Behavior of matrix parameters and their correlation to micro-pollutant degradation during treatment of real wastewater by carrier-bound photocatalytic ozonation

Simon Mehling* a, *, Tobias Schnabelb and Jörg Londonga

a Department of civil engineering, Professorship of Urban water management, Bauhaus-Universität Weimar, Weimar, Germany
b MFPA Weimar – Materials research and testing institute Weimar, Weimar, Germany

*Corresponding author. E-mail: simon.theodor.mehling@uni-weimar.de

ABSTRACT

Immobilized titanium dioxide catalysts were used within a photocatalytic immersion rotary body reactor, which was connected to substream ozonation unit to remove micro-pollutants from wastewater. Within this work data on the behavior of cumulative parameters during treatment of wastewater by photocatalysis and photocatalytic ozonation is provided. The investigated parameters are spectral absorption coefficient at 254 nm (SAC254), total organic carbon (TOC) and chemical oxygen demand (COD). All experiments were carried out using secondary effluent of the same wastewater treatment plant. For the parameter SAC254, consistent concentration curves and dependencies to operational parameters of the experimental system could be measured. The measurements of the parameters TOC and COD showed greater uncertainties, although basic trends could nonetheless be observed. A good linear correlation ($R^2 < 0.85$) between the reduction of SAC254 and 8 micro-pollutants for photocatalysis and photocatalytic ozonation was found. This confirms the suitability of the SAC254 as a control parameter for a large-scale application of a photocatalytic 4th treatment stage. A linear correlation between measured TOC and COD degradation rates was possible with a coefficient of determination of 0.58–0.86. The simultaneous decrease of TOC and COD is an indicator for a mineralization of the treated wastewater matrix.

Key words: anthropogenic micro-pollutants, photocatalysis, photocatalytic ozonation, titan dioxide, UV-A light, wastewater treatment

HIGHLIGHTS

• Correlation of SAC with micropollutant degradation during photocatalytic ozonation.
• Behavior of SAC, TOC, and COD in carrier-bound photocatalytic ozonation.
• Correlation of TOC and COD in carrier-bound photocatalytic ozonation.

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (http://creativecommons.org/licenses/by/4.0/).
INTRODUCTION

One of the major upcoming challenges of municipal wastewater management is the endangerment of drinking water resources and watercourses by anthropogenic micro-pollutants (Aemig et al. 2021). Within conventional wastewater treatment plants, these compounds, such as pharmaceuticals, industrial chemicals and pesticides, are only partially degraded and/or separated (Margot et al. 2015; Kanaujiya et al. 2019). Consequently, municipal wastewater represents a major input pathway for micro-pollutants (Gallé et al. 2019). Due to this necessity, processes for advanced wastewater treatment (4th treatment stage) have been developed and already implemented on a large scale. Conventional methods include adsorptive processes using powdered or granulated activated carbon and oxidative processes using ozone (Bourgin et al. 2018; Guillossou et al. 2019; Guillossou et al. 2020; Teichgräber et al. 2021). Advanced oxidation processes (AOP), which use hydroxyl radicals for oxidation at room temperature, are currently not used on an industrial scale as a 4th treatment stage (Kanakaraju et al. 2018). The main advantage of AOPs is the higher oxidation strength of hydroxyl radicals, which in principle allows complete mineralization of treated wastewater components (Kisch 2015; Kanakaraju et al. 2018). During photocatalysis with titanium dioxide, irradiation with UV-A light leads to charge separation of the semiconductor (Pitre et al. 2017). In this process, free electrons and electron holes are formed. These electron holes can form hydroxyl radicals through a reaction with water or hydroxide ions (Gaya & Abdullah 2008). In the presence of dissolved ozone, in addition to direct oxidation of micro-pollutants by ozone, reactive superoxides can also be formed (Mehrjouei et al. 2015). Furthermore, a reaction of the acceptor ozone with free electrons occurs, reducing the recombination rate and consequently increasing the concentration of hydroxyl radicals (Mecha & Chollom 2020).

Photocatalytic processes can be further differentiated according to the type of catalyst supply. On the one hand, the catalyst can be brought into contact with the water phase in particulate form. The advantage of this process is the high available catalyst area due to the small particle diameters. The main disadvantage of this variant is the need for complex nanoparticle separation (Mecha & Chollom 2020). The alternative is a carrier-bound process, where the catalyst is fixed to a carrier material, thus preventing the catalyst from being released from the reactor. A major challenge here is the formation of porous surfaces in the coating process. In this work, the behavior of various cumulative analytical parameters during treatment of real wastewater by photocatalysis and photocatalytic ozonation using a carrier-bound reactor is investigated. Analytical measurement of individual micro-pollutants is only possible using complex offline applications (Abegglen &
One goal is to quantify a control parameter that describes the total degradation of micro-pollutants. For this purpose the standard online parameter SAC254 is used. Also, the behavior of the cumulative parameters COD and TOC is investigated. The COD describes the total of all oxidative reactions, while the decrease in organic carbon – measured as TOC – allows assumptions about mineralization reactions (Márquez et al. 2014).

