Sunlight-driven photocatalysis of dissolved organic matter: Tracking by excitation emission matrix-parallel factor analysis and optimization using response surface methodology

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ABSTRACT

This study investigates the photocatalysis of dissolved organic matter (DOM) under ZnO-assisted artificial sunlight irradiation. Response surface methodology (RSM) based on central composite design (CCD) was utilized for design of experiments with ZnO dosage and pH. Fluorescence excitation-emission matrices coupled with parallel factor analysis (EEM-PARAFAC), dissolved organic carbon (DOC), and UV/Vis spectroscopy were used to track the DOM degradation during photocatalysis. EEM-PARAFAC analysis decomposed fluorescent DOM into two components (C1 and C2), identified as terrestrial humic-like organic matters. A pseudo-first-order DOM removal decreased with increased ZnO dosage, and were highest at pH 7 and lowest at pH 4. Response surface models of DOC, UV₂₅₄, C1 and C2 removals demonstrated statistically significant and well matched with a second-order polynomial equation based on analysis of variance (ANOVA). First-order terms were the highest contributor, in which ZnO dosage had the highest level of significance, to the DOM removal. The optimal conditions for the photocatalysis of DOM were found to be ZnO 0.3 g/L and pH 10, showing that the removals of DOC, UV₂₅₄, C1 and C2 were 57.9%, 94.5%, 100%, and 98.0%, respectively. In addition, ZnO showed a good stability and better photodegradation efficiency than TiO₂ in the DOM removal.

Keywords: Artificial Sunlight Irradiation, Central Composite Design (CCD), Dissolved Organic Matter (DOM), Parallel Factor Analysis (PARAFAC), Zinc Oxide (ZnO)

1. Introduction

Dissolved organic matter (DOM), found in every aquatic system, is a complex mixture of organic substances containing humic acids (HAs), fulvic acids (FA), aliphatic compounds, carbohydrates, and proteins [1–5]. Despite important roles of DOM in water bodies, an increase of DOM in surface water and wastewater has been a concern due to the potential negative impacts on the environment and human health.

DOM may have negative impacts on the water quality and overall efficiencies of treatment processes, such as increased coagulant and disinfectant demand, causing membrane fouling, causing yellow/brown color to water and cause taste and odor problems, promoted biological growth in the distribution system, increased disinfection by-products (DBPs) formation, and so on [1–3]. Especially, the primary concern of DOM present in water sources is related to the harmful DBPs generated from the disinfection process during

drinking water treatment. The DBPs-like trihalomethanes (THMs) and haloacetic acids (HAAs) are potential carcinogens, mutagenic, teratogenicity to humans [3]. Thus, it is an emerging issue in environmental science and engineering to achieve an effective removal of DOM from drinking water and wastewater sources.

In recent years, various advanced oxidation processes (AOPs) have been proposed for the removal of DOM [6–8] and organic pollutants [9–11]. Common approaches include UV-based irradiation, ozonation, heterogeneous photocatalysis, Fenton and photo/electro-Fenton processes, electrochemical oxidation, and ultrasound irradiation. Among the AOPs, heterogeneous photocatalysis has been demonstrated to be highly efficient, low-cost, environment-friendly, and sustainable technology for the DOM degradation and reducing the DBPs formation [12–19]. The mechanism of heterogeneous photocatalysis is based on the in-situ generation of highly reactive oxygen species (ROS) (e.g., $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$) which degrade organic pollutants into CO_2 , H_2O and other inorganic substance by irradiat-

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ing semiconductor catalysts (e.g., TiO_2 , ZnO , WO_3 , Fe_2O_3 , CdO , CdS , SnO_2 , etc.) with a light source (e.g., ultraviolet (UV), visible, or solar light) [20–23]. Typically, the electron-hole pairs ($e_{\text{CB}}^-/h_{\text{VB}}^+$) are generated by the light absorption of semiconductor photocatalyst [21–23]. Subsequently, the VB hole (h_{VB}^+) reacts with H_2O and OH^- to generating hydroxyl radicals ($\cdot\text{OH}$), while the CB electrons (e_{CB}^-) reacts with O_2 to generating superoxide radicals ($\text{O}_2^{\cdot-}$) [23–26]. These ROSs have strong oxidizing power to degrade many organic pollutants [22, 26]. In this approach, there are three pathways for DOM degradation, namely, oxidation by hydroxyl radicals, reduction by superoxide radicals, and adsorption by catalyst [6–8]. The efficiency of the photocatalytic processes is highly dependent on the light source and semiconductor catalysts. According to recent researches [13–17, 27–29], the majority of DOM photodegradation methods use UV light coupled with different catalysts (e.g., TiO_2 , ZnO). However, the amount of UV radiation in sunlight is limited (only 5–7%), greatly restricting practical application of the UV photocatalytic oxidation technology. Sunlight, a renewable, abundant, non-polluting, and cheap energy source [21, 26], can be used as a low-cost and sustainable replacement for UV light in the photocatalysis. Additionally, sunlight irradiation has been noted to change the characteristics on DOM [30, 31]. Thus, it is of great interest to use the solar/visible light as a light source in the photocatalytic degradation of DOM.

Though a few studies have focused on the degradation of DOM via solar photocatalysis using TiO_2 and modified- TiO_2 [18, 19], little research on visible/solar photocatalysis assisted by ZnO has been reported to date in our knowledge. ZnO , with its low-cost, non-toxicity, strong oxidation ability, and broad absorption range in the solar spectrum, can be a more efficient catalyst candidate than TiO_2 in the photocatalysis [22, 26]. Therefore, this study proposes a visible/solar photocatalytic process using ZnO for the degradation of DOM.

Dissolved organic carbon (DOC), ultraviolet/visible (UV/Vis) and fluorescence spectroscopy are commonly used analytical methods in DOM analyses. DOC provides information on the quantity of DOM in terms of organic carbon while UV/Vis spectroscopy shows the characteristics of DOM such as the aromaticity, molecular weight, hydrophobicity and hydrophilicity [32, 33]. Fluorescence spectroscopy, a non-destructive and highly sensitive optical technique, is commonly used for rapidly assessing DOM levels in aquatic environments [34]. Fluorescence EEM-PARAFAC technique is useful in tracking various DOM substances [33, 34]. The peak locations or intensities of individual PARAFAC constituents can be used to evaluate the water quality and treatment performance [34]. Recently, the EEM-PARAFAC was applied for tracing fluorescent DOM components in UV/ TiO_2 photocatalytic processes [13–15] and provided mechanistic understanding on transformation of DOM by the processes. However, to date, only few studies used EEM-PARAFAC to assess the photocatalytic degradation mechanism of DOM under ZnO -catalyzed sunlight irradiation system [15]. Therefore, a combination of traditional assessment parameters (e.g. DOC and UV parameters) and EEM-PARAFAC analysis is employed in this study to trace and provide further insight into the solar photocatalytic degradation of DOM using ZnO .

