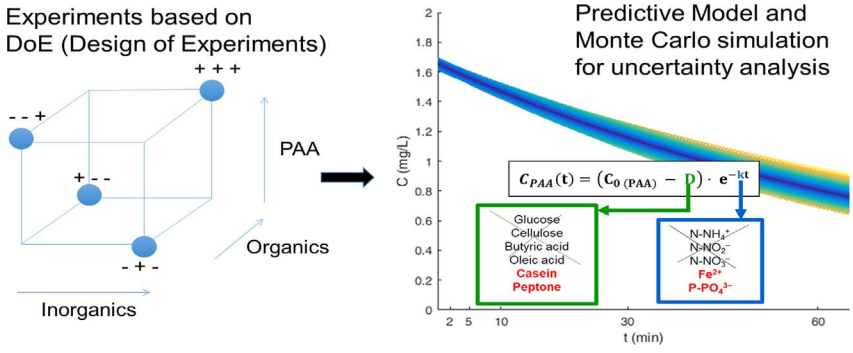
# Influence of inorganic and organic compounds on the decay of peracetic acid in wastewater disinfection

Laura Domínguez Henao, Riccardo Delli Compagni, Andrea Turolla, Manuela Antonelli*

Politecnico di Milano, Department of Civil and Environmental Engineering (DICA) – Environmental Section, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

The aim of this study was to evaluate the influence of the physical–chemical characteristics of wastewater on PAA decay, in multi-component solutions of inorganic and organic compounds (11 compounds in total) re-presentative of secondary effluents of wastewater treatment plants, disinfected at various PAA concentrations (2–5 mg/L). Batch experiments were defined using the statistical method of the Design of Experiments (DoE) in order to evaluate the effect of each compound and their interaction on PAA decay. Results showed that the organics consumed immediately a considerable amount of PAA, independently from the initial PAA con-centration, and consumption dropped rapidly to almost nil after 5 min, whereas PAA consumption due to the inorganics was slow, dependent on the initial PAA concentration and persisted until the end of the experiments (60 min). In detail, inorganics (such as reduced iron and orthophosphate) have shown to be the main drivers of the exponential decay: iron, particularly, has proved to directly consume PAA due to its catalysing capacity, whereas orthophosphate has shown to mainly interact with iron, acting as a chelating compound towards iron and consequently reducing the iron effect in consuming PAA. As for organics, proteins such as, casein and peptone, have been highlighted as the main cause of the initial PAA demand, probably due to the homolytic fission of PAA to generate peroxyl and hydroxyl radicals, which are known to have a high reactivity towards proteins. Finally, a model for predicting the residual PAA concentration was obtained and validated; uncertainty analysis was also performed by a series of Monte Carlo simulations to propagate input uncertainties to the model output.

## GRAPHICAL ABSTRACT




**Keywords:** Wastewater disinfection Peracetic acid, Decay rate, Oxidative demand Uncertainty analysis

Received 4 October 2017;
Received in revised form 13 December 2017;
Accepted 15 December 2017
Available online 16 December 2017

* Corresponding author.
*E-mail address:* manuela.antonelli@polimi.it (M. Antonelli).


Published Journal Article available at https://doi.org/10.1016/j.cej.2017.12.074

## 1. Introduction

The ongoing population growth has often challenged the water supply systems in many areas of the world [1], leading to severe shortage of water. Consequently, the reuse of treated wastewater to reduce the gap between water demand and available water resources is drawing increasing attention in recent years [2]. In particular, reclaimed water from treated municipal effluents is increasingly used as an alternative source for a wide range of applications, such as irrigation of public areas and crops, industrial use and groundwater recharge [3]. Regardless of the type of wastewater reuse, a disinfection stage is required in wastewater treatment plants (WWTPs) to ensure a good microbiological quality of the discharged effluent [4]. Chlorine-based compounds are still the most widespread disinfectants even though many studies [5–7] reported that reactions between chlorine and organic matter lead to the formation of carcinogenic disinfection by-products in the treated effluents. For this reason, alternative disinfecting agents, such as peracetic acid (PAA), were investigated for wastewater treatment over the past years [8]. PAA is a strong oxidizing agent with an oxidation potential higher than chlorine, which determines its high antimicrobial activity [9]. PAA has proved to be effective against many microorganisms including bacteria, viruses, bacterial spores and protozoan cysts [10–13], guaranteeing no appreciable re-growth after disinfection [14]. In addition, no harmful disinfection by-products (DBPs) are formed during PAA treatment [15–18]. Concerning the application of PAA disinfection in WWTPs, initial PAA concentration and contact time were widely studied as the most relevant operating parameters for determining PAA disinfection efficacy against microorganisms. In particular, several works [12,19–21] showed that initial PAA concentrations from 1 to 15 $mg_{PAA}\,L^{-1}$ and contact times from 15 to 60 min can result in proper disinfection of primary, secondary and tertiary effluents. However, PAA decomposes rapidly in water solution and the rate of this process is highly affected by the water matrix composition [8,9,12,13,22,23]. A key step for guarantying a sufficient disinfectant residual concentration to reach bacterial inactivation targets, avoiding excessive residuals consists in the assessment of the influence of wastewater characteristics on PAA decay, in terms of easy-to-measure parameters, thus on the actual PAA dose. Currently, experimental works on this topic are either missing or were carried out as preliminary assessments. In more detail, past studies [24–26] reported that the presence of some inorganic compounds induces the catalytic decomposition of PAA, especially transition metals, such as $Fe^{2+}$, $Mn^{2+}$, $Cu^{2+}$ and $Co^{2+}$. Regarding salinity, the study of Liu et al. [22] revealed that it has a significant effect on PAA decay. In contrast, the same authors found that water hardness had only a slight impact on PAA degradation. On the other hand, to the best author's knowledge, no research work investigated the potential effect on PAA decay of many common inorganic ions, as inorganic nitrogen compounds or phosphorus compounds. The effect of pH on PAA disinfection and stability has been reported by various authors [8,9,13,27], who have observed that pH values above 9 lead to higher PAA decomposition rates. Indeed, given that the $pK_a$ of PAA is 8.2, it is expected that at pH higher than this value the equilibrium will move toward the dissociated form ($CH_3CO_3^-$). According to Yuan et al. [27], the hydrolysis of PAA to acetic acid is only slightly affected by pH ranging from 5.5 to 9.0. This was confirmed by Pedersen et al. [23] who found that PAA decay was comparable at pH adjusted between values of 6.4 and 8.6, which are typical values for wastewaters. As a consequence, pH exhibits a moderate effect on PAA decay in the usual range that this parameter assumes in conventional treatment conditions in WWTPs. As for organic compounds, the majority of previous works [12,22,28–30] focused on the effect of the organic content in the effluent through macro-indicators, as COD or DOC, highlighting a general trend according to which the higher is the organic content higher is the PAA degradation. However, the extent of PAA degradation is different among the studies available at similar COD/DOC concentrations. This observation can be explained considering that organic compounds act differently on PAA decay depending on molecular characteristics, a major drawback of these macro-indicators is that they do not discriminate the individual effect of specific compounds, such as carbohydrates, lipids and proteins, in turn contained at different extent in WWTP effluents [31]. As for total suspended solids, although scarcely studied up to now, a significant PAA consumption has been outlined [12,19,20,30,32], but it has to be pointed out that most of the organic matter (around 86%) present in secondary effluents is expected to be in the soluble fraction [31,33]. Moreover, most of the past research works focused on investigating the effect of one factor at a time, without considering the occurrence of interaction effects between two or more factors.