By (Mecha et al. 2016), a decrease of SAC254 by about 35% was measured after 60 minutes treatment of secondary effluent by photocatalytic ozonation. Decreases in DOC of 50–75% were reported after 60 minutes of treatment. In the treatment of secondary effluent spiked with amoxicillin and diclofenac by (Moreira et al. 2015), 65% TOC was removed after 60 minutes of photocatalytic ozonation. The remaining TOC corresponded to the concentration of the transformation product oxamic acid within this experiments. By (Márquez et al. 2014), solar photocatalytic ozonation of secondary effluent achieved 50% TOC reduction after 3 hours of treatment. Photocatalytic ozonation of secondary effluent by (Aguinaco et al. 2012) achieved TOC reductions of 60–80% after 120 minutes. In (Fu et al. 2016), the degradation of n-butyl xanthate by photocatalysis and photocatalytic ozonation in ultrapure water was investigated. Here, a decrease in COD of 60% after 40 min of photocatalytic ozonation and 40% after 40 min of photocatalytic treatment was measured. By (Solís et al. 2016), for the treatment of diuron in ultrapure water, a decrease in TOC of 80% was achieved after 2 h of treatment. For ozonation, the TOC reduction was only 25%. It should be noted that the ozone dose used was 600 g/m³ after 2 hours of treatment. Within ozonation as a 4th treatment stage, ozone doses of approximately. 8 g/m³ are usually used for the same TOC. For these high ozone doses a strong influence of the indirect ozonation reaction can be assumed. (Kang et al. 2021) investigated the photocatalytic ozonation within a carrier-bound helix reactor for secondary effluent. A COD reduction from 124 to 45.8 mg/l (63%) and a TOC reduction from 79 to 32.5 mg/l (58%) were obtained after 57 minutes of treatment. The ozone dose used was about 1,500 g/m³ and the cumulative electrical power was 10.45 kW/m³. In summary, it can be concluded that by all described authors a significant reduction in one of the cumulative parameters (SAC, COD, TOC) by photocatalysis or photocatalytic ozonation could be demonstrated. However, in no case the behavior of COD and TOC was considered by measuring both parameters for multiple time points. Furthermore, in the experiments carried out by (Fu et al. 2016; Solís et al. 2016) ultrapure water was used, which means that no statement can be made on the formation of transformation products in an application as a 4th purification stage.

No literature values could be found on the influence of irradiation energy und ozone dose on these cumulative parameters within a carrier-bound photocatalytic system. Within this work, a simultaneous measurement of TOC and COD for a variety of operating parameters was used to provide an indication on the mineralization of the treated matrix by photocatalysis, ozonation and photocatalytic ozonation. A detailed investigation of the correlation of SAC and the degradation of a larger number of micro-pollutants could not be found either and thus represents a novelty of this work. The correlation of the degradation rates of micro-pollutants with the online measurable parameter SAC254 allows to develop an efficient control strategy for large-scale plants. In this way, a plant operation adapted to the time-related fluctuations of flow rates and micro-pollutant loads, can be achieved, making an minimization of operating costs possible. Due to the reciprocal quadratic relationship between quantum efficiency and irradiance, the cumulative energy input per treated wastewater volume can be reduced for low loads of the 4th treatment stage by an adapted reduction of the irradiance.

METHODS

Chemicals and materials
The catalyst material used was similar to previous works with more detailed descriptions in (Schnabel et al. 2020; Schnabel et al. 2021). During the coating process it was immobilized onto a V4A stainless steel mesh (316 L/1.4404) with a mesh size of 200 μm and a wire thickness of 100 μm. The coated catalyst material was a suspension of anatase-modified titanium dioxide nanoparticles of 14 nm diameter. The anatase content of the nanoparticles was 90% and the BET surface area was 50 m²/g. As an internal standard within the micro-pollutant analysis a 10 μg/l terbutryn (Sigma Aldrich) solution in methanol was used, which was purchased with a purity of 99.5%. For calibration of the micro-pollutant analysis calibration the following substances were used in analytical purity: amisulpride (Gentham Life Science), benztotriazole (Gentham Life Science), candesartan (BLD Pharma), carbamazepine (Sigma Aldrich), diclofenac (Cayman chemical Company), gabapentin (Gentham Life Science), 1-methylbenzotriazole (Chempure), and metoprolol (Sigma Aldrich). COD analysis was performed using LCK1414 cuvettes (Hach Lange) and a DR3900 photometer (Hach Lange). For the measurement of SAC254, ultrapure water was used as a blank for the photometric measurement. For the measurement of TOC, a calibration line was prepared
from aqueous potassium hydrogen phthalate (for analysis) solutions. The potassium hydrogen phthalate was purchased from sigma Aldrich. A platinum catalyst on ceramic supports from Analytik Jena was used as the catalyst for the thermal oxidation of the analysis.