The degradation efficiency of organic pollutants is strongly dependent on several operating parameters, including dosage, size, and structure of catalyst, pH level, irradiation time, light intensity,

temperature, and scavengers, etc. [12, 23, 35–39]. To investigate their effects on the photodegradation of DOM, response surface methodology (RSM), a widely used technique for analyzing and modeling experimental processes [29, 40, 41], was applied. We used central composite design (CCD) to generate necessary experimental runs. Therefore, the RSM-CCD was applied for assessment the effect of varying operating parameters and identifying the optimal conditions for the photocatalysis of DOM with ZnO under artificial sunlight irradiation.

In summary, this study aims at:

- 1) understanding of degradation mechanism by tracking water quality parameters and individual fluorescing components of DOM using EEM-PARAFAC modeling
- 2) assessing the photocatalytic degradation of DOM, including kinetics and effects of different operating conditions (ZnO dosage and pH) under ZnO -assisted simulated sunlight system finding the optimal operating conditions for the photodegradation of DOM using RSM-CCD.

2. Experimental Methods

2.1. Chemicals and Reagents

Humic acid (HA) used as a representative chemical of DOM and Zinc oxide (ZnO , MW: 81.39 g/mol, purity $\geq 99\%$) were purchased from Sigma-Aldrich (USA). Sodium hydroxide (NaOH , purity $\geq 93\%$) was obtained from Daejung Chemicals (South Korea). Sulfuric acid (H_2SO_4 , purity $\geq 96\%$) was purchased from Kanto Chemicals (Japan). By dissolving the HA in de-ionized water (DI water; $\geq 18.2 \Omega\text{-cm}^{-1}$) and filtering it through a $0.45\text{-}\mu\text{m}$ hydrophilic polytetrafluoroethylene (PTFE) membrane, a stock DOM solution with a concentration of $\text{DOC} = 10 \text{ mg/L}$. Other solutions were prepared using DI water and diluted as required.

2.2. Photocatalytic Experiments

The photocatalytic experiments were performed by a solar simulator (SLB300B, Sciencetech, Canada) equipped with a 300 W xenon short arc lamp (Ushio Inc., Japan) emitting a visible light with a wavelength range of 350–2,000 nm (Fig. S1). The radiant flux on the surface of samples was measured to $3.15 \pm 0.05 \text{ mW/cm}^2$ by a radiation intensity meter (UV-340C, Custom, Tokyo, Japan), which values were in similar levels to natural sunlight's intensities that were monitored during the experimental periods. The distance between the solution and the light source was maintained at $\sim 5 \text{ cm}$. While being gently stirred for uniform mixing, the 100-mL samples in a Pyrex reactor with water jacket were irradiated for 180 min at room temperature ($23 \pm 1^\circ\text{C}$) (Fig. S2).

Three initial pH levels of the solution (i.e., pH 4, 7, and 10) were generated by adjusting the solution with 1M H_2SO_4 and 1M NaOH . ZnO dosages were considered in 0.1, 0.2, and 0.3 g/L. At regular time intervals (0, 30, 60, 120 and 180 min), samples were taken and immediately filtered through $0.45\text{-}\mu\text{m}$ PTFE syringe filters to separate the ZnO powder from the solution.

2.3. Analytical Methods

DOC was determined using a TOC-V_{CPH} analyzer (Shimadzu, Japan).

UV/Vis spectra were recorded at a wavelength range of 200–800 nm using UV spectrophotometer (SPECORD 200 PLUS, Analytik Jena AG, Germany) with a 1-cm quartz cuvette. The single wavelength parameters such as UV₂₅₄, UV₂₈₀, UV₃₆₅, and Color₄₃₆ (UV₄₃₆), and the specific UV absorbance parameters SUVA₂₅₄, SUVA₂₈₀, SUVA₃₆₅, and SCOA₄₃₆ were determined from UV/Vis spectrum to monitor the changes of DOM during photocatalysis (Table S2).

A Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Inc, USA) was used to create the EEM fluorescence spectra by scanning the samples over an excitation range of 230–450 nm and over an emission range of 260–550 nm, both in 1-nm increments. The excitation and emission bandwidths were set as 10 nm, and the scanning speed was set as 9600 nm/min. To limit second-order Rayleigh scattering, we used a 290-nm cutoff for the samples. To minimize the inner filter effect, we diluted the samples, approximately to DOC = 1 mgC/L, before EEM measurements. The EEMs of the samples were subtracted from a water blank measured on the same day as the samples. The EEMs were further normalized by dividing them by a Raman peak area of 370–700 nm.

The morphological and crystalline characteristics of ZnO were observed by FE-SEM and XRD, as shown in Fig. S3. The FE-SEM image of ZnO shows its typical hexagonal prism morphology. XRD diffractogram of ZnO used in this study is exactly matched to the hexagonal wurtzite structure of ZnO (P6₃mc (#186), ICDD No. 96-901-1663), and the characteristic peaks are observed at 31.78°, 34.46°, 36.27°, 47.57°, 56.64°, 62.90°, 66.42°, 67.96°, 69.10° and 76.98° corresponding to (100), (002), (101), (012), (110), (013), (200), (112), (201) and (202) planes, respectively. The cell parameters of ZnO were determined to be $a = b = 3.2512 \text{ \AA}$, $c = 5.2051 \text{ \AA}$, $c/a = 1.60$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, and $\gamma = 120.00^\circ$, which are in good agreement with the standard values [P6₃mc (#186) with $a = b = 3.2490 \text{ \AA}$, $c = 5.2070 \text{ \AA}$, $c/a = 1.60$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, and $\gamma = 120.00^\circ$]. The crystallite size of ZnO was determined by the Scherer's formula [42] using (101) peaks in the XRD patterns. The average crystallite size calculated for ZnO was 71.36 nm.