The purpose of this study is firstly to identify which inorganic and organic compounds commonly present in the soluble fraction of wastewater can individually and/or jointly affect PAA decay, and secondly the development of a reliable mathematical model to predict residual PAA concentration over time as a function of the constituents of the WWTP effluent. In detail, eleven compounds were evidenced as potentially relevant for PAA decay based on a preliminary literature review as well as on the expertise of experimenters. Inorganic compounds were ammonia nitrogen ($NH^{4+}$), nitrate ($NO^{3-}$), nitrite ($NO^{2-}$), reduced iron ($Fe^{2+}$) and orthophosphate ($PO_4^{3-}$), whereas organic compounds were surrogates of carbohydrates (glucose and cellulose), lipids (butyric and oleic acids) and proteins (peptone and casein). Experiments were divided in two experimental plans, one for inorganics and one for organics, which were defined using the statistical method of the Design of Experiments (DoE). This methodology allowed to evaluate the effect exerted by each compound and to evidence the occurrence of interaction effects. After the development of the model and its validation by a set of experiments in which inorganics and organics displaying a significant effect were simultaneously present, an uncertainty analysis was performed by Monte Carlo simulations to propagate the input uncertainties to model output.

## 2. Materials and methods

### 2.1. Reagents and experimental setup

PAA technical grade solution (VigorOx® WWTII) was supplied by PeroxyChem (USA), whose composition as weight percentage is 15% of peracetic acid, 23% of hydrogen peroxide and 16% of acetic acid. The PAA concentration in the commercial solution was checked monthly by iodometric titration [34]. All chemicals were reagent grade purchased from Sigma Aldrich (USA), except for DPD (N,N-diethyl-p-phenylenediaminesulphate) salt that was purchased from Hach Lange (USA). All the stock solutions for the inorganic compounds were prepared according to Standard Methods [35]. The stock solutions containing the organic compounds or their surrogates, were prepared to have a concentration 1000 $mg\,L^{-1}$ in terms of COD for each compound. The calculations required to prepare the stock solutions were based on the Theoretical Oxygen Demand (ThOD) values of each organic compound [36].

1-h PAA decay tests were performed in completely mixed batch reactors (1 L glass beakers) mixed by magnetic stirrer in dark conditions at room temperature (20 ± 1 °C). In each beaker, a given aliquot of the stock solutions, according to the experimental plan described in Sections 2.3 and 2.4, was added to deionized water and the pH of the solutions was adjusted to 7.5 at the beginning of the tests with sodium hydroxide (NaOH) or sulphuric acid ($H_2SO_4$) and monitored during the tests. After pH adjustment, a selected aliquot of PAA stock solution was added to obtain the given PAA initial concentration. Samples were collected at five contact times (2, 5, 10, 30 and 60 min). Preliminary tests were performed in deionized water to estimate PAA decay in absence of inorganic and organic compounds (blank tests). Experiments were performed in triplicate for three initial PAA concentrations (2, 5 and 10 $mg_{PAA}\,L^{-1}$).

### 2.2. Experimental plan for inorganics and organics

Two fractional factorial designs, one for inorganics (paragraph 2.3) and one for organics (paragraph 2.4), were defined to identify the most important factors affecting PAA decay within a large number of compounds and to assess the occurrence of interaction effects. The choice of having two separate experimental plans was based on two main reasons: (i) a unique experimental plan would have required too many experiments and, (ii) the chemical properties of molecules, as size, polarity, type of molecular bonds, are such that interaction effects between inorganic and organic compounds are neither expected nor, in case of occurrence, comparable with PAA decay generated by the interaction between two inorganics or two organics [37]. Moreover, the fractional factorial design was selected due to sequential assembly feature allowing experimenters to modulate and develop the design to increase the degree of detail when needed [38].

### 2.3. DoE for inorganics

As a first step, the decay of two initial PAA concentrations (2 and 10 $mg_{PAA}\,L^{-1}$) over time was tested in 16 batch experiments where 5 inorganic compounds (factors) were combined at two pre-defined concentrations (levels) according to a fractional factorial design of resolution V (Table 1): (A) ammonia nitrogen, (B) nitrate, (C) nitrite, (D) reduced iron and (E) orthophosphate. The levels were set as follows: A and B (0.5 and 25 $mg\,L^{-1}$ as N), C (0.1 and 1 $mg\,L^{-1}$ as N), D (0.1 and 5 $mg\,L^{-1}$) and E (1 and 5 $mg\,L^{-1}$ as P). Each experiment was repeated three times for a total of 96 experiments. As a second step, PAA decay at 2 and 10 $mg_{PAA}\,L^{-1}$ was also evaluated in presence of either D or E at the following concentrations: 0.1 and 5 $mg\,L^{-1}$ for D, 1 and 5 $mg\,L^{-1}$ for E. Each experiment was performed in triplicate for a total of 24 experiments. The stability of nitrite over 1 h was verified in preliminary tests by dosing the maximum concentration of nitrite with and without all other inorganic compounds at the highest concentration used in the experimental plan.

### 2.4. DoE for organics

Firstly, the decay of two initial PAA concentrations (2 and 10 $mg_{PAA}\,L^{-1}$) over time was tested in 16 batch experiments where 6 compounds (factors), namely (A) glucose, (B) cellulose, (C) butyric acid, (D) oleic acid, (E) casein and (F) peptone, were combined at two pre-defined levels (10 and 35 $mg\,L^{-1}$ in terms of COD) according to a fractional factorial design of resolution IV (Table 1). Surrogates of compounds B, C and D were used for the tests, namely carboxymethylcellulose, sodium butyrate and sodium oleate, respectively. Each experiment was repeated three times for a total of 96 experiments. Secondly, the following steps have been accomplished: (i) the execution of a full factorial design to evaluate the combined effect of factors E and F on PAA decay at 5 $mg_{PAA}\,L^{-1}$, and (ii) the evaluation of PAA decay at 2 and 5 $mg_{PAA}\,L^{-1}$ in presence of either E or F at the concentrations of 10 and 35 $mg\,L^{-1}$ as COD for both factors. Twelve experiments (4 for the full factorial and 8 for the single trials) were performed and replicated three times for a total of 36 experiments. Finally, (iii) the effect of urea as a single compound on PAA decay was tested by *ad hoc* experiments at two different concentrations of PAA (2 and 5 $mg_{PAA}\,L^{-1}$). In detail, the urea concentrations were set to have the same concentration of organic nitrogen present in both casein and peptone at their lowest and highest concentrations used in the decay experiments, namely 2 and 8 $mg\,L^{-1}$ as N.