**Experimental set-up and procedure**

The presented measurement data is an extension of the research results in (Mehling et al. 2021). Here, the reaction behavior of the parent substances of eight micro-pollutants was investigated and described in more detail in the same experimental set-up. The experiments were carried out in December 2020 and January 2021 at the Weimar Tiefurt wastewater treatment plant, Germany. The investigated unit was continuously fed with the dry weather effluent of the wastewater treatment plant. This pilot system consists of a photocatalytic rotating immersion reactor and an ozone generator and injector system.

Inside the photocatalytic reactor, 2.44 m² of catalyst surfaces are installed on 12 rotating disks with a diameter of 36 cm, whose non-submerged sides can be uniformly irradiated via adjustable UV-A LEDs. The reactor has a hydraulic volume of 25 liters, which is divided into 12 cascades by deflector plates between the catalyst disks. The individual reactor cascades are connected in series, thus achieving a plug-flow behavior of the reactor. Each individual cascade also has an inlet through which it can be fed with ozone-enriched water. The photocatalytic reactor setup is shown in Figure 1. The ozonation system consists of ozone generator, injection nozzle, tubular reactor, gas separation and ozone measuring equipment for gas and water phase. The ozone generated is fed via the injection nozzle to the tubular reactor, where high turbulence is provided to achieve rapid mass transfer from the gas phase to the water phase. The residual gas and ozone is removed from the system via the gas separator.

An overall flow diagram of the setup can be seen in Figure 2. The volume flow of the continuously filtered (50 μm) plant feed was controlled by a 3-way valve and a magnetic inductive flow meter (MID) (IFM SM6100). The feed is first passed through the photocatalytic reactor. A partial flow of its effluent was fed via a membrane pump to the ozonation system, where a dissolved ozone concentration of 6.5 mg/l was set by using a measuring electrode. Controlled by an MID measurement (IFM SM6100), a defined dose of this water was equally fed to the photocatalysis cascades. The experiments were carried out using previously unused catalysts. Between individual test steps, the water was drained from the system to minimize aging of the catalysts and thus ensure the same conditions for all test steps. Before each test step, the photocatalytic reactor was flushed with wastewater. Then the experimental parameters were set and the reactor was put into operation. In all investigations, an operating time corresponding to at least 1.5 times the hydraulic retention time was maintained in order to achieve a steady-state reactor operating condition. After this operation time, reactor feed and operation were stopped simultaneously and reactor feed and cascades 2, 4, 6, 8, 10 and 12 (numbered in flow direction) were sampled. Samples were cooled and stored in the dark until analysis. Analysis was performed a maximum of 14 days after sampling, with the exception of backup samples. The experimental program is divided into three steps:

![Figure 1](image1.png)  
*Figure 1 | Schematic 3D-Model of the investigated photocatalytic immersion body reactor © Lynatox GmbH, 2020.*
Investigation of photocatalytic treatment without ozone dosing
Investigation of ozone dosing without photocatalytic treatment.
Investigation of the reactor operation as photocatalytic ozonation.

In the first step of the experiments, three different electrical LED power settings of 50, 100 and 150 W/m² relative to the installed catalyst area were investigated. No ozone enriched water was dosed into the photocatalytic reactor during this step. In the second experimental step, TOC-related ozone doses of 0.2, 0.4 and 0.6 mg O₃/ mg TOC were fed to the reactor via the water phase. The UV-A LEDs were switched off during this step, but a rotation of the catalyst disks was performed. The ozone doses investigated were based on existing recommendations for ozonation plants as 4th treatment stages in German-speaking countries (Competence Center for Trace Substances NRW 2016; Competence Center for Trace Substances Baden-Württemberg 2018). For the investigation of photocatalytic ozonation, the plant was operated under LED irradiation and ozone dosage in the immersion body reactor. The combination of area-related radiation powers of 25, 50 and 100 W/m² and specific ozone doses of 0.2, 0.4 and 0.6 mg/mg were investigated. A summary of all parameter combinations tested can be seen in Table 1.

