



# A novel phenomenological model for streamlined prediction and online monitoring of organic micropollutant removal in full-scale wastewater ozonation<sup>☆</sup>

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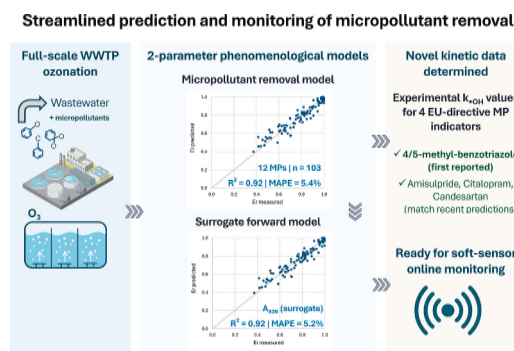
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## HIGHLIGHTS

- Two-parameter phenomenological model calibrated on full-scale ozonation
- Accurate 12 micropollutant removal predictions:  $R^2 = 0.92$ ;  $n = 103$
- Phenomenology-driven A436 surrogate model enables proxy-based online monitoring
- First experimental  $k_{OH}$  for 4 EU-directive MP indicators; 3 match recent predictions

## GRAPHICAL ABSTRACT



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## ABSTRACT

Ozonation is a leading option for advanced treatment in full-scale WWTPs, yet rapid prediction and online monitoring of organic micropollutant (MP) removal remain challenging. We propose an integrated, streamlined phenomenological framework that addresses both needs through two complementary models. The formulation rests on conventional ozone–radical kinetics, using the  $R_{ct}$  concept ( $\cdot OH$ -exposure/ $O_3$ -exposure) with an effective first-order ozone decay. After algebraic simplification, the model reduces to two identifiable parameters, and these assumptions were verified a posteriori by goodness-of-fit. Calibrated with full-scale observations, the two-parameter removal model accurately reproduced the behaviour of 12 MPs across 103 data points from three campaigns ( $R^2 = 0.92$ ; MAPE = 5.4%), with compound-wise errors of 0.4–10%. A key contribution is the experimental determination of  $k_{OH}$  for four directive-listed indicators, amisulpride, citalopram, candesartan, and 4/5-methyl-benzotriazole, experimentally determined by back-calculating  $k_{OH}$  from measured removals with the calibrated removal model. To the best of our knowledge, these constants have not previously been measured

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experimentally, and the new values closely match recent predictions for amisulpride, citalopram, and candesartan and provide the first reported  $k_{\text{OH}}$  for 4/5-methyl-benzotriazole. For online MP removal monitoring, we developed a surrogate-driven forward model built on the phenomenological formulation. A436 delivered the best balance of parsimony and accuracy, marginally outperforming A254: a joint two-parameter model, pooled across the same campaigns, achieved  $R^2 = 0.92$  and  $\text{MAPE} = 5.2\%$ . Overall, the framework links a minimal kinetic structure to easily measured signals, enabling rapid prediction and proxy-based monitoring under realistic conditions while providing new kinetic data that reduce uncertainty in indirect oxidation pathways.

## 1. Introduction

The European Union water policy on contaminants of emerging concern, reflected in the recently approved Urban Wastewater Treatment Directive (UWWTD) [1], will require the improvement of wastewater treatment plants (WWTPs) effectiveness for removing organic micropollutants (MPs), such as pharmaceutical compounds and anti-corrosive agents. The UWWTD mandates that within 20 years many plants can achieve a minimum 80% average removal for at least 6 indicator substances out of a 12-indicator list.

Currently conventional WWTPs can remove the more biodegradable contaminants, while the recalcitrant persist and must be addressed by alternative/additional processes. Ozonation and adsorption to activated carbon are two consolidated advanced treatment technologies for MP control, which are already used in several plants in Switzerland and in Germany [2,3]. Herein, the focus is on ozonation.

Ozone is a powerful but selective oxidant that reacts with dissolved compounds through two main mechanisms: (i) a direct molecular reaction, or (ii) an indirect pathway involving ozone decomposition and the generation of secondary oxidants, notably hydroxyl radicals ( $\cdot\text{OH}$ ), which subsequently oxidize solutes [4]. The balance between these pathways depends strongly on pH and on the water matrix composition, as ozone decomposes faster under alkaline conditions and the dissolved organic matter (DOM) in wastewater greatly influences ozone stability and hydroxyl radical formation [5,6]. Ozone can therefore react directly with MPs or indirectly, through hydroxyl radicals. A common approach to predict MP removal by ozonation at a full-scale WWTP is modelling ozonation through chemical kinetics, using the rate constants for the reactions of MP with ozone ( $k_{\text{O}_3}$ ) and hydroxyl radicals ( $k_{\text{OH}}$ ) and the exposure time to ozone and OH radical [7].

Due to the inability of directly monitoring the very low  $\cdot\text{OH}$  concentrations, most authors follow the experimental method proposed by Elovitz and von Gunten [8] and Elovitz et al. [6]. This method allows indirectly obtaining  $\cdot\text{OH}$ -exposure by measuring the decrease in concentration of an ozone-resistant compound yet very susceptible to hydroxyl radical ( $\cdot\text{OH}$  probe compound) and by using the  $R_{\text{ct}}$  concept, defined as the ratio of hydroxyl radical exposure/ozone exposure [7,9].

The  $\text{O}_3$ -exposure is usually obtained experimentally, directly through ozone decay curves [8] but an indirect measurement through the removal of very  $\text{O}_3$ -reactive compounds has also been referred [10]. Other approaches include deriving from literature values of waters with similar organic (DOM), and inorganic matrices (alkalinity, nitrite, and bromide concentrations) and for WWTPs with identical specific ozone doses [11].

Other approaches resort to mechanistic modelling of ozone chain reactions for calculating  $\cdot\text{OH}$  [12], or  $\text{O}_3$  exposures or decay [8,13].