**Table 1**
Experimental plan (fractional factorial design) for inorganic and organic compounds in coded units. The two levels of concentration for each compound are identified by '−' for low concentration value and '+' for high concentration value.

| Inorganics | | | | | Experiment | Organics | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | B | C | D | E | | A | B | C | D | E | F |
| − | − | − | − | + | 1 | − | − | − | − | − | − |
| + | − | − | − | − | 2 | + | − | − | − | + | − |
| − | + | − | − | − | 3 | − | + | − | − | + | + |
| + | + | − | − | + | 4 | + | + | − | − | − | + |
| − | − | + | − | − | 5 | − | − | + | − | + | + |
| + | − | + | − | + | 6 | + | − | + | − | − | + |
| − | + | + | − | + | 7 | − | + | + | − | − | − |
| + | + | + | − | − | 8 | + | + | + | − | + | − |
| − | − | − | + | − | 9 | − | − | − | + | − | + |
| + | − | − | + | + | 10 | + | − | − | + | + | + |
| − | + | − | + | + | 11 | − | + | − | + | + | − |
| + | + | − | + | − | 12 | + | + | − | + | − | − |
| − | − | + | + | + | 13 | − | − | + | + | + | − |
| + | − | + | + | − | 14 | + | − | + | + | − | − |
| − | + | + | + | − | 15 | − | + | + | + | − | + |
| + | + | + | + | + | 16 | + | + | + | + | + | + |

### 2.5. Validation of the model

The validation of the final model was performed by testing the consumption of two PAA concentrations (2 and 5 $mg_{PAA}\,L^{-1}$) in four *ad hoc* batch experiments where the inorganic and organic compounds that displayed a significant effect on PAA decay were added simultaneously, as shown in Table 2. In detail, four compounds namely (A) casein, (B) peptone, (C) reduced iron and (D) orthophosphate were combined at two pre-defined concentrations, which were set at the corresponding ones for each compound in the DoEs of inorganics and organics. Each experiment was performed in triplicate for a total of 24 experiments.

### 2.6. Analytical procedures

The residual PAA concentration was measured by a procedure adapted from the US EPA, namely the DPD – colorimetric method (method 330.5) for the determination of total chlorine concentration, as reported in Standard Methods [35]. In detail, collected samples were treated with 2 mL of potassium iodide (KI) (0.5 $mol\,L^{-1}$), 5 mL of phosphate buffer solution pH 5.5 (0.14 $mol\,L^{-1}$ of $Na_2HPO_4 * 12H_2O$, 0.34 $mol\,L^{-1}$ of $KH_2PO_4$, 0.0027 $mol\,L^{-1}$ of EDTA and 0.23 $mol\,L^{-1}$ $H_2SO_4$) and DPD salt to generate a transient colour formation. The colour intensity was measured by a spectrophotometer (Unicam UV/VIS 2) at 530 nm (optical path 40 mm) after 10 s from the addition of DPD salt. Since the absorbance value at 530 nm is linearly proportional to PAA concentration, a standard curve was prepared to describe the relation between absorption value and PAA concentration. In order to avoid the interference of $H_2O_2$ on the measurement, residual $H_2O_2$ was quenched before the addition of the DPD salt by adding 1 μg of bovine catalase (2900 units $mg^{-1}$).

Preliminary tests were performed to assess the interference of inorganic and organic compounds on the DPD – colorimetric method for the measurement of residual PAA concentration. In detail, two experiments (one with all inorganics and another one with all organics) were performed in absence of PAA. In each test the compounds were added at

**Table 2**
Experimental plan for the validation of the model. The two levels of concentration for each compound are identified by '−' for low concentration value and '+' for high concentration value.

| Experiment | Factor | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 1 | + | + | − | − |
| 2 | + | + | + | + |
| 3 | − | − | − | − |
| 4 | − | − | + | + |

the highest concentrations used in the experimental plans and four repetitions were carried out.

The stability over 60 min of the nitrite ion ($NO_2^-$) in solution at the experimental conditions adopted was verified using a Hach Lange kit LCK 341. The COD of the stock solutions of organic compounds was measured by Hach Lange kit LCK 514, whereas the total nitrogen concentrations of the stock solutions of casein and peptone were measured by Hach Lange kit LCK 338. These analyses were performed using a spectrophotometer Dr. Lange XION 500. The pH was measured during the tests with a Eutech 6+ pH meter.

### 2.7. Data processing

The standard curve for PAA measurement was obtained through a linear least-square regression ($R^2 = 0.9995$). The equation is: $ABS = \alpha + \beta \cdot [PAA]$, where ABS is the absorbance value at 530 nm and [PAA] is the PAA concentration ($mg_{PAA}\,L^{-1}$). Estimated coefficients were: $\alpha = 0.0624$, $\beta = 0.5563$.

Values of residual PAA concentration measured during the tests were plotted over time for each experiment (5 PAA residual concentration in triplicate, for a total of 15 data points) and interpolated with a non-linear least-square regression using as models both the first-order kinetic model (Eq. (1)) and the Haas and Finch kinetic model (Eq. (2)) [39].

$$[PAA] = [PAA]_o \cdot e^{-kt} \quad (1)$$

$$[PAA] = ([PAA]_o - D) \cdot e^{-kt} \quad (2)$$

where $[PAA]_0$ is the initial PAA concentration ($mg_{PAA}\,L^{-1}$), k is the decay kinetic rate constant ($min^{-1}$) and D is the initial oxidative consumption ($mg_{PAA}\,L^{-1}$). Mathworks Matlab R2015a software was used for the estimation of coefficients. Furthermore, the estimated coefficients were used as inputs in Minitab 17 software for the statistical analysis of data. As for the uncertainty analysis, a Monte Carlo simulation framework has been coded in Mathworks Matlab R2015a.

## 3. Results and discussion

### 3.1. Preliminary tests

The preliminary tests demonstrated the stability of nitrite in solution under different conditions over 1-h contact time, making nitrite adequate for the experimentation. As for the interference tests on PAA measurements due to inorganic and organic compounds, a negligible effect was observed in all the performed experiments: absorbance values were always below the lowest extreme of the standard curve, corresponding to PAA concentration of $0.176\,mg_{PAA}\,L^{-1}$, suggesting that inorganic and organic compounds do not bias PAA measurement.

Concerning the blank tests, the regression of experimental data by the Haas and Finch kinetic model [39] evidenced the negligible role of oxidative demand on PAA decay (p-values > .05) with values lower than $0.03\,mg_{PAA}\,L^{-1}$ for all tested concentrations, meaning that first-order kinetic model is adequate to describe PAA decay in deionized water. Estimated values for the decay kinetic rate constant $k_{blank}$ differed depending on the initial PAA concentration as shown in Table 3. Finally, $k_{blank}$ was modelled as reported by Eq. (3), resulting from linear interpolation among initial PAA concentrations and estimated $k_{blank}$ values ($R^2 = 0.9439$, N = 3):

$$k_{blank} = 0.00128 - 6.25e^{-5} \cdot [PAA]_0 \quad (3)$$

### 3.2. Effect of inorganics on PAA decay

The Haas and Finch kinetic model demonstrated to fit better all experimental data for inorganics than first-order kinetic model, as reported in Supplementary Material (Figs. S1 and S2). In particular, PAA decay exhibited a scarce oxidative demand (ranging intervals 1.8–12.4% and 1.5–11.5% for an initial PAA concentration of 2 and $10\,mg_{PAA}\,L^{-1}$, respectively) followed by a pronounced exponential decay (up to 14 and 18 times higher than $k_{blank}$ for 2 and $10\,mg_{PAA}\,L^{-1}$, respectively). In Fig. 1 the model coefficients for the 16 experiments with corresponding confidence intervals at 95% of significance are reported. The decay rate constants have been normalized in respect to the decay rate constant of the blank tests ($k_{blank}$).