Analytical methods
The analysis of micro-pollutant using LC-MS/MS followed the methodology of (Schmidt et al. 2018) as in previous publications (Schnabel et al. 2020). The HPLC used was a Dionex R3000 system with autosampler and gradient pump. As an eluent ultrapure water with 1 mmol/l ammonium acetate and acetonitrile with 0.1% acetic acid was used. As the analytical separation column a Phenomenex Synergy 2.5 μm hydro PP column measuring 100 · 2 mm was used. The gradient was run from 4% acetonitrile to 96% acetonitrile in 28 minutes with a flow of 0.25 ml/min. The injection volume was 100 μl sample, which was mixed with 10 μl internal standard. The detection was carried out using a Sciex API 4000 triple quadrupole mass...
spectrometer with electro spray ionization. For each substance two multiple reaction monitoring mass transitions were evaluated. Within this work the following micro-pollutants were analyzed: amisulpride, benzotriazole, candesartan, carbamazepine, diclofenac, gabapentin, 1-methylbenzotriazole and metoprolol. The COD analysis was carried out according to the standard manufacturer's instructions. SAC254 was measured using a 1 cm fused silica curette using a Macherey Nagel UV-VIS spectrophotometer against a blank of ultrapure water. The methodology is described in (DIN 38404-3-3). Results were expressed in absorbance 1/cm. The measurement was made at 254 nm. The TOC was measured, following (Miller et al. 1993), with a Multi N/C analyzer from Analytik jena. The inorganic carbon was removed from 5 ml of sample by blowing out with oxygen after the addition of 100 μl of 1 molar hydrochloric acid. During the measurement, a control determination of the inorganic carbon was carried out by adding phosphoric acid. The organic carbon was determined after catalytic combustion of 1 ml sample solution in the oxygen stream at 800°C on a platinum catalyst. The carbon dioxide formed was detected by non-dispersive near infrared spectroscopy. Calibration of the measurement system was performed equidistantly with 10 points between 1 and 10 mg/l using potassium hydrogen phthalate solutions. Blank values and control standards were measured regularly as quality assurance measures. The detection limits were calculated from the calibration. The samples were pre-filtered in the photocatalytic System, so no further filtration was made. With the exception of the SAC254 all analytical measurements were carried out in duplicate.

**Kinetic and modelling – evaluation methodology**

The reaction rates of a heterogeneous photocatalysis or photocatalytic ozonation seem to follow the Lagmuir-Hinshelwood model (Lin et al. 2009; Asenjo et al. 2013). Here, the reaction rate is calculated according to the following formula (3):

\[
\frac{dC}{dt} = -k_{LH} \frac{K_L C_{eq}}{1 + K_L C_{eq} + \sum_{i=1}^{n} K_i C_i (i = 1, n)}
\]

(3)

where \( r \) is the reaction rate, \( k_{LH} \) is the specific rate constant, \( K_L \) is the langmuir constant and \( C_{eq} \) the equilibrium concentration. \( K_i \) and \( C_i \) are the adsorption constant and concentration of every contained substance at any given time. For low concentrations (e.g., the degradation of micro-pollutants), the term \( 1 + K_L C_{eq} + \sum_{i=1}^{n} K_i C_i (i = 1, n) \) can be neglected, resulting in a pseudo-first-order reaction (Lazar et al. 2012) (4):

\[
\frac{dC}{dt} = k_{LH} K_L C_{eq} = k C_{eq}
\]

(4)

| number | LED-power [W/m²] | ozone dose [mg O₃/mg TOC] |
|--------|-----------------|--------------------------|
| 1.1    | 50              | –                        |
| 1.2    | 100             | –                        |
| 1.3    | 150             | –                        |
| 2.1    | –               | 0.2                      |
| 2.2    | –               | 0.4                      |
| 2.3    | –               | 0.6                      |
| 3.1    | 25              | 0.2                      |
| 3.2    | 25              | 0.4                      |
| 3.3    | 25              | 0.6                      |
| 3.4    | 50              | 0.2                      |
| 3.5    | 50              | 0.4                      |
| 3.6    | 50              | 0.6                      |
| 3.7    | 100             | 0.2                      |
| 3.8    | 100             | 0.4                      |
| 3.9    | 100             | 0.6                      |
where $k$ is the reaction rate constant. The assumption of a 1st order reaction is also confirmed by the practical observations of many authors (Mehrjouei et al. 2015). The measured values of SAC254 as well as the concentrations of TOC and COD are composed additively by the concentrations of all substances in the investigated matrix. Assuming a 1st order reaction of all substances contained in a matrix, a 1st order reaction can be expected for the behavior of the cumulative parameters SAC254, TOC and COD. However, studies on the treatment of real wastewater samples by photocatalytic processes showed a substance-specific degradation behavior, with individual substances (e.g. due to lack of adsorption) showing almost no degradation (Mecha & Chollom 2020). Consequently, a subdivision of cumulative parameters into reactive and nearly inert parts, as seen in the results of (Márquez et al. 2014) can be made. For the reactive part, an exponential and independent from the initial concentration trend for measured values over the treatment period is to be expected for small variation of the initial concentration. For this reason, in addition to a representation as absolute measured values, a relative representation as $c/c_0$ values is also presented for the investigated cumulative parameters. Due to the presumed inlet concentration independence, the correlation of measured values for micro-pollutants with the SAC254 was performed for their percentage decrease relative to the respective initial concentration. The linear parameter fit was performed with Origin Pro. It was further determined that the intercept of the y-axis occurs at $y = 0$. This results in the following formula for the parameter fit (5):

$$\frac{c_{0,MP} - c_{i,MP}}{c_{0,MP}} = r \cdot \frac{c_{0,SAC} - c_{i,SAC}}{c_{0,SAC}}$$

where $c_{i,MP}$ is the respective micro-pollutant concentration and $c_{0,MP}$ is the corresponding influent concentration. $c_{i,SAC}$ is the SAC254 measured value and $c_{0,SAC}$ the corresponding inlet measurement. The parameter fit for the correlation of TOC and COD is carried out analogously (6):

$$\frac{c_{0,TOC} - c_{i,TOC}}{c_{0,TOC}} = r \cdot \frac{c_{0,COD} - c_{i,COD}}{c_{0,COD}}$$