Altogether, to forecast the removal of a specific micropollutant in a WWTP, it is necessary to conduct ozonation bench-scale tests with the wastewater to obtain information about  $\text{O}_3$  decomposition and  $\cdot\text{OH}$ -exposure and the rate constants  $k_{\text{O}_3}$  and  $k_{\text{OH}}$  for those micropollutants must be known. To facilitate practical implementation, simplified predictive frameworks have also been proposed, such as the chemical credit approach of Pang et al. [14], which combines  $\text{O}_3/\text{TOC}$  ratios,  $\text{O}_3$  exposure, reaction rate constants and structural classifications to estimate compound removal.

Reported  $k_{\text{O}_3}$  values for MPs span several orders of magnitude,

whereas  $k_{\text{OH}}$  values are typically  $10^8$ – $10^9 \text{ M}^{-1} \text{ s}^{-1}$  [4,9,15]. These rate constants are usually determined in bench-scale kinetic experiments by monitoring MP decay in ozone solutions and applying competition kinetics with a reference compound of known reactivity [9]. As an alternative, computational approaches have been developed:  $k_{\text{O}_3}$  can be estimated by quantitative structure-activity relationship (QSAR) analysis, by using empirical chemical descriptors, such as Hammett and Taft constants (for aromatic and aliphatic compounds, respectively [16] or quantum molecular orbital descriptors [17]. For  $k_{\text{OH}}$ , the group contribution method (GCM) [16,17], assuming additivity of reactivity from functional groups, with each group assigned a specific contribution factor, has been widely used. Other approaches resort to using quantitative structure-property relationship (QSPR) modelling [18] and, more recently, to machine learning (ML) approaches based on molecular fingerprints (e.g., through the web application pySiRC, a python simulator of rate constants of oxidative processes of organic pollutants) [19].

Although numerous rate constants for both oxidants had already been published, to the best of our knowledge only recently have predicted, rather than experimental,  $k_{\text{OH}}$  values been reported for many, though not all, MPs relevant to urban wastewater, including certain pharmaceuticals and anticorrosive agents listed in the UWWTD [11].

Because laboratory analysis of MPs is costly, time-consuming, and not broadly available, WWTPs need faster decision-support information. A practical route is to leverage online-measurable surrogate parameters within smart monitoring frameworks, where virtual (soft) sensors combine these signals with process data to yield continuous, cost-effective, near-real-time estimates that complement periodic laboratory validation, as is to be required by the new UWWTD. Among available surrogates, changes in UV/Vis absorbance have been repeatedly used to infer MP abatement and to control ozone dosing [5,20–22], and fluorescence (EEM/PARAFAC) has been explored to enhance such proxy models [20,23]. In parallel, DOM concentration, typically quantified as dissolved organic carbon (DOC, mg C/L), is widely used to normalize specific ozone dose (g  $\text{O}_3$ /g C), providing essential context on matrix reactivity, even if it is not a direct surrogate of micropollutant removal [24,25].

This study presents two novel phenomenological models for full-scale wastewater ozonation: (i) a prediction model that builds on standard mechanistic modelling via chemical kinetics and reduces to an easily interpretable, closed-form equation for MP removal; and (ii) a monitoring model derived from that prediction model by assuming first-order decay of UV/Vis absorbance as a function of the transferred ozone dose, thereby expressing MP removal directly in terms of online-measurable surrogates. The models are tested and calibrated with full-scale WWTP ozonation data comprising 103 observations (from three campaigns) for 12 MPs spanning wide ranges of ozone and hydroxyl-radical reactivity. Together, they provide a practical toolkit: a mechanistically informed yet streamlined predictor for MP removal optimization, and a proxy-based formulation suitable for online monitoring and control and soft-sensor integration using routine plant signals. By calibrating the prediction model against full-scale data, we derived new experimental  $k_{\text{OH}}$  values for four compounds listed in the EU directive.

## 2. Materials and methods

### 2.1. Ozonation campaigns in Lordelo WWTP

Full-scale ozonation campaigns were conducted at Lordelo WWTP, located in Guimarães (Portugal) and operated by TRATAVE. With an average flowrate of 19,000 m<sup>3</sup>/d (dry weather), this plant has a high input of textile effluents (51% average of total flowrate). The treatment line (Fig. S1) comprises activated sludge with oxygen injection, sand filters and tertiary ozonation (CFV20-Dégremont Technologies, pure oxygen fed; 20 kg/h maximum ozone production, corresponding to 30 g O<sub>3</sub>/m<sup>3</sup> for the average flow). The plant has two ozone contact towers (usually only one line is working), each with three chambers in series with a total volume of 400 m<sup>3</sup> where ozone is injected through ceramic diffusers.

Three ozonation campaigns were conducted between September and October 2024, each campaign testing three doses, between 14 and 30 g O<sub>3</sub> generated/m<sup>3</sup>, corresponding to transferred ozone doses (TOD) of 11.6 to 24.2 g O<sub>3</sub>/m<sup>3</sup> (85% transfer efficiency) and to organic matter-normalised ozone dose of 0.4–1.0 g O<sub>3</sub>/g C. During the campaigns, the average inlet wastewater flowrate was 606–660 m<sup>3</sup>/h, thus the hydraulic retention time in the ozone contact tower was 36–40 min.

In each campaign, samples were collected from both the inlet and outlet of the ozone contact tower, corresponding to the filtered secondary effluent (LOR-E-FIL.M) and the treated effluent (LOR-E-EFL), respectively, as shown in Fig. S1. A 5-h composite sample was collected for LOR-E-FIL.M, while three grab samples were taken for LOR-E-EFL, each corresponding to a different ozone dose. A 1.5 h stabilization period, a lag time of at least 3 times the hydraulic retention time on the ozone chamber and predefined after a preliminary test, was applied before sampling the ozonated water for each dose.

### 2.2. Analytical parameters and analytical methods

Water samples were monitored for regular water quality parameters and for MPs.