**Table 3**
Main statistics and regression estimates of $k_{blank}$ for the first-order kinetic model (SE: Standard Error; CI: confidence interval at 95% of significance; N: number of data used for the fitting).

| $[PAA]_0$ ($mg_{PAA}\,L^{-1}$) | $k_{blank}$ ($min^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | Estimate | SE | CI (95%) | $R^2$ | p-value | N |
| 2 | 0.0012 | 0.0001 | 0.0010, 0.0015 | 0.9013 | < .000 | 15 |
| 5 | 0.0009 | 0.0001 | 0.0006, 0.0012 | 0.8000 | < .000 | 15 |
| 10 | 0.0007 | 0.0001 | 0.0005, 0.0009 | 0.8400 | < .000 | 15 |

### 3.3. Effect of inorganics on oxidative demand

With regard to the oxidative demand, a rigorous analysis of data did not highlight any statistically significant correlation between the D values and the presence of inorganics. Therefore, a graphical inspection (often efficient for data obtained using DoE methods) was adopted. D values in Fig. 1a can be sub-grouped as follow: from experiment 1 to 7, where the D values are low (with exception of experiment 2 for $10\,mg_{PAA}\,L^{-1}$) and the confidence intervals are narrow, and from experiment 8 to 16, where high D values and wide confidence intervals are observed (with the exception of experiment 8 where a very narrow confidence interval is observed for both initial PAA concentrations). Specifically, these two modes for confidence intervals are not fortuitous, being the same trend also noticeable for $k/k_{blank}$ values of Fig. 1b. In fact, experiments from 9 to 16 were performed with high iron concentration (see Table 1). A variability analysis subsequently determined a strong relation between the variability of D values and the presence of iron (Supplementary Material, Fig. S3). As for the means of D values, the highest values were observed for experiment 8 ($0.25 \pm 0.03$ and $1.15 \pm 0.25\,mg_{PAA}\,L^{-1}$ for 2 and $10\,mg_{PAA}\,L^{-1}$, respectively), where iron and orthophosphate are present at low concentration, whereas ammonia nitrogen, nitrate and nitrite are present at high concentrations. In detail, the contribution of each of these nitrogen compounds on oxidative demand can be observed by looking at D values of experiments 2, 3 and 5, where only ammonia nitrogen, or nitrate, or nitrite were present at high concentration (see Table 1). It is important to highlight that the addition of these values ($0.27 \pm 0.13$ and $1.27 \pm 0.40\,mg_{PAA}\,L^{-1}$ for 2 and $10\,mg_{PAA}\,L^{-1}$, respectively) is statistically comparable (confidence interval at 95% of significance) with the D value of experiment 8, meaning that the effect of these compounds is additive, and no interaction between these inorganics occurs. As a consequence of these considerations, *ad hoc* experiments were performed in absence of iron to precisely investigate the effect that ammonia nitrogen, nitrate and nitrite have on oxidative demand. In particular, a full factorial design was carried out (Supplementary Material, Table S1). Experimental results evidenced negligible D values ranging from no consumption to maximum values of $0.04 \pm 0.02$ and $0.12 \pm 0.06\,mg_{PAA}\,L^{-1}$ respectively for 2 and $10\,mg_{PAA}\,L^{-1}$, confirming the additive effect. However, estimated D values are low with respect to those in Fig. 1a, meaning that oxidative demand is mainly generated by iron or orthophosphate or an interaction between them.

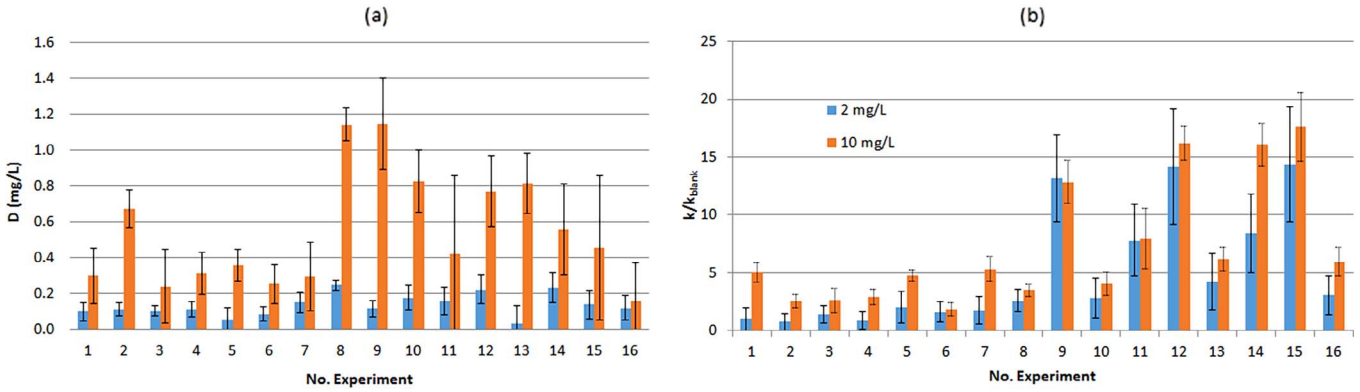



**Fig. 1.** Oxidative demand D (a) and normalized decay rate constant $k/k_{blank}$ (b) of Haas and Finch kinetic model for experiments at 2 and 10 $mg_{PAA}\,L^{-1}$ on inorganics. Confidence intervals at 95% of significance are reported.

### 3.4. Effect of inorganics on decay rate

As for the decay rate constants, reported in Fig. 1b, the statistical analysis was accomplished through a step-wise regression that sorted each compound by the relevance in affecting the decay rate. Data analysis, as shown in Fig. 2, highlighted that iron, orthophosphate and their interaction are the only significant factors (confidence level at 95%). Subsequently, *ad hoc* experiments were performed to investigate the experimental sub-space of iron and orthophosphate towards null values of one or both compounds, as shown in Fig. S4 of Supplementary Material, and to incorporate the experimental data from blank tests. Finally, a least-square regression was used to interpolate a linear model as reported by Eq. (4):

$$k = k_{blank}(b_0 + b_1 \cdot Fe^{2+} + b_2 \cdot PO_4^{3-} + b_{12} \cdot Fe^{2+} \cdot PO_4^{3-}) \quad (4)$$

Table 4 shows the main statistics and regression estimates for the models at 2 and 10 $mg_{PAA}\,L^{-1}$ while a graphical representation of the model is given in Fig. S5 in Supplementary Material. The choice to interpolate data with a linear model is reasonable (p-value for the lack-of-fit test higher than .05). Both models describe experimental data satisfactorily ($R^2$ equals to 0.8870 and 0.9420), with high accuracy on predictions ($R^2_{pred}$ equals to 0.8247 and 0.9119). Residual analysis (not reported) assessed the appropriateness of linear regression hypothesis (normality and homoscedasticity).