Here, $c_{i,TOC}$ is the TOC concentration and $c_{0,TOC}$ the corresponding feed concentration. $c_{i,COD}$ is the associated COD concentration and $c_{0,COD}$ is the inlet measurement.

RESULTS

The results of the SAC254 measurements are shown in Figure 3 for all test series. In all test series, a significant reduction in SAC254 of 20–55% was achieved after 60 minutes. For experimental step 1, there is an increase in SAC254 reduction with increasing irradiance. Similarly, an increase in ozone dose in experimental step 2 is associated with an increased SAC254 decrease. Within experimental step 3, many parameter combinations showed similar SAC254 curves. Only parameter combinations with low ozone doses (0.2 and 0.4 mg/mg) and irradiances (25 and 50 W/m$^2$) showed lower SAC254 reductions. It is evident that there is a limitation of the reaction rate of the reactor independent of the tested operating parameters. The same behavior was also observed for the reaction rates of the studied micro-pollutants (Mehling et al. 2021). Consequently, similar SAC reductions as in (Mecha et al. 2016) could be achieved. However, in (Mecha et al. 2016), the ozone input dose used was 1,250 g/m$^3$ and the cumulative electrical energy demand of the UV lamp was 214 kWh/m$^3$. In this work, ozone doses of 1.6–4.8 g/m$^3$ were used. The cumulative energy demand for 60 minutes of LED radiation was 2.44–14.65 kWh/m$^3$.

The results of the TOC measurements for all test series are shown in Figure 4. A clear variability of the inlet concentrations can be seen for experimental step 1. Furthermore, the measurements show large uncertainties and large concentration leaps between individual cascades in individual measurement series. In experimental step 1 a decrease of TOC by 20–40% was measured. However, the inlet concentrations of steps 1.1 and 1.2 appear inconsistent, so the high reduction rates of up to 40% must be critically questioned. In experimental step 2, lower measurement uncertainties are present and reduction rates of 10–20% are achieved as a function of the ozone dose. In experimental step 3 reduction rates of 0–20% were achieved. Individual measurement series show significant increases in the measured TOC concentrations between individual cascades. There seems to be a correlation between the TOC reduction, the ozone doses and irradiation powers used, which is, however, overlaid by a large fluctuation of the measured values within and between individual tests. Lower TOC reductions were achieved compared to the literature (Aguinaco et al. 2012; Márquez et al. 2014; Kang et al. 2021). However, TOC degradation rates in this source were measured using higher input ozone doses from 660 to 250 g/m$^3$ and differing radiation sources and powers.
The results of the COD measurements of all test series are shown in Figure 5. Here, within the duplicate measurements, large measurement errors were found in some cases. It is noteworthy that the concentration leaps observed in the TOC measurements are repeated, but for other measuring points. In experimental step 1, similar COD reductions of 15–20% were observed for all irradiances. In experimental step 2, ozone dose-dependent reduction rates of 5–20% were achieved.

**Figure 3** | Measured SAC254 values for photocatalysis (a), ozonantion (b) and photocatalytic ozonation (c) and relative concentration curves within the reactor for photocatalysis (d), ozonantion (e) and photocatalytic ozonation (f).

The results of the COD measurements of all test series are shown in Figure 5. Here, within the duplicate measurements, large measurement errors were found in some cases. It is noteworthy that the concentration leaps observed in the TOC measurements are repeated, but for other measuring points. In experimental step 1, similar COD reductions of 15–20% were observed for all irradiances. In experimental step 2, ozone dose-dependent reduction rates of 5–20% were achieved.
In experimental step 2.3, a large concentration leap was measured in cascade 2. For experimental step 3 a behavior analogous to the TOC measurements was observed. Small COD reductions of approximately 10% were measured for parameter combinations with low ozone dose and LED power. For many measurement within this step, significant concentration fluctuations between individual reactor cascades can be observed. Likes to TOC measurements the reduction rates of the COD where smaller compared to literature, which can be explained by the lower input of ozone and radiation.