2.4. PARAFAC Modeling

PARAFAC was used to extract the components from the dataset of EEMs. Under PARAFAC analysis, the EEM dataset is decomposed into a set of trilinear terms (F) and a residual array. The underlying EEM spectra are estimated by minimizing the sum of the squared residuals of the trilinear model as follows [27, 34]:

$$x_{ijk} = \sum_{f=1}^F a_{if} b_{jf} c_{kf} + \varepsilon_{ijk}, \quad i = 1, \dots, I; j = 1, \dots, J; k = 1, \dots, K \quad (1)$$

where x_{ijk} is the fluorescence intensity for the i_{th} sample at emission wavelength j and excitation wavelength k , a_{if} is directly proportional

to the concentration of the f_{th} fluorophore in the i_{th} sample (defined as scores), and b_{jf} and c_{kf} are the estimates of the emission and excitation spectra, respectively, for the f_{th} fluorophore. F represents the number of components in the model, and ε_{ijk} is the residual variability not accounted for by the model.

PARAFAC modeling was performed using MATLAB 7.0 (Mathworks, MA, USA) with the DOMFluor Toolbox (<http://www.models.life.ku.dk>). The maximum fluorescence intensity ($F_{\max}$) values of the individual components were used to represent their relative concentrations. The degradation efficiency of DOM in terms of individual components is calculated using $F_{\max}$ value. The determination and validation of components in the model were performed using split-half validation, explained variation ($> 99.9\%$), core consistency diagnostic ($> 85\%$), Tucker's congruence coefficient, and the spectral analysis of the excitation and emission loadings. The EEM data for the PARAFAC model were obtained based on 125 EEM data. Details of the PARAFAC can be found in other studies [13–15, 34].

2.5. Design of Experiment

This subsection describes the design process of experiments to investigate the degradation efficiency of DOM under solar photocatalysis. First, two main experimental factors, denoted as A for ZnO dosage (g/L) and B for pH, were selected as the independent variables. The range and levels of each independent variable are given in Table 1. The degradation efficiency of DOM in terms of DOC, UV₂₅₄, and PARAFAC components was used as response functions (Y). Second, using statistical software (Minitab Ver.18., State College, PA), a two-factor-three-level CCD with 13 experimental runs was designed. These experimental runs included a complete factorial design with (2^n) experiments, 4-star points, and 5 central points. Third, after we obtained the results, the experimental data were fitted to the second-order (quadratic) polynomial models, which had a common expression as follows [21, 29, 41]:

$$Y = b_0 + b_1 A + b_2 B + b_{12} AB + b_{11} A^2 + b_{22} B^2 \quad (2)$$

where Y is the response function, A and B are independent parameters, b_0 is the model constant, b_1 and b_2 are the linear coefficients, b_{12} is the interaction coefficients, and b_{11} and b_{22} are the quadratic coefficients.

An analysis of variance (ANOVA) was employed to test and produce response surface graphs from the experimental data. The quality and goodness-of-fit of the models were evaluated using the F -values, p -values, coefficients of determination (R^2), adjusted R^2 , and predicted R^2 . The quantitative effects of the independent variables were determined based on the ANOVA results (F -values and p -values). Percentage contributions (PCs) for each individual

Table 1. Experimental Ranges and Levels of the Independent Operating Variables for RSM-CCD Experimental Design

Experimental parameters	Symbol Coded	Levels			Star point $\alpha = 1.414$	
		-1	0	1	+ α	- α
ZnO dosage (g/L)	A	0.1	0.2	0.3	0.34	0.06
pH	B	4	7	10	11.24	2.76

variable were calculated as [21, 41]:

$$TPC_i = \frac{\sum_{i=1}^n SS_i}{\sum_{i=1}^n SS_i + SS_{ij} + SS_{ii}} \times 100 \quad (3)$$

$$TPC_{ij} = \frac{\sum_{i=1}^n \sum_{j=1}^n SS_{ij}}{\sum_{i=1}^n \sum_{j=1}^n SS_i + SS_{ii} + SS_{ij}} \times 100 \quad (4)$$

$$TPC_{ii} = \frac{\sum_{i=1}^n SS_{ii}}{\sum_{i=1}^n \sum_{j=1}^n SS_i + SS_{ii} + SS_{ij}} \times 100 \quad (5)$$

where TPC_i , TPC_{ij} , and TPC_{ii} are the total percentage contribution of the first-order, interaction, and quadratic terms, respectively, and SS_i , SS_{ij} , and SS_{ii} are the computed sum of squares for the first-order, interaction, and quadratic terms, respectively. Finally, the optimal conditions to maximize the DOM degradation were determined from the multiple responses fitted RSMs.

3. Results and Discussion

3.1. Characterization of DOM

The UV/Vis spectra of the DOM are depicted in Fig. S4 (a). There was a decrease in the absorbance as the wavelength increased. The spectra showed a strong absorbance in the UV/Vis range (200–800 nm), particularly in the UV region with no extrema, indicating that the DOM contained a relatively high amount of aromatic or polyphenolic organic compounds [8, 16]. Furthermore, $SUVA_{254}$ values were higher than 4 ($SUVA_{254} = 4.52 \pm 0.13$ (L/mg·m)), revealing that the DOM mainly contained hydrophobic and aromatic compounds [16–18]. These observations demonstrated that the DOM was primarily composed of hydrophobic compounds with high molecular weights (HMWs).

The EEM fluorescence spectroscopy was used to explore the position of fluorescence peaks to identify the source and composition of DOM. The EEM of the DOM (Fig. S4 (b)) showed that there were broad and strong peaks at emission wavelengths above ~350 nm, commonly referred to as humic-like peak [16–18, 34]. The EEM-PARAFAC analysis successfully decomposed fluorescent DOM into two components (C1 and C2), which were identified as terrestrial humic-like organic matters (Fig.S5 and Table S3). Based on the F_{max} values of PARAFAC components, C1 (58%) was more dominant than C2 (42%). As shown in Fig.S5, C1 had a peak at an Ex/Em of 261 nm/≥ 500 nm, exhibiting a broad excitation spectrum and gradual emission above 350 nm. C1 represented a combination of peak A and peak C, implying that C1 is expected to absorb light in the UVC and UVA (wavelengths greater than

320 nm) regions [17, 27, 34]. Meanwhile, C2 had a peak at an Ex/Em of < 230 nm/438 nm, with a shoulder peak at an excitation range of 300–350 nm. C2 appeared to be a peak A, implying that C2 was easily photodegraded by UVC light, as the peak excitation wavelength for this component occurred in this region of light [17, 34]. The C2 peak, compared to that of C1, was likely to be blue-shifted in both excitation and emission spectra, which would indicate that C1 had a higher molecular weight and was more hydrophobic than C2.