Summarizing, reduced iron proved to be the most important factor affecting PAA decay (p-value for $b_1 < .0001$ for both initial PAA concentrations), probably due to its capacity to catalyze PAA decomposition, as discussed by Yuan et al. [24]. On the other hand, orthophosphate does not affect PAA decay (p-value for $b_2$ equals to .887 and .500 for 2 and 10 $mg_{PAA}\,L^{-1}$, respectively). However, the term is kept in the model for hierarchical reasons, whereas significantly interacts with iron (p-value for $b_{12} < .0001$ for both PAA concentrations). The chemical effect of this interaction can be attributed to the role of orthophosphate in acting as chelating compound towards iron, inhibiting its catalysing effect towards PAA. In accordance with the literature [40–45], phosphate molecules can surround heavy metals avoiding their precipitation (known as sequestration), as it occurred in present case, in which no precipitate was observed during experiments. Based on experimental data, when both compounds are at high concentration, the orthophosphate is enough to sequester iron, leading to $k/k_{blank}$ values that are comparable with those observed when low concentration of iron is present. On the other hand, when iron and orthophosphate are at high and low concentration respectively, orthophosphate do not sequester iron completely, resulting in the highest $k/k_{blank}$ values observed. As for the role of initial PAA concentration, the two models can be statistically considered different (see Fig. S5b in Supplementary Material which shows that the confidence intervals do not overlap), meaning that the initial PAA concentration affects PAA decay. In particular, modeling results demonstrate that the higher the initial PAA concentration, the stronger the PAA interaction with iron and orthophosphate leading to a fast PAA decay. Finally, supposing a linear behavior between the coefficients of models and the initial PAA concentration, a unique formulation for decay rate constants is proposed in the equations:

$$b_0 = 0.943 + 0.185 \cdot [PAA]_0 \quad (5)$$

$$b_1 = 2.286 + 0.086 \cdot [PAA]_0 \quad (6)$$

$$b_2 = 0.005 + 0.138 \cdot [PAA]_0 \quad (7)$$

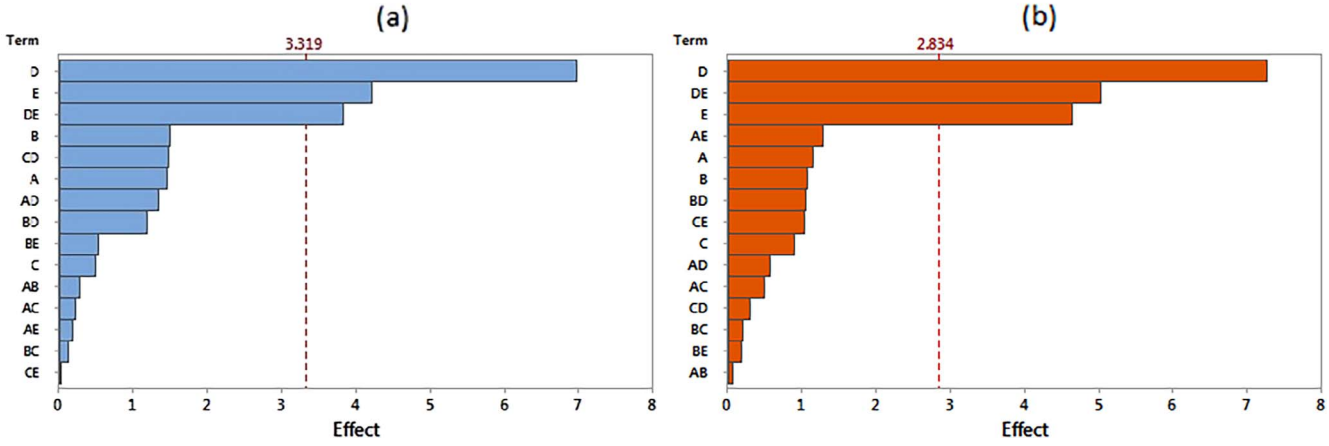



**Fig. 2.** Pareto chart showing factors affecting PAA decay rate at 2 (a) and 10 (b) $mg_{PAA}\,L^{-1}$: the red dashed line represents the significance threshold at 0.05.

**Table 4**
Main statistics and regression estimates of the model for the effect of inorganics on PAA decay rate.

| $[PAA]_0$ ($mg_{PAA}\,L^{-1}$) | Symbol | Estimate | SE | CI (95%) | t-Value | p-value |
|---|---|---|---|---|---|---|
| 2 | $b_0$ | 1.312 | 0.761 | −0.286, 2.910 | 1.72 | .102 |
| | $b_1$ | 2.459 | 0.238 | 1.958, 2.960 | 10.31 | < .000 |
| | $b_2$ | 0.033 | 0.231 | −0.453, 0.519 | 0.14 | .887 |
| | $b_{12}$ | −0.367 | 0.069 | −0.512, −0.222 | −5.31 | < .000 |
| | $R^2 = 0.8870$; $R^2_{adj} = 0.8682$; $R^2_{pred} = 0.8247$; N = 21; Lack-of-fit (p-value) = .706 | | | | | |
| 10 | $b_0$ | 2.788 | 0.661 | 1.399, 4.177 | 4.22 | .001 |
| | $b_1$ | 3.149 | 0.207 | 2.714, 3.585 | 15.19 | < .000 |
| | $b_2$ | 0.144 | 0.201 | −0.278, 0.566 | 0.72 | .500 |
| | $b_{12}$ | −0.531 | 0.060 | −0.657, −0.405 | −8.85 | < .000 |
| | $R^2 = 0.9420$; $R^2_{adj} = 0.9323$; $R^2_{pred} = 0.9119$; N = 21; Lack-of-fit (p-value) = .610 | | | | | |

$$b_{12} = -0.326 - 0.020 \cdot [PAA]_0 \quad (8)$$

### 3.5. Effect of organics on PAA decay

The regression on experimental data at $2\,mg_{PAA}\,L^{-1}$ highlighted a sizeable oxidative demand within the first five minutes (D values ranging between 9.1% and 27.2% of the initial PAA concentration) followed by a smooth exponential decay (k values from 1 to 8 times higher than $k_{blank}$) (see also Fig. S6 of Supplementary Material for model fitting). Fig. 3 shows the model coefficients for the 16 experiments with the corresponding confidence interval at 95% of significance. Contrarily to the results for inorganics, only oxidative demand values were processed by statistical analysis: as for decay rate constants, the high variability results in mean values not statistically different (ANOVA test with p-value > .05). Moreover, the small values of normalized decay rate constants lead to conclude that organics slightly affect PAA decay after the first five minutes. Consequently, it can be inferred that all organics are oxidized by PAA in a short time and their oxidized products, which cannot further affect significantly PAA decay, remain in solution; however, the influence of these reaction by-products on PAA decay could explain the observed k values slightly higher than the $k_{blank}$. Nevertheless, further investigations are needed.

As for $10\,mg_{PAA}\,L^{-1}$ initial PAA concentration, the high variability of the experimental data lead to poor quality of raw data (Supplementary Material, Fig. S8). The reason for this outcome is not clear and further investigations are needed. Furthermore, based on the assumption that the high initial PAA concentration could have been the cause of the poor quality of the raw data, an extra DoE has been performed at the intermediate concentration of $5\,mg_{PAA}\,L^{-1}$. In this case, a full factorial design in two factors has been run. The choice of these factors comes from the results of the step-wise regression for the D values at $2\,mg_{PAA}\,L^{-1}$, later detailed in paragraph 3.3.1, where only proteins (casein and peptone) were highlighted as influencing factors for PAA decay. At $5\,mg_{PAA}\,L^{-1}$ a strong oxidative demand within the first five minutes was observed (D values ranging between 4.0% and 12.8% of the initial PAA concentration) followed by a negligible exponential decay (k values ranging from 1 to 3 times higher than the $k_{blank}$).