Regular water quality parameters were analysed using standards methods (Table S1 in Supplementary information) and included pH, temperature, alkalinity, conductivity, chloride, bromide, total suspended solids (TSS), turbidity, total and dissolved organic carbon (TOC and DOC), UV absorbance at 254 nm (A254), absorbance at 436 nm (A436) and UV transmittance at 254 nm (T254), chemical and biochemical oxygen demand (COD and BOD5), colour-scanning, ammoniacal nitrogen (N-NH<sub>4</sub>), nitrate (N-NO<sub>3</sub>), nitrite (N-NO<sub>2</sub>), total nitrogen (N-total), and total phosphorus (P-total).

Thirty-four MPs (Table S2 in Supplementary information), including the 12 listed in UWWTD and other pharmaceutical compounds and metabolites, were analysed by UHPLC-MS/MS as described in supplementary material (text S1, Tables TS1.1–1.6, Fig. TS1.1) and further detailed in Paíga et al. [26].

From the total of 34 MPs analysed, 16 were not quantified in the filtered secondary effluent (13 were never quantified and 3 were not quantified in some campaigns). For two MPs the experimental constants  $k_{O_3}$  and  $k_{OH}$  were not available and for four MPs the constants  $k_{OH}$  were not available. Therefore, 12 compounds with available  $k_{O_3}$  and  $k_{OH}$  constants, and quantified in the filtered secondary effluent, were used for calibration of the removal model.

### 2.3. Filtered secondary effluent quality

The quality of the filtered secondary effluent (LOR-E-FIL.M) during the three ozone campaigns is presented in Table S3 (supplementary information).

All campaigns showed neutral pH values (7.2–7.6) and low particle concentrations, with TSS below 5 mg/L and turbidity under 1.9 NTU. Compared to the characteristics of other studies on MP removal by

ozonation (presented in Table S3), significantly higher levels of salts, nutrients and organic matter were observed, reflected in elevated alkalinity (376–660 mg/L CaCO<sub>3</sub>), conductivity (2.8–4.2 mS/cm), chloride (610–880 mg/L), bromide (0.4–0.5 mg/L), ammonia (17–31 mg/L N), DOC (22–25 mg C/L) and COD (78–93 mg/L O<sub>2</sub>). LOR-E-FIL.M also showed high colour strength (0.10–0.13 cm<sup>-1</sup> for A436 and 19–24 for colour scan) and A254 (0.97–1.1 cm<sup>-1</sup>). These characteristics are justified by the high input of textile wastewater in Lordelo WWTP together with the modest nitrification in the activated sludge treatment upstream. Among all campaigns, Campaign 3 exhibited the most distinct secondary effluent quality, marked by the lowest salt load, as indicated by reduced alkalinity, electrical conductivity, and chloride concentrations.

### 2.4. Modelling of micropollutants removal

Considering a parallel second order reaction mechanism between the micropollutant and O<sub>3</sub> and •OH, which can be expressed by Eqs. (1) and (2)



yields [7]:

$$-\ln\left(\frac{[MP]}{[MP]_0}\right) = k_{O_3} \int [O_3] dt + k_{OH} \int [\bullet OH] dt \quad (3)$$

where  $k_{O_3}$  and  $k_{OH}$  are the second-order reaction rate constants of the micropollutants (MP) with ozone and •OH, respectively, and  $\int [O_3] dt$  and  $\int [\bullet OH] dt$  are the ozone and OH radical exposures, respectively [7].

Resorting to the *Rct* concept [8] described in the introduction:

$$Rct = \frac{\int [\bullet OH] dt}{\int [O_3] dt} \quad (4)$$

Eq. (3) can be simplified to [8]:

$$-\ln\left(\frac{[MP]}{[MP]_0}\right) = (k_{O_3} + k_{OH} \cdot Rct) \int [O_3] dt \quad (5)$$

For modelling the ozone decay in the water, a pseudo first-order decay was considered. Phenomenologically, the order of the decay reaction with respect to ozone is comprised between 1 and 2, with many studies considering that a first-order kinetic describes the decay process reasonably accurately [25,27]. Other studies, following a mechanistic approach, resort to a two-step decrease, characterized by a fast initial decrease of ozone (instantaneous ozone demand), followed by a second phase in which ozone decreases with first-order kinetics [28].

Considering a pseudo first-order ozone decay, the ozone depletion can then be mathematically described as:

$$\frac{d[O_3]}{dt} = k_d \cdot [O_3] \quad (6)$$

which, by integration, yields

$$[O_3] = [O_3]_0 \cdot e^{-k_d t} \quad (7)$$

where  $k_d$  is the pseudo first-order reaction constant for ozone decomposition and  $[O_3]_0$  is the initial (molar) ozone concentration.

The ozone exposure ( $\int [O_3] dt$ ) can then be calculated by:

$$\int_0^t ([O_3]_0 \cdot e^{-k_d t}) dt = \frac{[O_3]_0}{k_d} (1 - e^{-k_d t}) \quad (8)$$

Combining Eq. (5) with Eq. (8), yields:

$$-\ln\left(\frac{[MP]}{[MP]_0}\right) = (k_{O_3} + k_{OH} \cdot Rct) \cdot \frac{[O_3]_0}{k_d} (1 - e^{-k_d t}) \quad (9)$$

Defining the MP removal efficiency ( $Er$ ) as:

$$Er = 1 - \frac{[MP]}{[MP]_0} \quad (10)$$

where  $[MP]_0$  is the initial MP concentration, the removal efficiency can be described by:

$$Er = 1 - e^{-(k_{O_3} + k_{\bullet OH} \cdot Rct) \cdot \frac{(1 - e^{-k_d t})}{k_d} \cdot [O_3]_0} \quad (11)$$

In Eq. (11), both  $Rct$  and  $k_d$  are water specific, i.e., may depend on temperature, pH, alkalinity, and type of dissolved organic matter (DOC, UV absorbance) [8,13].  $Rct$  is time-invariant and independent of the ozone dose [8].