Additionally, the chemical characteristics of the DOM (i.e., Sigma-Aldrich HAs) have been reported in the literatures [4, 5, 8]. The elemental composition of HAs are approximately 55.6–68.98% C, 5.26–5.5% H, 0.74–4.5% N, 1.2–4.24% S, and 34.4–43.45% O. The HAs are mainly composed of phenolic, carboxylic acid, enolic, quinone, and other functional groups. The carboxylic (4.38 ± 0.03 meq·g⁻¹C) and phenolic (2.71 ± 0.34 meq·g⁻¹C) groups are the main functional groups, while the quinones are responsible for the formation of reactive oxygen species in HAs.

3.2. Photocatalytic Degradation of DOM

3.2.1. UV/Vis spectroscopic analysis

Fig. S6 (a) illustrates the UV/Vis spectrum for the DOM during the photocatalysis process with 0.2 g/L of ZnO dosage at pH 7. The absorbance decreased as the reaction time increased; moreover, there was a rapid reduction in the absorbance for the photocatalysis with ZnO in suspension. The UV/Vis absorption remained constant after 180 min of irradiation, indicating that complete mineralization could not be achieved. The UV parameters were determined and given in Table 2.

There was a rapid reduction in all single wavelength absorbance in the order of $Color_{436} > UV_{365} > UV_{280} > UV_{254}$, as expressed in Fig. S6 (b). The UV_{254} values showed that the DOM chromophores, mostly consisting of large aromatic rings, might have been rapidly decomposed into smaller non-aromatic structures [13–17]. As shown in Table 2, both UV absorbance ratios of treated DOM continuously increased during the photocatalysis process. The A_{250}/A_{365} ratio implied a decrease in the aromaticity and molecular weight, while the A_{254}/A_{436} ratio implied a high removal rate of color-forming moieties [16, 17]. Additionally, a reduction in the molecular weight was also observed based on the increase of slope ratio (S_R) during the process [16, 17].

Fig. S6 (c) shows the $SUVA$ values of DOM during the photocatalysis process. We observed a considerable decrease in all $SUVA$ values, implying a reduction in aromatic halogen attack sites, a decrease in the molecular size, and an elimination of quinones [14–17]. Specifically, there was a substantial reduction in $SUVA_{254}$

Table 2. UV/Vis Parameters of DOM During Solar Photocatalytic Degradation Process with 0.2 g/L ZnO Dosage at pH 7

Time (min)	UV ₂₅₄	UV ₂₈₀	UV ₃₆₅	Color ₄₃₆	SUVA ₂₅₄	SUVA ₂₈₀	SUVA ₃₆₅	SUVA ₄₃₆	A ₂₅₀ /A ₃₆₅	A ₂₅₄ /A ₄₃₆	S _R
0	0.5520	0.4525	0.1721	0.0781	4.63	3.80	1.44	0.66	3.27	7.07	0.86
30	0.3814	0.2933	0.1102	0.0484	3.45	2.65	1.00	0.44	3.55	7.88	1.07
60	0.2462	0.1783	0.0648	0.0258	2.44	1.76	0.64	0.26	3.91	9.54	1.27
120	0.0537	0.0231	0.0052	0.0011	0.62	0.27	0.06	0.01	10.85	48.82	3.26
180	0.0246	0.0079	0.0012	0.0001	0.36	0.12	0.02	0.00	22.58	246.00	10.00
Removal (%)	95.54	98.25	99.30	99.87	92.18	96.93	98.78	99.78			

(over 90% of initial values) which could be explained by the preferential removal of aromatic chromophores over aliphatic moieties, followed by the transition of the DOM to non- or less-UV-absorbing substances. The reduction in $SUVA_{254}$ also implied that HMW DOM was rapidly decomposed into organic compounds of lower molecular weight (LMW) [14–17]. This observation was supported by the lower DOC removal values compared to UV_{254} values at the same reaction time. Furthermore, a strong linear correlation was observed between $SUVA_{254}$ and DOC ($R^2 = 0.98$), indicating that the decreases in $SUVA_{254}$ could be used as indicators of DOC removal efficiency during the photocatalytic degradation of DOM.

3.2.2. Fluorescence EEM

Fig. S7 illustrates the EEM contour plots of DOM with 0.2 g/L of ZnO dosage at pH 7 during the photocatalysis process. The photocatalysis led to a continuous reduction in the fluorescence intensity and changes in the shape of the EEM plots. After 180-min irradiation, the fluorescence intensity for the measured wavelengths was almost zero, with no clear peak. The decreased fluorescence intensity in the EEM plots implied that the preferential photocatalytic degradation of DOM caused the breakdown of HMW fractions and the formation of LMW fractions [16–18]. This observation was similar to the previously reported photodegradation of DOM [16–19].

3.2.3. Photocatalysis of DOM: kinetics and degradation efficiency

The photocatalytic degradation efficiency of DOM was analyzed based on the removals of DOC, UV_{254} , and F_{max} values of the two PARAFAC components. Upon photocatalysis, all degradation rates were found to be a pseudo-first-order kinetic model ($R^2 = 0.90$ – 1.00), which had also been reported in other studies to describe the photodegradation of DOM [13–17, 27].

After 180-min treatment, the DOC removals varied from 19.18% to 62.61% while UV_{254} removals were in the range of 55.20% to 96.18%. Overall, greater removal efficiencies of UV_{254} than DOC were found, and the reasons can be as the followings. First, the terminal functional groups (e.g., hydroxyl and carboxyl) of the aromatic compounds reinforced the adsorption affinity of the surface of the catalyst particles [13–16]. Second, some of the DOM chromophores were partially transformed into non-UV-absorbing compounds (e.g., LMW organic acids, alcohols, etc.) in the photochemical reaction [14–17], thus those non-UV-absorbing moieties are responsible for DOC unremoved.

The photodegradation behaviors of the two PARAFAC components were analyzed using F_{max} values. The degradation kinetics based on F_{max} were fitted with a pseudo-first order kinetic model ($R^2 = 0.94$ – 0.99). After 180-min irradiation, the C1 removals varied from 67.61% to 100%, and the highest removal was observed after 120-min irradiation at a ZnO dosage of 0.3 g/L and pH 7. The C2 removals were found to be in 12.38% to 99.45%.

F_{max} removal and degradation rate of C1 were higher than those of C2, which could be explained by the excitation and emission wavelengths of each component. Both PARAFAC components were identified as terrestrial humic-like organic matters; however, C1 represented a combination of peak A and peak C, showing longer excitation and emission wavelengths than C2. With peaks at longer wavelengths, C1 could be associated with the structural con-

densation and polymerization of DOM [18, 34]. Indeed, previous researches reported more pronounced fluorescence at longer emission wavelengths in the EEMs of larger size and/or more hydrophobic DOM fractions [13–19]. Therefore, the results indicated the preferential adsorption of more hydrophobic and larger DOM molecules onto minerals and/or nanoparticles, which has also been reported in previous studies [13–15]. In addition, C2 would be less excited by visible light than C1 due to shorter excitation wavelengths of C2 compared to that of C1.