### 3.6. Effect of organics on oxidative demand

In Fig. 4, D values at $2\,mg_{PAA}\,L^{-1}$ (obtained from the fractional factorial design) and $5\,mg_{PAA}\,L^{-1}$ (obtained from the full factorial design) are reported. It is important to point out that D values at $2\,mg_{PAA}\,L^{-1}$ can be used for the comparison, thanks to the projection property of the fractional factorial design. In fact, the planned fractional factorial design has resolution IV and projectivity III, meaning that if two of the 6 factors are inert, the design results in a complete $2^4$ full factorial design with the remaining factors. Consequently, the fractional factorial design at $2\,mg_{PAA}\,L^{-1}$ can be projected from a six-dimensional space to a two-dimensional space considering only casein and peptone, that were evidenced as statistically significant.

As shown in Fig. 4, mean values at 2 and $5\,mg_{PAA}\,L^{-1}$ almost coincide, suggesting that the organic compounds are limiting the reaction with PAA for both initial PAA concentrations. Finally, *ad hoc* experiments were performed to investigate the experimental sub-space of casein and peptone towards null values of one or both compounds, and to incorporate the results from the blank test. A linear least-square regression was used to interpolate a linear model as reported by Eq. (9):

$$D = b_3 + b_4 \cdot caseine + b_5 \cdot peptone \quad (9)$$

In Table 5 the main statistics and regression estimates for the model are shown. The choice to interpolate data by a unique model for both initial PAA concentrations is justified by the complete overlap between the confidence intervals of D values at 2 and $5\,mg_{PAA}\,L^{-1}$, indicating a

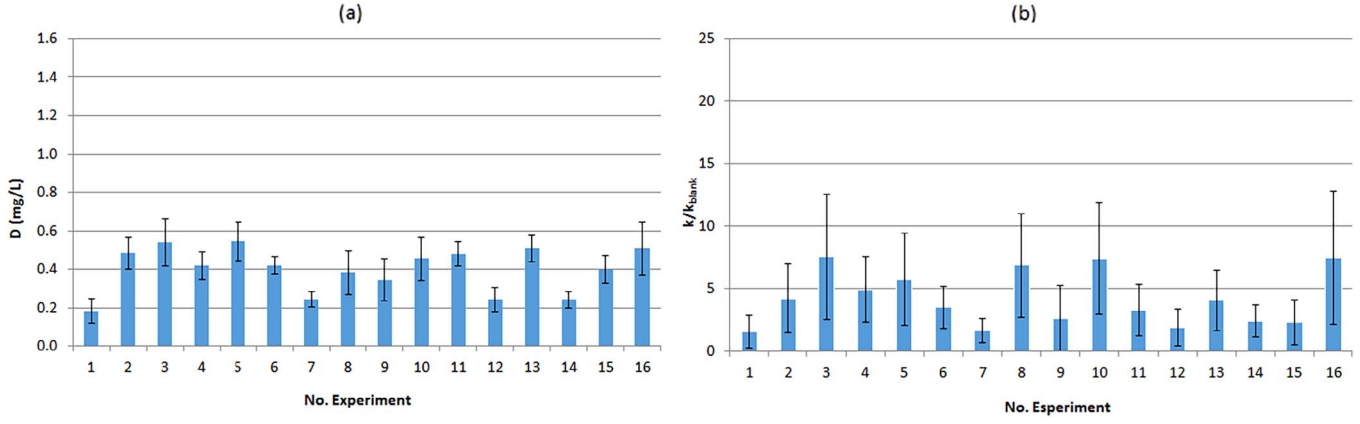



**Fig. 3.** Oxidative demand D (a) and normalized rate constant $k/k_{blank}$ (b) of Haas and Finch kinetic model for experiments at $2\,mg_{PAA}\,L^{-1}$ when organics are present. The confidence intervals are at 95% of significance.

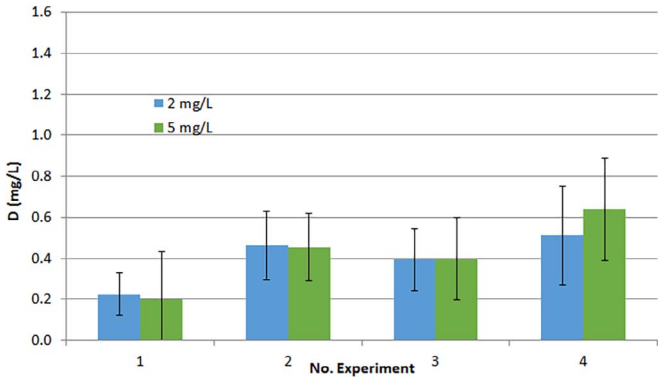



**Fig. 4.** Oxidative demand D of Haas and Finch kinetic model for experiments at 2 and 5 $mg_{PAA}\,L^{-1}$ when organics are present. The confidence intervals are at 95% of significance.

**Table 5**
Main statistics and regression estimates of the model for the effect of organics on PAA oxidative demand.

| Symbol | Estimate | SE | CI (95%) | t-Value | p-value |
|---|---|---|---|---|---|
| $b_3$ | 0.046 | 0.018 | 0.010, 0.083 | 2.61 | .014 |
| $b_4$ | 0.009 | 0.006 | 0.008, 0.010 | 9.98 | < .000 |
| $b_5$ | 0.006 | 0.006 | 0.005, 0.007 | 15.37 | < .000 |

$R^2 = 0.9205$; $R^2_{adj} = 0.9153$; $R^2_{pred} = 0.9032$; N = 34; Lack-of-fit (p-value) < .044

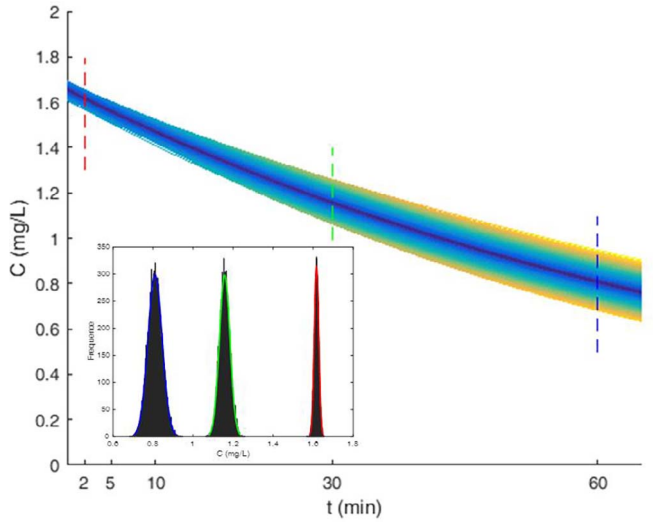



**Fig. 5.** Results of the exemplary Monte Carlo simulation for $10^4$ simulations. In the detail the output distribution (approximated by a normal pdf) of the model at three different sections (2, 30 and 60 min).