### 3. Results and discussion

#### 3.1. Fitting the removal of micropollutants during ozonation in the WWTP

As a first approach for modelling the MP removal efficiency, it was considered that the term  $\frac{k_d}{(1 - e^{-k_d t})}$  of Eq. (11) was constant and represented by  $k'_d$  and the following equation was used to fit the observed removals:

$$Er = 1 - e^{-(k_{O_3} + k_{\bullet OH} \cdot Rct) \cdot \frac{[O_3]_0}{k'_d}} \quad (12)$$

where the parameters to compute were  $Rct$  and  $k'_d$ .

Given the somehow different water characteristics of the three campaigns (Table S3), more markedly in campaign 3, which corresponds to a water with lower alkalinity, conductivity, and organic carbon, the data of each campaign, each comprising 12 MPs, was fitted independently, with the first and second campaigns containing 35 data points and the third campaign containing 33 data points. For each campaign, the  $Rct$  and  $k'_d$  values were calculated, in the total of six parameters. Nevertheless, given the not so significant different water characteristics, the data of all the campaigns were also fitted altogether, with the model, thus, comprising only two parameters and a total of 103 data points.

To assess the goodness-of-fit of the models, the coefficient of determination ( $R^2$ ) and the Mean Absolute Percentage Error (MAPE, Eq. (S1)) were calculated. Two modelling approaches were compared: (i) fitting each campaign independently (six parameters in total) and (ii) fitting all campaign data jointly (two parameters). For this comparison, four metrics were evaluated: global  $R^2$ , MAPE (Eq. (S1)), and adjusted  $R^2$  (Eq. (S2)), for which higher values indicate a better fit, and the Akaike Information Criterion (AIC, Eq. (S3)), for which lower values indicate greater model parsimony [29].

The computed parameters and the goodness-of-fit values are presented in Table 1.

By analysing the goodness-of-fit values of both approaches, it can be concluded that both models describe the removals very well ( $R^2 = 0.92$  and MAPE = 5.4% for the three sets independently vs.  $R^2 = 0.89$  and MAPE = 6.7% for the three sets together). When comparing the adjusted  $R^2$  and AIC values of both models, it can be concluded that the model considering the three sets independently performs better (adjusted  $R^2 =$

0.91 and AIC = −604 for the three sets independently vs. adjusted  $R^2 = 0.89$  and AIC = −583 for the three sets together) and this modelling approach was, therefore, herein adopted.

Fig. 1a) shows MP removal functions derived for each dose versus the  $k_{O_3} + k_{\bullet OH} \cdot Rct$  values and the corresponding data points, whereas Fig. 1b) shows the predicted removals vs. the measured removals. It can be observed that the model accurately describes the removals of the 12 measured MP removals across 103 observations, with the predicted values clustered along the 1:1 line, although with a light tendency to overpredict the removals for lower ozone doses. This lead us to conclude that the simplification of eq. (12) is valid for our system.

From the fittings produced,  $Rct$  values in the range of  $2.0 \times 10^{-5}$  to  $3.0 \times 10^{-5}$  and  $k'_d$  values between  $55 \text{ s}^{-1}$  and  $68 \text{ s}^{-1}$  were obtained. Using the definition of  $k'_d$  and considering the hydraulic residence time of ozone in the reactor ( $\approx 2400 \text{ s}$ ),  $k_d$  values between  $55 \text{ s}^{-1}$  and  $68 \text{ s}^{-1}$  were obtained ( $k_d \approx k'_d$  for these conditions; for  $k_d' \lesssim 4 \times 10^{-3} \text{ s}^{-1}$  different values are obtained). This pseudo first-order constant for ozone decay in the water is unusually high when compared to published values, which lie in the range of  $10^{-3}$ – $10^{-2} \text{ s}^{-1}$  in secondary effluents and reclaimed waters [6,9,25,30,31]. Nevertheless, the waters in these studies possess lower organic content, lower alkalinity, no or minor industrial contribution or colour content, factors that increase ozone decay. On the other hand, it can also be due to a very high instantaneous ozone demand, which according to Hogard et al. [30] can be in the range of 58–80% of the DOC concentration. From our results and given the high DOC and colour content of the wastewater herein studied, we believe that ozone decomposition is controlled by direct reactions between ozone and highly reactive moieties of the DOM rather than by the autocatalytic chain reaction, as already previously hypothesized by Buffle et al. [5], thus strengthening the validity of our modelling approach.

The  $Rct$  value is also higher than the usually reported values, which commonly lie in the range of  $10^{-6}$ – $10^{-9}$  [5,6,9,25], though values in the range of  $10^{-5}$  have also been reported [11,30]. The higher  $Rct$  value herein derived is due to the low ozone exposure herein calculated ( $4 \times 10^{-6}$  to  $1 \times 10^{-5} \text{ M s}$ ), linked to the high ozone decomposition. The computed  $O_3$  exposure is lower than commonly reported values for similar ozone doses ( $10^{-5}$  to  $10^{-2} \text{ M s}$ ) [5,6,25], though for low  $O_3$  doses ( $0.1$ – $0.25 \text{ g O}_3/\text{g DOC}$ ),  $O_3$  exposures in the range of  $10^{-6} \text{ M s}$  have been reported [11,30]. The  $\bullet OH$  exposures herein calculated,  $8 \times 10^{-11}$  to  $2 \times 10^{-10} \text{ M s}$ , are in the ranges commonly reported ( $10^{-11}$  to  $10^{-10} \text{ M s}$ ) [6,11,30].