Figure S8 shows the comparison of DOM removals and degradation rates calculated using DOC, UV_{254} , and F_{max} values of the PARAFAC components at 0.2 g/L ZnO and pH 7. The removals calculated using the F_{max} of the two components (100% for C1 and 98.42% for C2) were consistently higher than those calculated using UV_{254} (95.67%) and DOC (43.52%). The degradation rate of C1 was 11.31-fold and 8.46-fold higher than those calculated using DOC and UV_{254} , while the degradation rate of C2 was 1.93-fold and 1.56-fold higher than those calculated using DOC and UV_{254} , respectively. These results were supported by previous reports [13–15] which demonstrated that fluorescent components were much more sensitive to UV light than other non-fluorescent structures. The higher degradation of fluorescence components compared to UV-absorbing moieties (i.e., UV_{254}) could also be explained by the fluorescence arising from the $\pi^* - \pi$ transitions in DOM molecules and its quick elimination under UV irradiation [13–15].

3.2.4. Effects of operational parameters

Effect of ZnO dosage: The effects of ZnO dosages (0.1, 0.2, and 0.3 g/L) at pH 7 on the degradation of DOM are depicted in Fig. 1 (a) and (b). The DOM removal and apparent degradation rate (k_{app}) increased considerably as the ZnO dosages increased from 0.1 g/L to 0.3 g/L. Specifically, the DOM removal and k_{app} increased by $\Delta 29.61\%$ and 2.52-fold for DOC, by $\Delta 2.89\%$ and 1.24-fold for UV_{254} , by $\Delta 4.46\%$ and 173-fold for C1, and by $\Delta 0.75\%$ and 1.35-fold for C2. It could be because more active sites become available with increasing of ZnO dosage, and thus facilitating the $\cdot OH$ generation.

Effect of pH: The effects of pH (4, 7, and 10) on the degradation of DOM at 0.2 g/L of ZnO are expressed in Fig. 1 (c) and (d). The DOM removal and k_{app} were in the order of pH 7 > pH 10 > pH 4. This observation could be explained due to the ionization of DOM and the zeta potential (ZP) of ZnO at different pH levels. In particular, in HA molecules, the acidic functional groups (e.g., $-COOH$ and $-OH_{phenolic}$) would be more ionized as the aqueous pH increased because pK_{a-COOH} and pK_{a-OH} have been reported to be 4.7 and 12.5, respectively [4, 5]:

HAs were negatively charged over a wide pH range (2.0–10.7). The ZP of ZnO was positive at a pH range of 6.7–9.3 and negative otherwise (the pH_{ZPC} for ZnO is 9.0 ± 0.3), according to the following reactions [22, 26, 43]:

Fig. 1. Effects of ZnO dosage and pH on the photocatalytic degradation of DOM: Effect of ZnO dosage at pH 7 - (a) DOM removal and (b) Degradation rate; Effect of pH at ZnO 0.2 g/L - (c) DOM removal and (d) Degradation rate.

Therefore, at pH 7, ZnO and HA had opposing charges, and the electrostatic attraction between HA molecules and the ZnO surface would lead to a more rapid exposure of the HAs to reactive oxygen species (especially $\cdot\text{OH}$), resulting in the maximum DOM removal and k_{app} . On the other hand, at pH 4 and 10, both the HAs and ZnO were negatively charged, thus there would be a strong repulsive force between the HA molecules and the ZnO surface. Consequently, there would be limited chances for the HA molecules to contact with reactive oxygen species near the ZnO surface, decreasing removal and k_{app} .

In addition, the DOM removal and k_{app} were always higher at pH 10 than those at pH 4. This observation could be explained by two reasons. First, it has been reported that ZnO can be photo-oxidized at pH 4 (acidic conditions), as given in Eq. (9) [22, 44]. Meanwhile, ZnO can be dissolution to $\text{Zn}(\text{OH})_4^{2-}$ at pH 10 (alkaline conditions), as given in Eq. (10) [22, 44]. The dissolution of ZnO into Zn^{2+} and $\text{Zn}(\text{OH})_4^{2-}$ would slow the mass transport rate and consequently reduce the active surface area of ZnO. Second, acidic conditions (i.e., less OH^-) were less favorable for the generation of $\cdot\text{OH}$ by the hole oxidation of OH^- , lowering the efficiency of the attack of hydroxyl radicals on DOM and the photocatalytic oxidation rate [21, 27].

3.3. Optimization of DOM Degradation Using RSM Based on CCD

In the present study, a two-factor-three-level CCD consisting of 13 experimental runs was employed to optimize the photocatalytic degradation efficiency of DOM. Four predicted responses – Y1 (DOC removal), Y2 (UV₂₅₄ removal), Y3 (C1 removal), and Y4 (C2 removal) – were expressed as second-order polynomial equations of two independent variables, A (ZnO dosage) and B (pH), which are provided in Eqs.(11)-(14). The predicted and experimental values of the four responses with two independent variables are summarized in Table 3.

$$\text{Y1 (DOC removal)} = -23.85 + 156.1 A + 8.98 B - 135.7 A^2 - 0.5826 B^2 + 5.18AB \quad (11)$$

$$\text{Y2 (UV}_{254} \text{ removal)} = -42.19 + 519.8 A + 18.73 B - 700.0 A^2 - 0.946 B^2 - 16.32 AB \quad (12)$$

$$\text{Y3 (C1 removal)} = -9.90 + 337.3 A + 16.85 B - 425 A^2 - 0.875 B^2 - 11.23 AB \quad (13)$$

$$\text{Y4 (C2 removal)} = -207.6 + 918 A + 47.85 B - 954 A^2 - 2.258 B^2 - 45.50 AB \quad (14)$$

Table 3. Two-Factors-Three-Level Central Composite Design for The Photocatalytic Degradation of DOM