**Table 6**
Input values and correlation matrix used for the exemplary Monte Carlo simulation.

| Input values | Coefficient | Correlation matrix | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $b_0$ | $b_1$ | $b_2$ | $b_{12}$ | $b_3$ | $b_4$ | $b_5$ |
| $[PAA]_0 = 2\,mg_{PAA}\,L^{-1}$ | $b_0$ | 1 | −0.65 | −0.76 | 0.51 | | | |
| | $b_1$ | −0.65 | 1 | 0.49 | −0.78 | | | |
| $Fe^{2+} = 4\,mg\,L^{-1}$ | $b_2$ | −0.76 | 0.49 | 1 | −0.68 | | | |
| $PO_4^{3-} = 1\,mg\,L^{-1}$ | $b_{12}$ | 0.51 | −0.78 | −0.68 | 1 | | | |
| | $b_3$ | | | | | 1 | −0.59 | −0.59 |
| casein = 25 $mg\,L^{-1}$ | $b_4$ | | | | | −0.59 | 1 | −0.07 |
| peptone = 10 $mg\,L^{-1}$ | $b_5$ | | | | | −0.59 | −0.07 | 1 |

non-dependence from this parameter. Instead, a linear model is not the most reasonable for data interpolation (p-value for the lack-of-fit test lower than .05). However, the moderately high values of R-square ($R^2 = 0.9205$) and predicted R-square ($R^2_{pred} = 0.9032$) indicate that the model is enough accurate and predictive.

In conclusion, both casein and peptone individually affect oxidative demand (p-value < .001 for both $b_3$ and $b_4$) while no interaction seems to occur, as also supported by a forward step-wise regression that has excluded the interaction term. Moreover, casein seems to consume more PAA than peptone ($b_3 > b_4$). The oxidative demand determined by these compounds can be attributed to the role of PAA in acting as a protein denaturant [46,47]. In fact, the peroxyl and hydroxyl radicals that PAA forms through homolytic fission might oxidize sulfhydryl and sulfur bonds present in proteins. It can be inferred that PAA acts towards protein compounds as it does with microorganisms, mainly attacking the lipoprotein in the cytoplasmic membrane and disrupting the chemiosmotic function of the cell [48–51]. However, this hypothesis requires specific investigations to be confirmed.

As a final step, an easy-to-measure indicator of organic compounds that displayed a significant effect on PAA decay has been assessed. Casein and peptone are a protein and a peptide respectively, both consisting of chains of amino acids, which are mainly formed by an amine and a carboxyl group. Particularly, amines are nitrogen-containing groups that allow to differentiate proteins from other organic compounds such as carbohydrates and lipids. Therefore, experimental results stress the previous statements about the ineffectiveness of conventional macro-indicators of organic content. Accordingly, in the view of referring the presented model to a unique indicator, the organic nitrogen could represent a valuable alternative. In order to verify such hypothesis, the effect of urea on PAA decay was evaluated by *ad hoc* experiments. However, as reported in Fig. S7 in Supplementary Material no significant effect was observed with respect to blank tests, indicating that not all organic nitrogen but protein nitrogen affects PAA decay. In conclusion, the experimental evidence suggests that the model can be expressed in terms of protein nitrogen if the values for the coefficients are re-calculated and merged by considering the composition of the two organic compounds (0.138 $mg_{protein\ nitrogen}\,mg_{caseine}^{-1}$, 0.130 $mg_{protein\ nitrogen}\,mg_{peptone}^{-1}$). The result is $b_{4\text{-}5} = 0.123$, that is a unique coefficient for describing the influence of protein nitrogen on PAA decay. For the application of this model to WWTP effluents, given the issues related to analytical determination, the protein nitrogen can be roughly estimated as a percentage of the total organic nitrogen, according to data in literature for various types of effluents and sources [52,53].

### 3.7. Uncertainty analysis and validation of the model

Eqs. (3), (4) and (9) were integrated in the Haas and Finch kinetic model (e.2) in order to obtain a unique model for predicting the residual PAA concentration over time as a function of inorganics, organics and initial PAA concentration. Subsequently, the uncertainty analysis was performed in three steps: (i) identification and quantification of

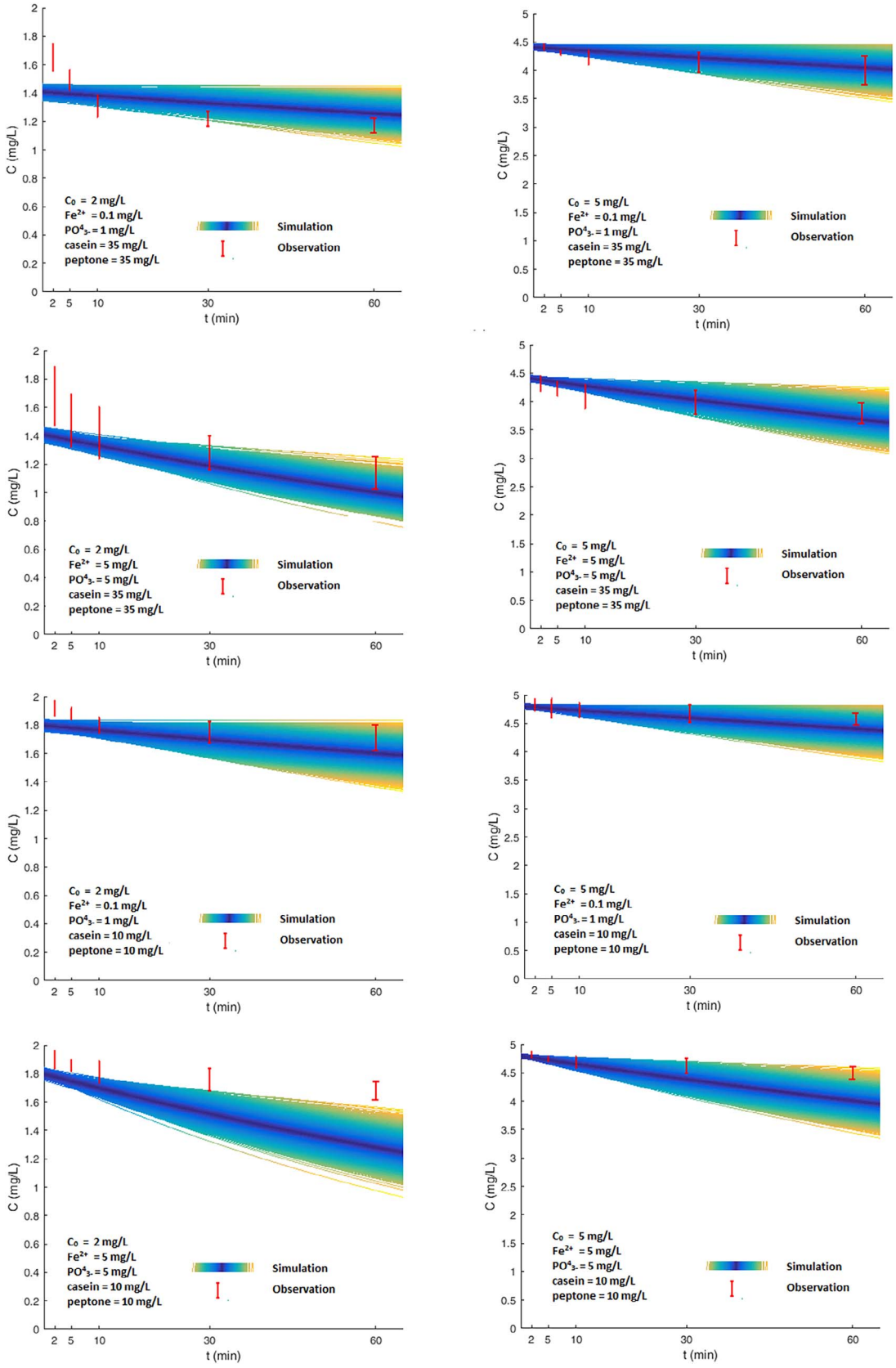



**Fig. 6.** Experimental (mean ± CI) and simulated data for the validation of PAA decay model.

uncertainty in model inputs, (ii) propagation of the uncertainties through a Monte Carlo simulation, and (iii) statistical analysis of the model results.