Fig. 2 shows the remaining fraction ( $1 - Er$ ) and the predicted model curves as a function of the effective ozone concentration for benzotriazole and venlafaxine and Fig. S2 (supplementary information) shows the same representations for the other 10 MPs (caffeine, hydrochlorothiazide, ibuprofen, ketoprofen, fluoxetine, irbesartan, naproxen, sulfamethoxazole, carbamazepine, and diclofenac). As can be observed, all MPs are quite accurately described by the model, with MAPE values ranging from 0.4% (diclofenac) to 10% (caffeine and ibuprofen) and  $R^2$  values ranging between 0.40 (caffeine) and 0.94 (benzotriazole), except for the MPs that show very high and very small removal variations (1 to 4 percentual points) with the ozone dose (naproxen, sulfamethoxazole, and diclofenac). These MPs, thus, possess negative  $R^2$  values (indicated by a “—” sign in the graphs of Fig. S2), because the removal varies only marginally with dose and  $R^2$  becomes non-informative under such near-

**Table 1**  
Computed parameters and goodness-of-fit values of the fittings.

| Set       | $Rct$                 | $k'_d \text{ (s}^{-1}\text{)}$ | $R^2$      |        | Adjusted $R^2$ | MAPE (%)   |        | AIC  |
|-----------|-----------------------|--------------------------------|------------|--------|----------------|------------|--------|------|
|           |                       |                                | Individual | Global |                | Individual | Global |      |
| 1         | $2.34 \times 10^{-5}$ | 55.2                           | 0.90       | 0.92   | 0.91           | 5.5        | 5.4    | −604 |
| 2         | $2.05 \times 10^{-5}$ | 59.7                           | 0.91       |        |                | 7.4        |        |      |
| 3         | $2.99 \times 10^{-5}$ | 68.0                           | 0.94       |        |                | 3.2        |        |      |
| 1 + 2 + 3 | $2.40 \times 10^{-5}$ | 60.4                           |            | 0.89   | 0.89           |            | 6.7    | −583 |

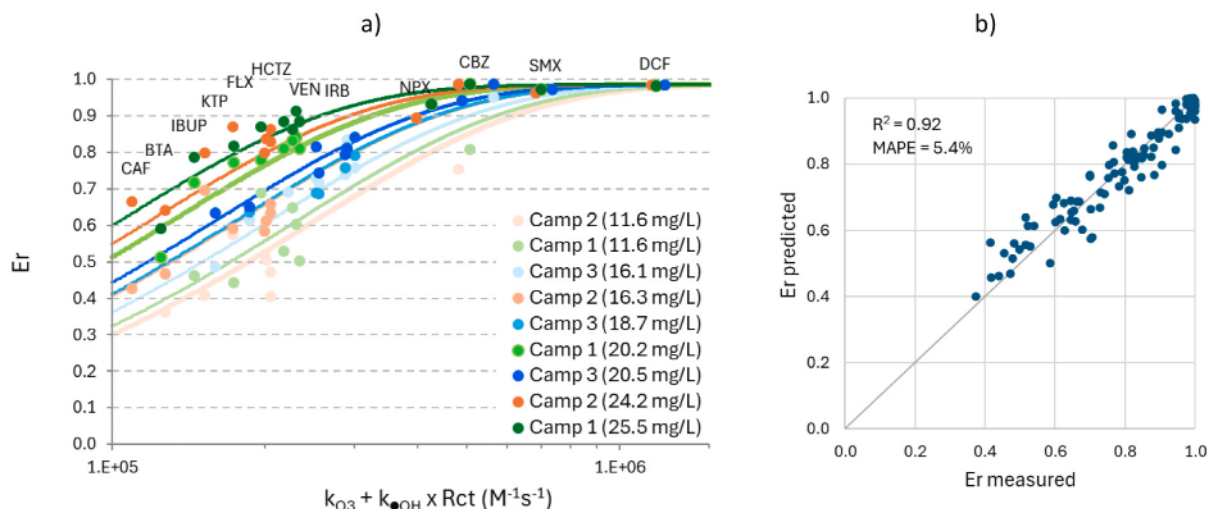


**Fig. 1.** a) MP removal functions derived for each ozone dose at LOR vs  $k_{O_3} + k_{OH} \cdot R_{ct}$  values and the corresponding data points, and b) predicted removals vs. measured removals (the line represents  $y = x$ ).

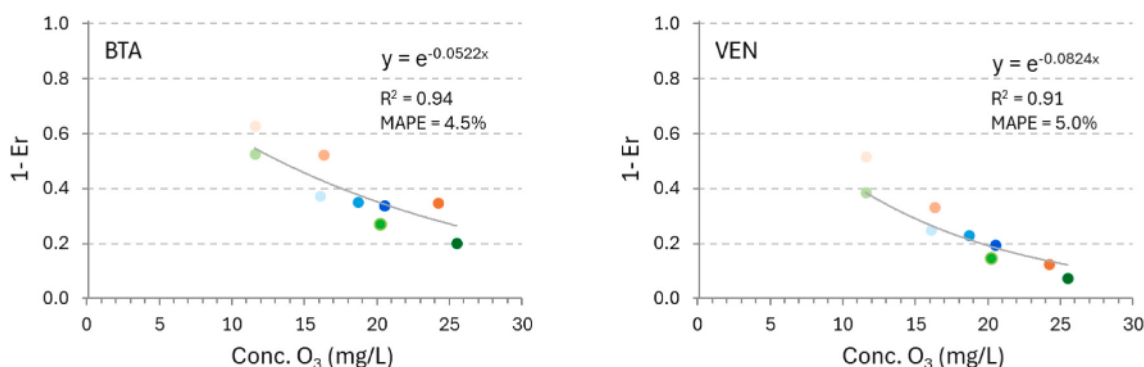


**Fig. 2.** Benzotriazole and venlafaxine remaining fractions (1-Er) as function of effective ozone concentration. Data points of each campaign (colour code of Fig. 1a) and model curves in grey.

saturation conditions.

