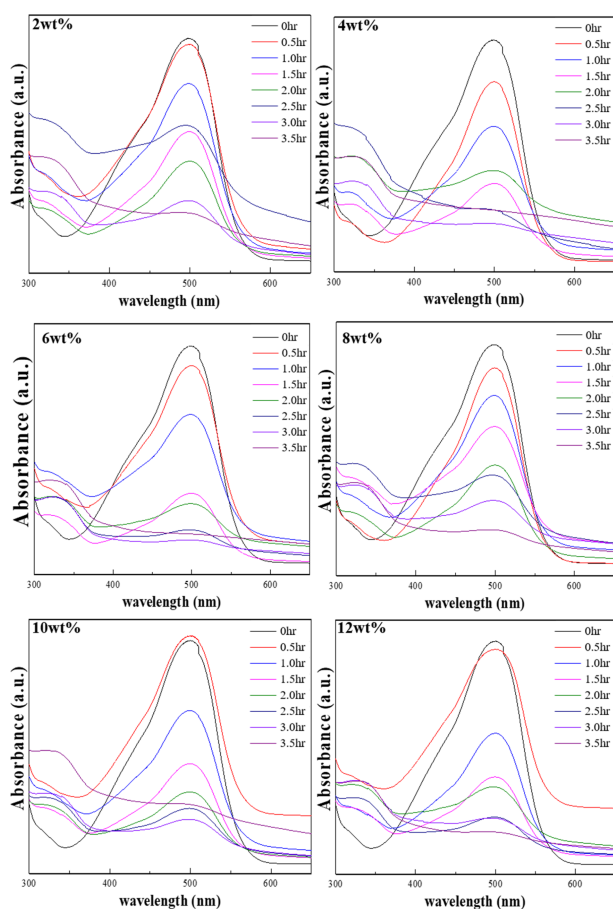


Fig. 8. MR absorbances owing to the photocatalytic reaction with time at different TiO₂ concentrations: (a) 2 wt%, (b) 4 wt%, (c) 6 wt%, (d) 8 wt%, (e) 10 wt%, and (f) 12 wt%.

of the microstructure of the glass fiber substrate according to the amount of TiO₂ added. This was analyzed using a scanning electron microscope (JSM-7610F, JEOL) analyzer.

When the same amount of TiO₂ was coated on the same area, it was assumed that the coating performance was the same if a certain amount remained on the substrate without peeling off. The coating performance was compared by focusing on peeling according to the concentration of TiO₂.

The amount of coating on the fiber increased as the amount of TiO₂ increased; however, excessive particles per unit area of the glass fiber adhered at more than 8 wt%.

The results of comparing the photocatalytic efficiency according to the difference in the TiO₂ concentration in the coating solution with reaction time is shown in Fig. 10. The absorbance was measured when the TiO₂ concentration was varied from 2 to 12 wt% and the reaction time was increased to 30 min at 5-min intervals.

A better photocatalytic efficiency was observed for 4-6 wt%

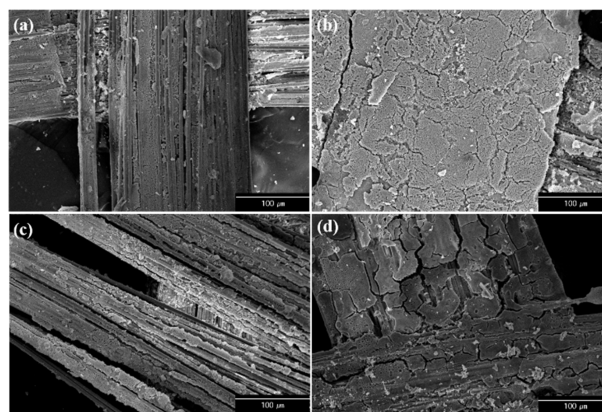


Fig. 9. SEM images of glass fiber coating at different TiO₂ amounts: (a) 2 wt%, (b) 4 wt%, (c) 6 wt%, (d) 8 wt%.

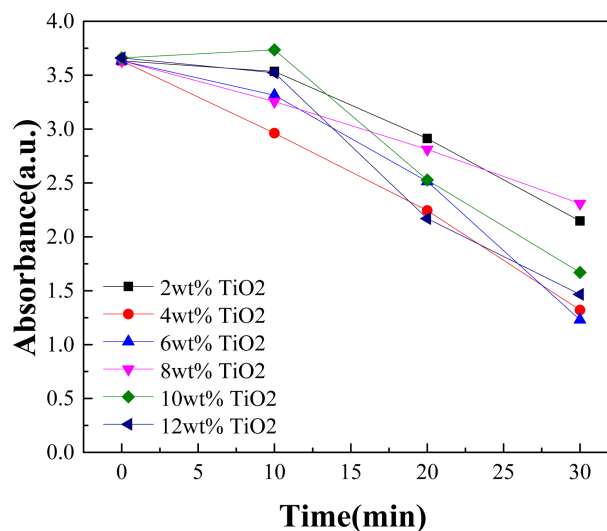


Fig. 10. MR absorbance change according to TiO₂ concentration with reaction time.