Exp.	ZnO dosage (g/L)	pH	Predicted response models (Y) (%)							
			Y1 (DOC removal)		Y2 (UV ₂₅₄ removal)		Y3 (C1 removal)		Y4 (C2 removal)	
			Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
	A	B								
1	0.10	10.00	28.50	27.14	76.19	79.16	85.22	89.46	74.44	81.74
2	0.20	7.00	43.04	43.52	95.54	95.67	100.00	100.00	98.97	98.37
3	0.30	10.00	56.11	57.86	95.79	94.49	100.00	100.46	99.36	97.99
4	0.20	7.00	43.85	43.52	95.87	95.67	100.00	100.00	97.97	98.37
5	0.20	7.00	43.81	43.52	95.84	95.67	100.00	100.00	97.93	98.37
6	0.20	11.24	41.17	40.93	89.34	88.07	98.17	94.28	94.01	87.93
7	0.20	7.00	43.09	43.52	95.34	95.67	100.00	100.00	98.77	98.37
8	0.34	7.00	62.61	60.33	96.18	99.44	100.00	104.04	99.45	110.11
9	0.20	2.76	25.07	25.13	67.48	69.22	67.61	74.23	12.38	27.51
10	0.30	4.00	42.04	43.58	94.39	90.95	100.00	93.02	98.96	82.60
11	0.06	7.00	19.18	21.28	66.70	63.91	80.26	78.96	50.08	48.48
12	0.20	7.00	43.78	43.52	95.77	95.67	100.00	100.00	98.22	98.37
13	0.10	4.00	20.64	19.08	55.20	56.04	71.75	68.55	19.39	11.70

Table 4. ANOVA Results of The Response Surface Quadratic Models for The DOM Removal (%) in Terms of DOC, UV₂₅₄, C1, and C2 Removal (%)

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Y1, DOC removal					
Model	1978.49	5	395.7	137.830	0.000
Residual	20.1	7	2.87		
Lack of fit	19.41	3	6.47	38.02	0.002
Pure error	0.68	4	0.17		
Total	1998.59	12			
$R^2 = 0.9899$, Adjusted $R^2 = 0.9828$, Predicted $R^2 = 0.9304$					
Y2, UV₂₅₄ removal					
Model	2462.9	5	492.58	74.61	0.000
Residual	46.21	7	6.6		
Lack of fit	46.01	3	15.34	307.86	0.000
Pure error	0.2	4	0.05		
Total	2509.11	12			
$R^2 = 0.9816$, Adjusted $R^2 = 0.9684$, Predicted $R^2 = 0.8695$					
Y3, C1 removal					
Model	1580.92	5	316.18	14.36	0.001
Residual	154.14	7	22.02		
Lack of fit	154.14	3	51.38	14.36	0.001
Pure error	0	4	0.00		
Total	1735.05	12			
$R^2 = 0.9112$, Adjusted $R^2 = 0.8477$, Predicted $R^2 = 0.3683$					
Y4, C2 removal					
Model	11404.10	5	2280.82	20.86	0.000
Residual	765.30	7	109.33		
Lack of fit	764.40	3	254.80	1125.78	0.000
Pure error	0.90	4	0.23		
Total	12169.40	12			
$R^2 = 0.9371$, Adjusted $R^2 = 0.8922$, Predicted $R^2 = 0.5532$					

Two statistical measures (F-value and p -value) were used to evaluate the quality of the models. As shown in Table 4, the F-values of the four models (Y1 = 137.83, Y2 = 74.61, Y3 = 14.36 and Y4 = 20.86) were greater than the 0.05 F critical value ($F_{0.05,5,7} = 3.97$) [45], demonstrating the high statistical significance of the

four regression models. Low p -values were also observed (≤ 0.001 for all models), further indicating the significance of these models. Thus, the four models explained the measured data well, with the corresponding coefficients demonstrating high significance.

R^2 , adjusted R^2 and predicted R^2 were used to measure the

degree of fit for the models. In this study, R^2 values were $Y1 = 0.9899$, $Y2 = 0.9816$, $Y3 = 0.9112$ and $Y4 = 0.9371$, showing that the second-order polynomial models were reliably fitted to the experimental results. The R^2 values of the four models were in the order of $Y1 > Y2 > Y4 > Y3$. The highest R^2 obtained for the model of DOC removal (Y1) indicated that 98.99% of the total variation could be represented by the established model, expressing a satisfactory quadratic fit. Adjusted R^2 values were $Y1 = 0.9828$, $Y2 = 0.9684$, $Y3 = 0.8477$ and $Y4 = 0.8922$, which were close to the R^2 value for each model, and this indicates a good correlation among the factors of the process using the CCD design. Predicted R^2 values were $Y1 = 0.9304$, $Y2 = 0.8695$, $Y3 = 0.3683$ and $Y4 = 0.5532$, showing that the Y1 model was the best fitted among the models. The low values in predicted R^2 for Y3 and Y4 (i.e., the removals of C1 and C2) are thought because there were remaining fractions of organic substances that do not respond to the light, but account for contents of organics as the more fluorescing DOMs are degraded to non-light absorbing organics.

In addition to the results of ANOVA and R^2 values, diagnostic plots also confirmed a good agreement between the model prediction and the experimental data (Fig. S9). Therefore, the four regression models were statistically significant and could be used to predict the photodegradation of DOM.

The quantitative effects of each independent variable on DOM are summarized in Table 5. In the four models, all first-order terms

(A and B) were statistically significant (p -values < 0.05). More specifically, in the Y1 model, the two first-order terms and one quadratic term (B^2) were statistically significant (p -values < 0.05). In the Y3 model, the two first-order terms and two quadratic terms (A^2 and B^2) were statistically significant (p -values < 0.05). In the Y2 and the Y4 models, all terms (A, B, A^2 , B^2 , and AB) were statistically significant (p -values < 0.05). Figure S10 illustrates the PCs of the variables in the four models. We observed the highest contribution (i.e., TPC) by the first-order terms (89.25% for Y1, 63.22% for Y2, 63.12% for Y3, and 63.65% for Y4). The quadratic terms were the second highest contributor (10.26% for Y1, 32.03% for Y2, 34.10% for Y3, and 29.97% for Y4). Moreover, ZnO dosage (A) showed the highest level of significance, with a contribution of 76.69% for Y1, 49.34 for Y2, 38.52 for Y3, and 32.46 for Y4.