**Figure 4** | Measured TOC concentrations for photocatalysis (a), ozonation (b) and photocatalytic ozonation (c) and relative concentration curves within the reactor for photocatalysis (d), ozonation (e) and photocatalytic ozonation (f).
The results of a linear parameter fit for measured degradation rates of micro-pollutants and SAC254 are shown in Figure 6. For most of the micro-pollutants a good correlation ($R^2 > 0.8$) was achieved. For benzotriazole and methylbenzotriazole a different behavior was observed. Due to an increase in concentration between reactor feed and subsequent cascades in test 1.2, negative reduction rates were calculated, which do not correspond to the other tests in this series of experiments.

**Figure 5** | Measured COD concentrations for photocatalysis (a), ozonation (b) and photocatalytic ozonation (c) and relative concentration curves within the reactor for photocatalysis (d), ozonation (e) and photocatalytic ozonation (f).
For the investigation of a sole ozone dosage within the rotating immersion reactor, the results of the linear parameter fit between SAC254 and micro-pollutant degradation rates are shown in Figure 7. A good to very good correlation ($R^2 > 0.9$) was obtained for all micro-pollutants except gabapentin. For amisulpride and metoprolol, a non-linear behavior is indicated, which, however, cannot be quantified on the basis this dataset.

**Figure 6** | Linear correlation of SAC254 and micro-pollutant reduction rates of amisulpride (a), bezontriazole (e), candesartan (b), carbamazepine (f), diclofenac (c), gabapentin (g), methylbenzotriazole (d) and metoprolol (h) for treatment with photocatalysis.
The results of the correlation analysis of SAC254 to micro-pollutant degradation rates for investigation step 3 are shown in Figure 8. Good to very good accuracies ($R^2 \geq 0.9$) were achieved for all micro-pollutants in this case. The determined slopes show similar amounts compared to the purely photocatalytic treatment, if good coefficients of determination were achieved. Compared to experimental step 2, the large slope of diclofenac is apparent, which is a result of the high affinity of diclofenac for photocatalytic degradation within the system.

Figure 7 | Linear correlation of SAC254 and micro-pollutant reduction rates of amisulpride (a), bezontriazole (e), candesartan (b), carbamazepine (f), diclofenac (c), gabapentin (g), methylbenzotriazole (d) and metoprolol (h) for treatment with ozone.
For all 3 experimental steps, a correlation between the TOC and COD degradation rates was found as shown in Figure 9. Slopes from 1.69 to 0.60 and correlation coefficients ($R^2$) from 0.86 to 0.60 were determined in the experiments. The highest slope with a good coefficient of determination was determined in experimental step 1. The ozonation in experimental step 2

---

**Figure 8** | Linear correlation of SAC254 and micro-pollutant reduction rates of amisulpride (a), bezontriazole (e), candesartan (b), carbamazepine (f), diclofenac (c), gabapentin (g), methylbenzotriazole (d) and metoprolol (h) for treatment with photocatalytic ozonation.
resulted in a lower slope with a similarly good coefficient of determination. Within experimental step 5, the photocatalytic ozonation, the lowest slope was determined. Here, however, a correlation was only possible to a limited extent due to fluctuating TOC and COD measurements. Especially for a treatment by ozone alone, the increased reduction rates of TOC

**Figure 9** | Linear correlation of TOC and COD reduction rates for photocatalysis (a), ozonation (b) and photocatalytic ozonation (c).
compared to the literature are notable. In large-scale plants using higher ozone doses (approximately 0.8 mg/mg), only 10% reductions of COD and TOC are observed (Abegglen & Siegrist 2012). The measured TOC reductions must therefore not only be influenced by the reaction with ozone but also by the reactor itself. It is suspected that non-stationary adsorption processes on the catalyst material exert this influence. In addition, it can be assumed that despite the prefiltration of the reactor inlet, particulate carbon was introduced or formed within the reactor system. This would explain the observed concentration leaps of TOC and COD between individual reactor cascades.

It is therefore difficult to assess the mineralization performance of the reactor system. However, the simultaneous decrease of TOC and COD by similar amounts is a positive indication for high mineralization rates. It can be assumed that TOC provides information about the overall mineralization reactions, while COD provides information about the total oxidative reactions (transformation and mineralization). The simultaneous decrease of TOC and COD is therefore an indicator for the mineralization rate of the treated wastewater matrix by photocatalysis and photocatalytic ozonation. It is assumed that the slope of the determined linear correlation enables a statement about the mineralization rate of a reactor configuration. For a 100% mineralization rate, this slope should theoretically approach 1. This assumes that all compounds within the matrix are either degraded in equal proportions or have the same COD/COD ratio. In practice, neither of these assumptions is true, which means that calculated slopes only allow qualitative statements to be made. Consequently, when photocatalysis alone is used as the reaction mechanism, the reactor shows significantly higher mineralization. This can be explained by the absence of direct selective oxidation reactions of ozone with the wastewater matrix.