TiO₂ than when TiO₂ 8 wt% or more was added. The experimental results, in which peeling occurred at 8 wt% or more, reduced the absorbance characteristics (Fig. 9). When all these results were comprehensively analyzed, TiO₂ concentrations of 4 and 6 wt%, which showed the highest efficiency for a short period without peeling, were determined to be the optimal conditions. Compared with conventional water quality analysis methods, most of the MR decomposed within 30 min, which validated that this analysis was dozens of times faster than those of conventional methods.

3.2 Design and fabrication of a photocatalytic TOC analyzer

The amount of CO₂ generated when a 6 wt% TiO₂-coated substrate was placed in a 75 ppm TC (total carbon) standard

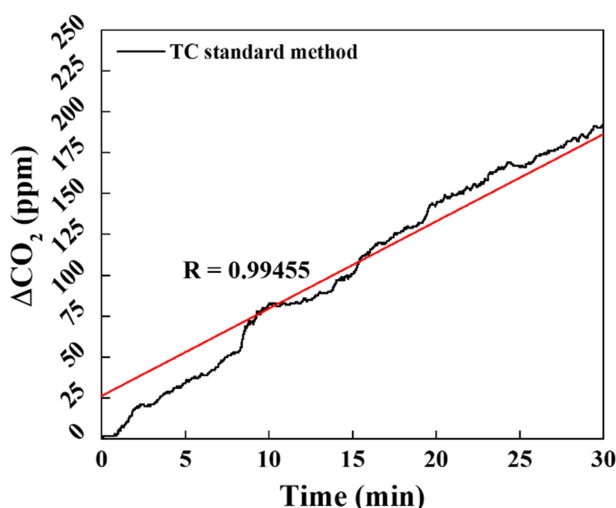


Fig. 11. CO₂ generation during photocatalytic reaction with a TC standard concentration of 75 ppm and a 6 wt% TiO₂-coated substrate.

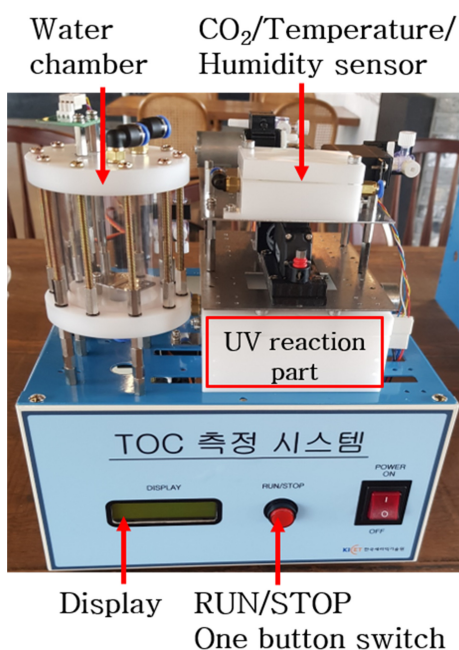


Fig. 12. TOC equipment of the developed photocatalytic oxidation method.

solution and irradiated with UV is shown in Fig. 11; the amount of CO₂ increases linearly with reaction time. The TOC concentration of the injected sample can be measured by calculating the linearly increasing amount of CO₂ generated as an upward slope, and based on these results, the TOC concentration could be used as a real-time water quality analysis sensor [14].

A UV-based photocatalytic TOC analyzer using an inorganic binder and a glass fiber substrate is shown in Fig. 12. The entire analysis system was designed and manufactured independently.

According to the measurement method of the produced analyzer, sampled water entering the intake chamber caused a photocatalytic reaction at the UV reaction unit to generate CO₂; the generated CO₂ was measured using a sensor to analyze TOC and 5 mL of water was used for one measurement.

The CO₂ measurement method of the manufactured TOC analyzer was applied with the photocatalytic NDIR (non-dispersive infrared) method; other parameters, such as temperature and humidity could be measured in addition to the CO₂ measurement. The measured results can be checked in real time on the display device of the analyzer, and the measured data can be wirelessly transmitted to the water quality monitoring system. TOC was measured in the range of 0 to 5000 mg/L (ppm) and the measurement cycle was within 15 min.

4. CONCLUSIONS

This study designed and manufactured a TOC analysis system using a photocatalytic reaction and proposed a method to coat TiO₂ photocatalyst materials on a glass fiber substrate with an inorganic binder to improve their photoreaction properties. The photocatalytic reaction efficiency was validated based on the change in absorbance reduction owing to MR decomposition.

An analysis method using photocatalytic reactions has been proposed to resolve the problem of errors in organic carbon measurements by removing CO₂-generating elements using inorganic binders that do not contain organic carbon components. Additionally, by comparing the photoreaction properties according to TiO₂ changes of up to 2-12 wt% using a glass-fiber substrate with excellent coating properties, we observed that peeling did not occur at 6 wt%, exhibiting the highest efficiency.

The first self-produced photocatalytic TOC analyzer in this study had a simpler structure and shorter measurement time than the conventional TOC analysis method, enabling efficient analysis. This is expected to be effectively applied to real-time water quality monitoring systems in the future with low energy consumption and simple processes.

ACKNOWLEDGMENT

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