Using full-scale calibration and two parameters, our phenomenological formulation reproduced the removals of 12 micropollutants over 103 observations (Fig. 1b) with  $R^2 = 0.92$  and MAPE = 5.2% (compound-level MAPE 0.4–10%;  $R^2$  up to 0.94; Fig. 2 and Fig. S2). In contrast, Zimmermann et al. [25] transferred a hydraulics-plus-kinetics mechanistic model calibrated with laboratory batch tests to a full-scale ozonation stage; while trends were captured, the model overpredicted several compound abatements by up to a factor of 2.5, which the authors attributed to colloid shielding and  $R_{ct}$  mismatches; slowly ozone-reactive MPs could be predicted within a factor of  $\sim 1.5$  using batch data from the same plant. More recently, Meyer et al. [11] determined laboratory  $k_{O_3}$  (87 parent compounds, 130 metabolites) and combined these with predicted  $k_{OH}$  and plant-specific oxidant exposures to model abatement in three full-scale WWTPs, reporting good agreement ( $R^2 = 0.47$ – $0.79$ ) between modelled and observed field removals. Complementarily, Atallah Al-asad et al. [12] calibrated a mechanistic DOM-fractionation model on lab ozone-decay data and validated at full scale: predictions were good for high ozone-reactive compounds (e.g., diclofenac, carbamazepine), whereas for compounds with intermediate ozone reactivity (e.g., benzotriazole, metoprolol) were underestimated by an  $R_{ct}$  approach though improved when radical chain reactions were explicitly modelled.

Together, these studies show that lab-based mechanistic calibration can predict full-scale removals, but performance may strongly depend on accurately transferring oxidant exposures and matrix effects. By

comparison, our full-scale-calibrated two-parameter phenomenological model attains comparable or superior accuracy across 12 MPs with minimal model complexity.

### 3.2. Novel experimental determination of $k_{OH}$ for four directive-listed micropollutants

Given that the developed model accurately predicted the removals of 12 micropollutants with known second-order rate constants for ozone ( $k_{O_3}$ ) and hydroxyl radicals ( $k_{OH}$ ), the model-derived values of  $R_{ct}$  and  $k_d'$  (one pair per campaign) were considered reliable. These values were then used to fit, via Eq. (12), the removals of amisulpride, citalopram, candesartan, and 4/5-methyl-benzotriazole. These four compounds are included among the 12 indicators listed in the revised UWWTD. From this fitting procedure,  $k_{OH}$  values were calculated. To the best of our knowledge, these constants have not previously been determined experimentally and were only recently predicted [11].

Their fittings are presented in Fig. 3 (for the remaining fractions, 1-Er) and the  $k_{OH}$  constants obtained are presented in Table 2.

As can be observed, the four MPs are well described by the model, with MAPE values ranging from 6% (citalopram and 4/5-methyl-benzotriazole) to 11% (amisulpride and candesartan) and  $R^2$  values ranging between 0.71 (amisulpride) and 0.96 (4/5-methyl-benzotriazole).

The determined  $k_{OH}$  constants were compared to the predicted values reported by Meyer et al. [11], obtained through the two approaches they identified as the most reliable, QSPR and pySiRC,

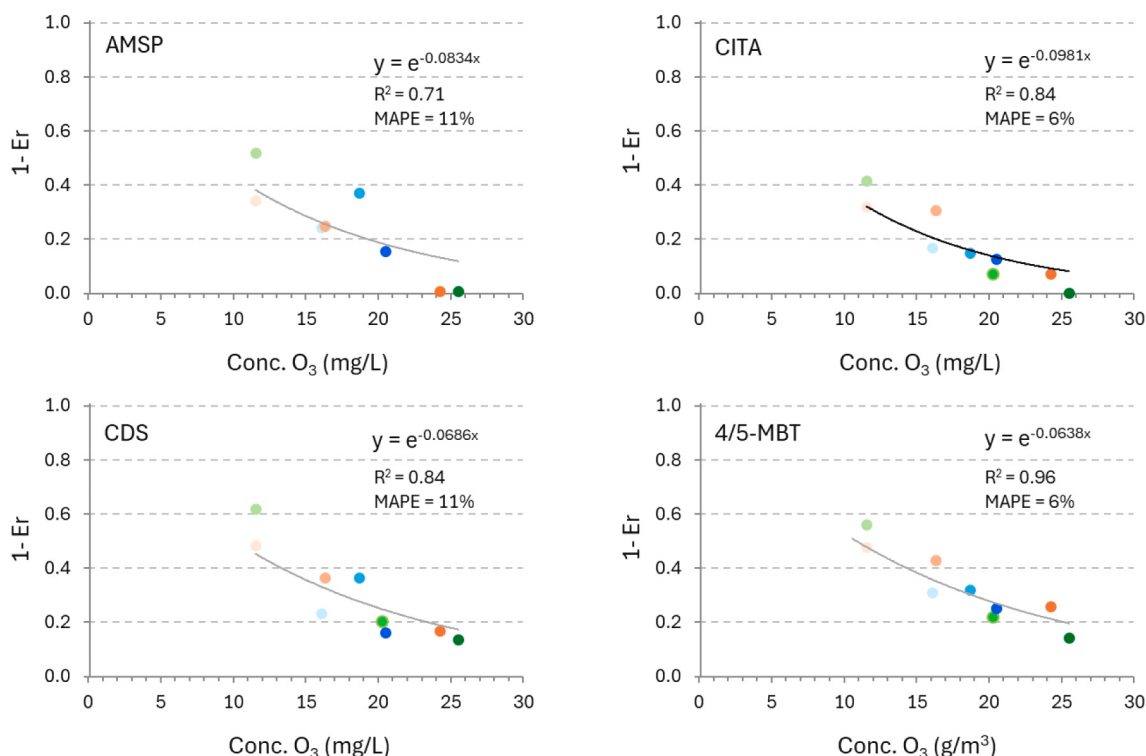


**Fig. 3.** Amisulpride, citalopram, candesartan, and 4/5-methyl-benzotriazole remaining fractions (1-Er) as function of effective ozone concentration. Data points of each campaign (color code of Fig. 1a) and model curves in grey.