CONCLUSIONS

The aim of this work was to provide a data set on the behavior of the cumulative parameters SAC254, TOC and COD during treatment of wastewater treatment plant secondary effluent by photocatalysis and photocatalytic ozonation. For the parameter SAC254, consistent concentration curves and dependencies to operational parameters of the experimental system could be measured. The measurements of the parameters TOC and COD showed greater uncertainties, although basic trends could nonetheless be observed. In future work, it should be possible to reduce the measured uncertainty by excluding the measurement of particulate substances (sample filtration). Furthermore, proof of continuous reactor operation, for example by online measurement technology, should be integrated into experimental designs.

A good to very good linear correlation between the reduction of SAC254 and 8 micro-pollutants for a treatment using photocatalysis and photocatalytic ozonation could be measured. This confirms the suitability of the SAC254 as a control parameter for a large-scale application of a photocatalytic 4th treatment stage. This enables an energy-saving reactor control, which can compensate volume and concentration fluctuations in the wastewater treatment plant effluent.

Within all experimental steps a decrease of the parameters TOC and COD was observed. A linear correlation between measured degradation rates was possible with a coefficient of determination of 0.58–0.86. The simultaneous decrease of TOC and COD is therefore an indicator for a good mineralization rate of the treated wastewater matrix especially via photocatalysis. The degree of mineralization, as well as the formation and harmfulness of any transformation products that may be formed, should be investigated by further research using this methodology coupled with non-target analysis. This question determines the general suitability and design of photocatalytic processes for wastewater treatment as well as the necessity of complex post-treatment processes (e.g. biologically active sand filtration).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Abegglen, C. & Siegrist, H. 2012 Mikroverunreinigungen aus kommunalem Abwasser Verfahren zur weitergehenden Elimination auf Kläranlagen (Micropollutants from Municipal Wastewater Process for Further Elimination in Sewage Treatment Plants). Federal Office for the Environment BAFU.

Aemig, Q., Hélias, A. & Patureau, D. 2021 Impact assessment of a large panel of organic and inorganic micropollutants released by wastewater treatment plants at the scale of France. Water Research 188, 116524. doi:10.1016/j.watres.2020.116524.

Aguinaco, A., Beltrán, F. J., García-Araaya, J. F. & Oropesa, A. 2012 Photocatalytic ozonation to remove the pharmaceutical diclofenac from water: influence of variables. Chemical Engineering Journal 189–190, 275–282.
Asenjo, N. G., Santamaría, R., Blanco, C., Granda, M., Álvarez, P. & Menéndez, R. 2013 Correct use of the Langmuir–Hinshelwood equation for proving the absence of a synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon. *Carbon* 55, 62–69.

Bourgin, M., Beck, B., Boehler, M., Borowska, E., Fleiner, J., Salhi, E., Teichler, R., Gunten, U. v., Siegrist, H. & Mc Ardell, C. S. 2018 Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: abatement of micropollutants, formation of transformation products and oxidation by-products. *Water Research* 129, 486–498. doi:10.1016/j.watres.2017.10.036.

Competence Center for Trace Substances Baden-Württemberg (Ed.) 2018 *Handlungsempfehlungen für die Vergleichskontrolle und den Betrieb von Verfahrenstechniken zur gezielten Spurenstoffelimination* (Recommendations for Action for Comparative Control and the Operation of Process Technologies for Targeted Trace Substance Elimination).

Competence Center for Trace Substances NRW (Ed.) 2016 *Anleitung zur Planung und Dimensionierung von Anlagen zur Mikroschadstoffelimination* (Instructions for Planning and Dimensioning Plants for Micropollutant Removal).

DIN 38404-3-3 2005 German Standard Methods for the Examination of Water, Waste Water and Sludge - Physical and Physical-Chemical Parameters.

Fu, P., Feng, J., Yang, H. & Yang, T. 2016 Degradation of sodium n-butyl xanthate by vacuum UV-ozone (VUV/O3) in comparison with ozone and VUV photolysis. *Process Safety and Environmental Protection* 102, 64–70. doi:10.1016/j.psep.2016.02.010.

Gallé, T., Pittois, D., Bayerle, M. & Braun, C. 2019 An immission perspective of emerging micropollutant pressure in Luxembourgish surface waters: a simple evaluation scheme for wastewater impact assessment. *Environmental Pollution (Barking, Essex : 1987)* 253, 992–999. doi:10.1016/j.envpol.2019.07.080.

Gaya, U. I. & Abdullah, A. H. 2008 Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 9 (1), 1–12. doi:10.1016/j.jphotochemrev.2007.12.003.

Guillossou, R., Le Roux, J., Mailler, R., Vulliet, E., Morlay, C., Nauleau, F., Gasperi, J. & Rocher, V. 2019 Organic micropollutants in a large wastewater treatment plant: what are the benefits of an advanced treatment by activated carbon adsorption in comparison to conventional treatment? *Chemosphere* 218, 1050–1060. doi:10.1016/j.chemosphere.2018.11.182.