Three-dimensional (3D) surfaces and two-dimensional (2D) contours of DOM degradation efficiency (%) as predicted by four models (Y1, Y2, Y3 and Y4) are given in Fig. 2. Both ZnO dosage and pH had positive effects on DOM removal. The direct relationship between these two factors and the DOM degradation efficiency was also illustrated by the positive coefficients of A and B in all four models as expressed in Eqs. (10)-(13). Specifically, when the ZnO dosage increased from 0.1 g/L to 0.3 g/L, DOM removal also increased by 24.50% for DOC, 34.91% for UV_{254} , 24.47% for C1, and 70.90% for C2 at pH 4 compared to increases of 30.72% for DOC, 15.33% for UV_{254} , 11.00% for C1, and 16.25% for C2 at pH 10. The effect of ZnO dosage on the DOM degradation

Table 5. ANOVA Results for The Four Quadratic Models for DOM Photocatalytic Degradation

Quadratic model	Factor	Coefficient	F-Value	p-Value	Sum of squares	Percentage contribution (%)	Remark
Y1 (DOC removal)	Intercept	-23.85					
	A	156.10	531.11	0.000	1524.7	76.69	Significant
	B	8.98	86.97	0.000	249.7	12.56	Significant
	A^2	-135.70	4.46	0.072	12.8	0.64	No
	B^2	-0.58	66.61	0.000	191.2	9.62	Significant
	AB	5.18	3.36	0.109	9.7	0.49	No
Y2 (UV_{254} removal)	Intercept	-42.19					
	A	519.80	191.18	0.000	1262.2	49.34	Significant
	B	18.73	53.8	0.000	355.2	13.88	Significant
	A^2	-700.00	51.62	0.000	340.8	13.32	Significant
	B^2	-0.95	76.38	0.000	504.3	19.71	Significant
	AB	-16.32	14.52	0.007	95.9	3.75	Significant
Y3 (C1 removal)	Intercept	-9.90					
	A	337.30	28.57	0.001	629.1	38.52	Significant
	B	16.85	18.25	0.004	401.8	24.60	Significant
	A^2	-425.00	5.71	0.048	125.7	7.70	Significant
	B^2	-0.88	19.58	0.003	431.2	26.40	Significant
	AB	-11.23	2.06	0.194	45.4	2.78	No
Y4 (C2 removal)	Intercept	-207.60					
	A	918.00	34.74	0.001	3797.9	32.46	Significant
	B	47.85	33.39	0.001	3650.0	31.19	Significant
	A^2	-954.00	5.79	0.047	632.9	5.41	Significant
	B^2	-2.26	26.29	0.001	2873.7	24.56	Significant
	AB	-45.50	6.83	0.035	746.8	6.38	Significant

Fig. 2. 3D response surface graphs and 2D contour plots for DOM photocatalytic degradation: (a1) & (a2) - DOC removal, (b1) & (b2) - UV₂₅₄ removal, (c1) & (c2) - component 1 removal, and (d1) & (d2) - component 2 removal.

efficiency can be explained by an increased number of available active sites on the surface of photocatalyst, leading to an increase of $\cdot\text{OH}$ generation, and thus facilitating the photodegradation of DOM. Likewise, as pH level increased from 4 to 10, DOM removal increased by 8.07% for DOC, 23.12% for UV₂₅₄, 20.91% for C1, and 70.05% for C2 at 0.1g/L of ZnO dosage and by 14.28% for DOC, 3.54% for UV₂₅₄, 7.44% for C1, and 15.39% for C2 at 0.3g/L of ZnO dosage. Moreover, Figure S11 displayed the plot of pH effect (one of the main effects) on DOM degradation efficiency. It was observed that the DOM degradation efficiency was in the order of pH 7 (neutral) > pH 10 (alkaline) > pH 4 (acidic). As abovementioned in Section 3.1, this result was due to the ionization of DOM and the zeta potential of ZnO at different pH levels.

In order to optimize the operating parameters for the DOM degradation efficiency, which is expressed by the multiple responses of DOC, UV₂₅₄, C1 and C2, a desirable function was applied in this study. The desirable function, as defined a maximum DOM degradation efficiency, was set as maximum DOC, UV₂₅₄, C1 and C2 removals with the ZnO dosage in the range of 0.1 g/L to 0.3

g/L and within the pH of 4 to 10. The optimal condition for the maximum DOM degradation was found to be at ZnO of 0.3 g/L and pH 10, in which the 180-min removals of DOC, UV₂₅₄, C1 and C2 were predicted to be 57.9%, 94.5%, 100.0%, and 98.0%, respectively. The predicted values by the statistical model were validated by the experimental data, where the results were very close to the predicted values, showing the removals of DOC, UV₂₅₄, C1 and C2 to 56.11%, 95.79%, 100.0%, and 99.4%, respectively.

3.4. Mechanisms of Photocatalytic Degradation

The proposed reaction mechanisms for the visible/solar photocatalytic degradation of DOM using ZnO are expressed in the set of equations (Eqs. (15)-(32)) (Fig. S12). Basically, when ZnO is irradiated with simulated sunlight containing photonic energy ($h\nu$), $h\nu_{\text{VB}}$ and conduction band (CB) electron (e_{CB}^-) pairs are produced, as given in Eq. (15) [21–23]. The $h\nu_{\text{VB}}$ reacts with H_2O and hydroxide ions (OH^-) to form $\cdot\text{OH}$ (Eqs. (17)-(18)) [22–24]. The reduction of dissolved or adsorbed O_2 to $\text{O}_2^{\cdot-}$ by CB electrons is depicted in Eq. (19) [24–26]. The $\text{O}_2^{\cdot-}$ was converted to H_2O_2 via disproportionation with protons (Eq. (20)) or formed $\text{HO}_2^{\cdot}$ via protonation, which had a short lifetime due to the rapid reaction with $\text{O}_2^{\cdot-}$ or $\text{HO}_2^{\cdot}$ to form the more stable H_2O_2 (Eq. (21)-(22)) [23–25]. The one-electron reduction of H_2O_2 produced $\cdot\text{OH}$ (Eq. (23)), while H_2O_2 could also react with $\text{O}_2^{\cdot-}$ to form $\cdot\text{OH}$ (Eqs. (24)-(25)) [21–24]. The formation of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ could attack DOM at or near the ZnO surface, then being able to oxidize and reduce the DOM molecules into CO_2 , H_2O , and degradation products (Eq. (26)) [14, 26–28]. According to previous studies [5], the reaction of $\cdot\text{OH}$ with HAS resulted in the release of LMW acids, amino acids, and ammonia. Moreover, it has been reported that the photobleaching of DOM after irradiation of simulated sunlight generated reactive species, including singlet oxygen ($^1\text{O}_2$), $\cdot\text{OH}$, triplet DOM states ($^3\text{DOM}^*$), $\text{O}_2^{\cdot-}$, and H_2O_2 , as given in Eqs. (27)-(32) [29–31]. Although these photogenerated reactive species were produced at low concentrations and had very short-lives, they had an important role in the degradation of DOM by photocatalysis process.