**Table 2**

Hydroxyl radical constants ( $k_{OH}$ ) obtained for amisulpride, citalopram, candesartan, and 4/5-methyl-benzotriazole.

| Compound                 | Label   | Category         | LOQ (ng/L) | $k_{O_3} \text{ M}^{-1} \text{ s}^{-1}$ | $k_{OH} \text{ M}^{-1} \text{ s}^{-1}$ |
|--------------------------|---------|------------------|------------|-----------------------------------------|----------------------------------------|
| Amisulpride              | AMSP    | Psychiatric drug | 1.6        | $1.5 \times 10^5$                       | $1.0 \times 10^{10}$                   |
| Citalopram               | CITA    | Psychiatric drug | 0.15       | $2.5 \times 10^4$                       | $1.1 \times 10^{10}$                   |
| Candesartan              | CDS     | Antihypertensive | 1.4        | $5.6 \times 10^2$                       | $8.7 \times 10^9$                      |
| 4/5-Methyl-benzotriazole | 4/5-MBT | Anticorrosive    | 21         | $5.7 \times 10^2$                       | $8.1 \times 10^9$                      |

available for amisulpride, citalopram and candesartan. The herein experimentally derived constants determined are in very good agreement with these predicted by Meyer et al. [11]:  $1.0 \times 10^{10}$  vs.  $(9.1\text{--}9.2) \times 10^9$  for amisulpride,  $1.1 \times 10^{10}$  vs.  $(0.89\text{--}1.2) \times 10^{10}$  for citalopram, and  $8.7 \times 10^9$  vs.  $(6.6\text{--}9.4) \times 10^9$  for candesartan. Accordingly, the  $k_{OH}$  constants derived in this work can be regarded as good approximations of the intrinsic second-order rate constants, although they should ideally be refined using more fundamental experimental techniques such as those described by Mathon et al. [9] and Von Gunten [28]. For 4/5-methyl-benzotriazole, to the best of our knowledge, its  $k_{OH}$  constant has not been previously reported.

When comparing the newly determined  $k_{OH}$  constants and published  $k_{O_3}$  constants for citalopram, 4/5-methyl-benzotriazole, and candesartan, with those of the other target compounds, we predict that citalopram will be abated by ozone to a degree similar to venlafaxine, whereas 4/5-methyl-benzotriazole and candesartan should display abatement profiles analogous to fluoxetine, respectively. Plotting their observed removal efficiencies against one another confirms these predictions (Fig. S3).

### 3.3. Establishing a proxy for online monitoring of micropollutants

The change in the UV/Vis absorbance of DOM has been widely used as an empirical parameter for predicting micropollutant removal during ozonation of wastewaters [5,20–22] and very good correlations have been found for ozone exposure [5] or the consumed ozone (TOD) [32],

the latter expressed as:

$$-\ln\left(\frac{Abs}{Abs_0}\right) = k_{Abs,O_3} \cdot TOD \quad (13)$$

where  $Abs$  and  $Abs_0$  are the final and initial UV/Vis absorbances,  $k_{Abs,O_3}$  is a pseudo first-order reaction kinetic constant of absorbance with ozone and TOD is the transferred ozone dose.

For testing this hypothesis, correlations between TOD and A254 and A436, a colour indicator, were assessed, with the data of all the campaigns fitted altogether (Campaigns 1–3) and separately (Campaign 1, Campaign 2, Campaign 3), following the same approach as when fitting the removal of MPs (Section 3.1). The fittings shown in Fig. S4 show very good correlations for both A254 and A436, when fitted together ( $R^2 = 0.994$  for A254 and  $R^2 = 0.995$  for A436) and when fitted separately ( $R^2 = 0.999\text{--}1.000$  for A254 and  $R^2 = 0.997\text{--}1.000$  for A436), confirming the validity of Eq. (13).

Thus, combining Eqs. (12) and (13), Eq. (14) is obtained for estimating MP removal:

$$Er = 1 - \left(\frac{Abs}{Abs_0}\right)^{\frac{k_{O_3} + k_{OH} \cdot R_{Cf}}{k_{Abs,O_3} \cdot k_d}} \quad (14)$$

With all variables and parameters fixed from the previous determinations, predicted versus measured removals were generated using both A254 and A436 as inputs to Eq. (14), testing two configurations, following the approach of Section 3.1: campaign-specific simulations

(six-parameter model) and a joint simulation across the three campaigns (two-parameter model). As shown in Fig. S5 and in Table S4, both surrogates perform strongly (A254:  $R^2 = 0.91$ , MAPE = 5.4%–5.8%; A436:  $R^2 = 0.92$  and MAPE = 4.9%–5.2%) and the AIC favoured the parsimonious A436 joint model (AIC = –615 vs. –611), which we therefore adopted.

Using absorbance at 436 nm as the surrogate, the resulting phenomenological forward model (Eq. (14)) accurately reproduced 12 measured MP removals across 103 observations (Fig. 4), with the predicted values clustered along the 1:1 line, with  $R^2 = 0.92$  and MAPE = 5.2%, indicating high explanatory power and low bias over the operative range ( $Er \approx 0.4$ –1). Importantly, these statistics result from forward simulation with previously determined parameters rather than re-fitting Eq. (14), underscoring that the simplified kinetics coupled to A436 captures the dominant drivers of ozone-based abatement.