Guillossou, R., Le Roux, J., Brossillon, S., Mailler, R., Vulliet, E., Morlay, C., Nauleau, F., Rocher, V. & Gaspéri, J. 2020 Benefits of ozonation before activated carbon adsorption for the removal of organic micropollutants from wastewater effluents. *Chemosphere* 245, 125530. doi:10.1016/j.chemosphere.2019.125530.

Kanakaraju, D., Glass, B. D. & Oelgemöller, M. 2018 Advanced oxidation process-mediated removal of pharmaceuticals from water: a review. *Journal of Environmental Management* 219, 189–207.

Kanauijia, D. K., Paul, T., Sinharoy, A. & Pakshirajan, K. 2019 Biological treatment processes for the removal of organic micropollutants from wastewater: a review. *Current Pollution Reports* 5 (3), 112–128. doi:10.1007/s40726-019-00110-x.

Kang, W., Chen, S., Yu, H., Xu, T., Wu, S., Wang, X., Lu, N., Quan, X. & Liang, H. 2021 Photocatalytic ozonation of organic pollutants in wastewater using a flowing through reactor. *Journal of Hazardous Materials* 410, 124277. doi:10.1016/j.jhazmat.2020.124277.

Kisch, H. 2015 *Semiconductor Photokatalysis- Principles and Applications*. Wiley VCH.

Lazar, M., Varghese, S. & Nair, S. 2012 Photocatalytic water treatment by titanium dioxide: recent updates. *Catalyst* 2012, 572–601.

Lin, Y., Ferronato, C., Deng, N., Wu, F. & Chovelon, J.-M. 2009 Photocatalytic degradation of methylparaben by TiO2: multivariable experimental design and mechanism. *Applied Catalysis B: Environmental* 88 (1–2), 32–41.

Margot, J., Rossi, L., Barry, D. A. & Holliger, C. 2015 A review of the fate of micropollutants in wastewater treatment plants. *WIREs Water* 2 (5), 457–487.

Márquez, G., Rodríguez, E. M., Beltrán, F. J. & Álvarez, P. M. 2014 Solar photocatalytic ozonation of a mixture of pharmaceutical compounds in water. *Chemosphere* 115, 71–78.

Mecha, A. C. & Chollom, M. N. 2020 Photocatalytic ozonation of wastewater: a review. *Environmental Chemistry Letters* 18 (5), 1491–1507.

Mecha, A. C., Onyago, M. S., Ochieng, A., Fourie, C. J. S. & Momba, M. N. B. 2016 Synergistic effect of UV–vis and solar photocatalytic ozonation on the degradation of phenol in municipal wastewater: a comparative study. *Journal of Catalysis* 341, 116–125.

Mehling, S., Schnabel, T. & Londong, J. 2021 Photocatalytic ozonation in an immersion rotary body reactor for the removal of micropollutants from the effluent of wastewater treatment plants. *Water Science and Technology*. doi:10.2166/wst.2021.617.

Mehriouei, M., Müller, S. & Möller, D. 2015 A review on photocatalytic ozonation used for wastewater and the treatment of wastewater. *Chemical Engineering Journal* 265, 209–219.

Miller, A. E. J., Mantoura, R. F. C. & Preston, M. R. 1993 Shipboard investigation of DOC in the NE Atlantic using platinum-based catalysts in a Shimadzu TOC-500 HTCO analyser. *Marine Chemistry* 41 (1–3), 215–221. doi:10.1016/0304-4203(93)90122-5.

Moreira, N. F. F., Orge, C. A., Ribeiro, A. R., Faria, J. L., Nunes, O. C., Pereira, M. F. R. & Silva, A. M. T. 2015 Fast mineralization and detoxification of amoxicillin and diclofenac by photocatalytic ozonation and application to an urban wastewater. *Water Research* 87, 87–96.

Pitre, S. P., Yoon, T. P. & Scianco, J. C. 2017 Titanium dioxide visible light photocatalysis: surface association enables photocatalysis with visible light irradiation. *Chemical Communications* 53 (31), 4335–4338. doi:10.1039/C7CC01952A.

Schmidt, S., Hoffmann, H., Garbe, L.-A. & Schneider, R. J. 2018 Liquid chromatography-tandem mass spectrometry detection of diclofenac and related compounds in water samples. *Journal of Chromatography A* 1558, 112–116. doi:10.1016/j.chroma.2018.01.037.
Solís, R. R., Rivas, F. J., Martínez-Piernas, A. & Agüera, A. 2016 Ozonation, photocatalysis and photocatalytic ozonation of diuron. Intermediates identification. Chemical Engineering Journal 292, 72–81. doi:10.1016/j.cej.2016.02.005.

Teichgräber, B., Jagemann, P., Hetschel, M., Bechtel, A. & Phan, L.-C. 2021 A module-based approach for elimination of organic micropollutants at wastewater treatment plants. Water Science and Technology 84 (2), 364–373. doi:10.2166/wst.2021.029.

First received 14 December 2021; accepted in revised form 31 January 2022. Available online 14 February 2022.