The photogenerated holes ($h\nu_B^+$), $\cdot\text{OH}$ and O_2^- are the main ROSs involved in the photocatalytic oxidation of organic pollutants. To assess the contributions of the main ROSs to the photocatalytic reactions under simulated sunlight irradiation, we conducted the radical- and hole-trapping experiments by introducing different scavengers including 1,4-benzoquinone (BQ, 0.01M), ethylene diamine tetraacetic acid disodium salt (EDTA-2Na, 0.01M), and tert-butyl alcohol (TBA, 0.01M) as the O_2^- , $h\nu_B^+$, and $\cdot\text{OH}$ scavengers, respectively. The radical- and hole-trapping experiments were carried out at an initial DOM concentration of 10 mgC/L, pH 7, ZnO concentration of 0.2 g/L, and scavenger concentration of 0.01 M. Figure S13 illustrates different photocatalytic degradations of DOM (using DOC and UV_{254} values) under the existence of different scavengers. Compared to the no-scavenger, the DOM removals decreased when BQ, EDTA-2Na or TBA were introduced, indicating that three ROSs contributed to the photocatalytic degradation of DOM. Specifically, the DOM removals decreased greatly when the TPA or EDTA-2Na was added, and DOC removals reduced to 7.23% and 9.82%, compared to 43.14% of no-scavenger, while the UV_{254} removals decreased to 60.07% and 68.31% from the 95.61% of no-scavenger. Meanwhile, the presence of BQ did not significantly affect the efficiency of DOM removal, meaning that the O_2^- could also contribute to the photocatalytic degradation of DOM, but not as much as $\cdot\text{OH}$ and the $h\nu_B^+$, and the contributing orders of active species would be $\cdot\text{OH} > h\nu_B^+ > \text{O}_2^-$. Based on these results, it can be concluded that the photodegradation of DOM was mainly driven by $\cdot\text{OH}$ and $h\nu_B^+$ and, and the photocatalytic degradation of DOM would be promoted by synergistic actions, i.e., more generation of $\cdot\text{OH}$ and $h\nu_B^+$ by visible light.

In order to assess the role of catalyst, light source, and combined catalyst and light efforts on the DOM degradation, a comparison of adsorption, photolysis, and photocatalysis of DOM was investigated under the experiment condition at 0.2g/L ZnO and pH 7. The total DOM removals and degradation rates calculated using DOC and UV_{254} for three processes are expressed in Fig.S14. The DOC removals were 2.94%, 10.21%, and 43.14% for photolysis, adsorption, and photocatalysis, respectively. The degradation rate for photocatalysis was higher than those for photolysis (18.56-fold) and adsorption (5.47-fold) (Fig. S14 (a)). Similarly, as shown in Fig. S14(b), UV_{254} removals were 4.11%, 19.51%, and 95.61% for photolysis, adsorption, and photocatalysis, respectively. The degradation rate for photocatalysis was greater than those for photolysis

(93.57-fold) and adsorption (16.96-fold). Therefore, the results demonstrated that adsorption by ZnO only or photolysis (sunlight only) had a minor contribution to DOM removal, whereas the photocatalysis significantly contributed to the DOM degradation.

In addition to the photocatalytic performance, the reusability of photocatalyst is also very important. To evaluate the photo-stability of the catalyst, recycled experiments for the photodegradation of DOM were performed. The experiments were implemented by recovering and reusing of ZnO in four serial cycles for DOM photo-degradation, and the results are depicted in Fig.S15(a). After four cycles, the total removals of DOM in terms of UV_{254} reduced from 95.0% to 86.2%. It might be due to the photocorrosion of ZnO under the sunlight irradiation (Eq. (33)), which is a serious drawback for ZnO-based photocatalysts [22, 44]. However, with a slight reduction in DOM degradation efficiency was observed after the four cycles, still ZnO could be an efficient photocatalyst for organic pollutants, and its reusability potential would be highly increased if the surface of the ZnO is modified. Furthermore, DOM photocatalytic efficiencies by using ZnO and two different TiO_2 catalysts (TiO_2 -AEROXIDE® P25 and TiO_2 -Sigma Aldrich) were compared, as shown in Fig. S15 (b). The DOM removals and degradation rates based on UV_{254} are comparatively presented in Fig. S15 (b). As observed, the degradation of DOM by two catalysts well fitted to a pseudo-first-order model ($R_{\text{ZnO}}^2 = 0.98$ and $R_{\text{TiO}_2}^2 = 0.95$). Both the removal and degradation rate when ZnO was used were higher compared to the results when two types of TiO_2 were used. Specifically, the DOM removal and degradation rate of ZnO catalyst is $\Delta = 6.1\%$ and 1.50-fold higher than those of TiO_2 P25 catalyst. The DOM removal and photodegradation rate of ZnO catalyst is $\Delta = 31.6\%$ and 3.01-fold higher than those of TiO_2 Sigma Aldrich catalyst. Therefore, we concluded that ZnO catalyst could be a good photocatalyst candidate for the photocatalytic degradation of DOM and other organic pollutants.

4. Conclusions

This study demonstrates that ZnO-assisted solar irradiation is one of the most promising green technologies for effective degradation of DOM in aqueous environments. DOM removal by photolysis or adsorption onto ZnO is negligible, and the photocatalysis plays an important role in the treatment. Tracking of DOM using EEM-PARAFAC during the photocatalytic processes shows that the degradation rates become different, depending on the characteristics of DOM. The organic matters with light-absorption and high molecular weights are degraded to low molecular weights, and non-light absorbing substances with organic carbon, resulting in lower removals of DOC than UV_{254} or fluorescing components. The ROS scavenging experiments providing DOM photocatalysis under sunlight irradiation, using ZnO, are mainly driven by $\cdot\text{OH}$ and $h\nu_B^+$. Comparisons between ZnO and two types of TiO_2 reveal that ZnO-assisted photocatalysis are more efficient than those with TiO_2 , demonstrating it as good photoactivity under visible light, demanding low energy. The application of RSM-CCD shows an overall good fit between the model prediction and the experimental

data, and the optimized conditions for maximum removal give insight into the practicability of the system. The sunlight-driven ZnO photodegradation can be further enhanced for better performance of the process by optimizing other parameters, and by modifying the photocatalytic systems.

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Author Contributions

T.T.N. (Ph.D. student) performed the experiments as with the data preparation for PARAFAC modeling and wrote the first draft. S.-N.N. (Research Professor) conceptualized the experimental methodology, performed the data analysis on PARAFAC modeling, acquired the funding and finalized the submitted version.

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