Overall performance is comparable to, or exceeds, reported both per-compound empirical relationships and global (multi-compound) formulations that link UV/Vis or fluorescence signals to MP removal in secondary effluents, supporting A436 as a robust proxy for near-real-time monitoring and control. Gerrity et al. [20] developed empirical regressions between  $\Delta A_{254}$  and total fluorescence ( $\Delta TF$ ) and the abatement of 18 MPs in bench-scale tests; they reported compound-specific fits with  $R^2 \approx 0.50$ –0.83, supporting the feasibility of using UV/fluorescence signals as surrogates for micropollutant removal. Pang et al. [14] showed linear correlations ( $R^2 > 0.9$ ) between  $\Delta A_{254}$  and  $\Delta TOC$  and overall removal of 58 compounds. Sgroi et al. [23], at pilot scale, examined six pharmaceuticals and obtained per-compound correlations with PARAFAC fluorescence components (humic-/tryptophan-like) and A254; each pharmaceutical required its own regression and A254 decreases were typically small during treatment. Stapf et al. [22], also at pilot scale, implemented online  $\Delta A_{254}$  for ozone process control in secondary effluent (no regressions reported), reinforcing UV absorbance as an operational indicator. From the broader compilation in Lim et al. [21], Park et al. [33] work stands out as a phenomenological formulation calibrated in lab for 13 MPs: using A254 the overall  $R^2$  was 0.92 (with per-compound  $R^2 \approx 0.82$ –0.95), and using total fluorescence the overall  $R^2$  was 0.92 (with per-compound  $R^2 \approx 0.86$ –0.96); however, this surrogate coupling added two calibration parameters beyond the two in the underlying removal model. Also summarized by Lim et al. [21], Bahr et al. [34] (pilot, 12 MPs) reported per-compound empirical A254 correlations with  $R^2 \approx 0.39$ –0.95, and Chon (lab, 6 MPs) reported per-compound A254 correlations with  $R^2 \approx 0.85$ –0.99. Taken together,

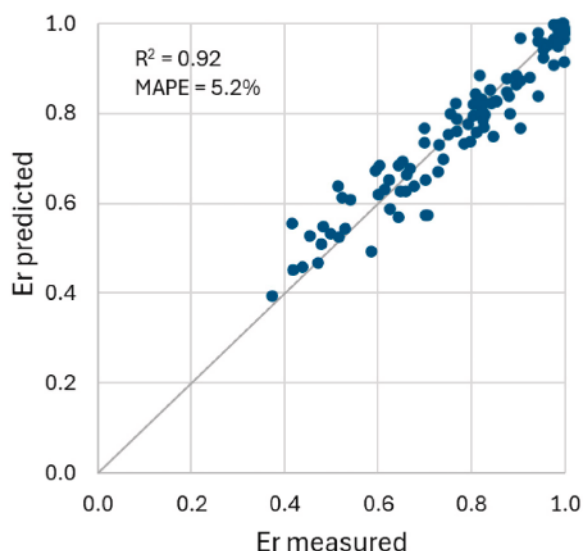


Fig. 4. Predicted removals, simulated by Eq. (14), vs. measured removals using A436 as proxy (the line represents  $y = x$ ).

most published surrogate–MP relationships are empirical; aside from Park et al.'s [33] work, we did not identify additional phenomenological surrogate models in these sources. Against this backdrop, our approach achieves literature-level accuracy while retaining a two-parameter phenomenological removal model and a two-parameter surrogate coupling (one shared, one distinct), with independent calibration of each component.

In our work, fluorescence spectroscopy data, analysed via PARAFAC of excitation–emission matrices (EEMs), were also tested as a proxy for MP removal and produced results comparable to those obtained with A254; accordingly, they are omitted for brevity.

#### 4. Conclusions

We proposed and tested a compact phenomenological framework for predicting and monitoring the removal of organic micropollutants during full-scale wastewater ozonation. First, a two-parameter removal model calibrated with full-scale observations accurately reproduced the behaviour of 12 micropollutants over 103 data points, yielding overall  $R^2 = 0.92$  and MAPE = 5.4%, with compound-wise errors from 0.4% to 10% and  $R^2$  up to 0.94; only compounds showing very small removal variation with ozone dose exhibited unstable  $R^2$ . The analysis supports the validity of the simplified kinetic model across the explored operating window and indicates only a mild tendency to overpredict at the lowest ozone doses.

Second, for online implementation, we developed and evaluated a surrogate-driven forward model based on the phenomenological formulation. Using A436 yielded the best balance between parsimony and accuracy: the two-parameter joint model (pooled across three campaigns) achieved  $R^2 = 0.92$ , MAPE = 5.2%, and the lowest AIC (–615), marginally outperforming A254 ( $R^2 = 0.91$ , MAPE = 5.8%). These results substantiate A436 as a practical proxy for near-real-time tracking and soft-sensor deployment.

A further contribution is the experimental determination of  $k_{OH}$  for four directive-listed micropollutants, obtained by inverse modelling from the measured removals of amisulpride, citalopram, candesartan, and 4/5-methyl-benzotriazole in our full-scale dataset, using the calibrated removal model with their  $k_{OH}$  as the only adjustable parameters. The resulting constants closely match recent predictions for amisulpride, citalopram and candesartan and constitute, to our knowledge, the first experimental value for 4/5-methyl-benzotriazole. This new kinetic evidence reduces uncertainty in indirect-oxidation pathways and strengthens calibration and validation of prediction and monitoring tools.

This approach has the advantage of reflecting real treatment conditions, accounting for water-matrix effects and operating parameters, and allowing simultaneous estimation for multiple compounds. The proposed framework is deliberately parsimonious, reducing data requirements and facilitating implementation in other facilities, while enabling integration into operational frameworks (e.g., setpoint definition, performance tracking, and early-warning monitoring). In contrast, bench-scale experiments are time-consuming, may not be feasible for large numbers of compounds, and rely on idealised conditions. Our full-scale modelling method, while capturing realistic treatment conditions, may be limited by the accuracy of measured removal efficiencies, assumptions embedded in the kinetic simplifications, and potential site-specific effects that may reduce transferability to other plants or matrices. Future work should validate the formulation across additional WWTPs, explore other surrogate inputs (e.g., fluorescence), potentially broaden the  $k_{OH}$  dataset, and integrate process-constraint modules (e.g., formation of bromate or other oxidation byproducts, energy/ozone efficiency) for plant-wide control.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.desal.2026.120060>.

## Data availability

Data will be made available on request.

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