As for the first step, model inputs were divided in two groups: a first group formed by inorganics ($Fe^{2+}$, $PO_4^{3-}$), organics (casein and peptone) and initial PAA concentration ($[PAA]_0$), which can be either measured or spiked into a water matrix with a certain precision and accuracy depending on instruments and labware, and a second group formed by model coefficients ($b_1$, $b_2$, $b_3$, $b_4$, and $b_5$), which are the results of the linear least-square regressions previously described. Uncertainties associated with the first group can be quantified only by a precise evaluation of the errors due to measurement and laboratory procedures (e.g., dilution error, sampling error, etc.). These uncertainties were not considered in the present work. Only uncertainties associated to the second group were quantified and propagated through the model, being normal probability density functions (normal pdf) assumed for all coefficients. In particular, at each function a mean and a standard deviation, respectively equal to the estimate value and the standard error of the coefficient, were assigned. Moreover, correlation between coefficients was taken into account by the correlation matrixes obtained from regression.

As for the second step, a classical Monte Carlo simulation was used to propagate coefficient uncertainties to the system output. Specifically, the code simulates $10^4$ lives of the system: for each life, all system coefficients are randomly sampled from correlated normal distributions and a value of k and D is calculated. Then, the residual PAA concentration is simulated over time. Fig. 5 shows the output of the Monte Carlo simulation carried out for the input values and the correlation matrix reported in Table 6.

As for the last step, the outputs of simulations were processed from a frequentist point of view. As an example, frequency histograms for exemplary Monte Carlo simulation results at three different times (2, 30 and 60 min) and the related interpolations with normal pdf (blue, green and red line) are shown in Fig. 5. The normal pdf fits the data with good accuracy and a confidence interval for residual PAA concentration can be easily obtained. For example, it can be concluded with a 95% of confidence that the predicted residual PAA concentration after 60 min ranges within 0.716 and 0.856 $mg_{PAA}\,L^{-1}$ (estimated mean and standard deviation of the normal pdf equals to 0.786 and 0.035 $mg_{PAA}\,L^{-1}$, respectively).

Finally, a series of *ad hoc* experiments were planned with a dual objective: (i) to validate the final model, and (ii) to detect the occurrence of interaction effects between inorganics and organics. In particular, PAA decay at two initial PAA concentrations, namely 2 and 5 $mg_{PAA}\,L^{-1}$, was evaluated in case of simultaneous presence of inorganics and organics. In Fig. 6 the experimental data with 95% confidence intervals were compared with simulated data under various operating conditions.

Overall, the model effectively predicts residual PAA concentrations for most of the tested cases. Additionally, these results highlight the absence of significant interaction effects between inorganic and organic compounds, confirming what was expected initially by the experimenters.

## 4. Conclusions

Inorganics and organics compounds displayed different roles in PAA decay, specifically inorganics affected the rate constant, being responsible for the PAA residual concentration at a given contact time, while organics defined the instantaneous PAA demand, indicating the required minimum initial PAA concentration. In particular, PAA decay rate was driven mainly by the presence of transition metals (reduced iron) and was slightly depending on initial PAA concentration. On the other hand, $PO_4^{3-}$ acts as a chelating agent, counteracting the effect of transition metals and stabilizing residual PAA concentration. Inorganic nitrogen compounds at concentrations typical of secondary effluents do not display any significant effect in determining PAA decay rate. As for the organics, among the compounds used as surrogates of the main components of secondary effluents, only proteins affected PAA initial demand, while carbohydrates and lipids did not display any effect. In detail, proteins consumed instantaneously a significant amount of PAA, independently from the initial PAA concentration, and PAA consumption dropped rapidly after 5 min to almost nil.

Based on experimental evidences, a unique predictive model has been formulated to define the most proper PAA dosage based on effluent chemical composition to obtain the actual concentration available for disinfection. The usefulness of this predictive model for PAA decay is in achieving specific bacteria inactivation targets avoiding disinfectant overdosage. This has not only economic implications, but also allows to prevent high residual concentrations of the disinfectant in the effluents, which might lead to toxic effects in aquatic ecosystems and the potential formation of genotoxic and mutagenic disinfection by-products.

## Acknowledgements

The research activity was supported by the company PeroxyChem (Philadelphia, USA) and by Fondazione Cariplo (Milan, Italy) (DrinkAble project, Grant #2014-1285). The valuable support of Luca Leonardi in performing some of the experimental tests is gratefully acknowledged.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.12.074.

## References

[1] D. Pimentel, M. Pimentel, World population, food, natural resources, and survival, World Future J. Gen. Evol. 59 (2003) 145–167.
[2] US Environmental Protection Agency, Guidelines for Water Reuse. Report EPA/625/R-04/108, Washington D.C., 2012.
[3] D. Bixio, C. Thoeye, J. De Koning, D. Joksimovic, D. Savic, T. Wintgens, T. Melin, Wastewater reuse in Europe, Desalination 187 (2006) 89–101.
[4] World Health Organization, Guidelines for Drinking-water Quality, Recommendations, Geneva, 2008.
[5] J.J. Rook, Formation of haloforms during chlorination of natural waters, Water Treat. Exam. 23 (1974) 234–243.
[6] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D.M. DeMarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research, Mutat. Res. 636 (2007) 178–242.
[7] S. Monarca, S.D.S.D. Richardson, D. Feretti, M. Grottolo, A.D.A.D. Thruston, C. Zani, G. Navazio, P. Ragazzo, I. Zerbini, A. Alberti, Mutagenicity and disinfection by-products in surface drinking water disinfected with peracetic acid, Environ. Toxicol. Chem. 21 (2002) 309–318.
[8] T. Luukkonen, S.O. Pehkonen, Peracids in water treatment: a critical review, Crit. Rev. Environ. Sci. Technol. (2016) 1–39.
[9] M. Kitis, Disinfection of wastewater with peracetic acid: a review, Environ. Int. 30 (2004) 47–55.
[10] M.G.C. Baldry, M.S. French, D. Slater, The activity of peracetic acid on sewage indicator bacteria and viruses, Water Sci. Technol. 24 (1991) 353–357.
[11] J. Koivunen, H. Heinonen-Tanski, Inactivation of enteric microorganisms with chemical disinfectants, UV irradiation and combined chemical/UV treatments, Water Res. 39 (2005) 1519–1526.
[12] J. Koivunen, H. Heinonen-Tanski, Peracetic acid (PAA) disinfection of primary, secondary and tertiary treated municipal wastewaters, Water Res. 39 (2005) 4445–4453.
[13] T. Luukkonen, J. Teeriniemi, H. Prokkola, J. Rämö, U. Lassi, Chemical aspects of peracetic acid based wastewater disinfection, Water SA 40 (2014) 73–80.
[14] M. Antonelli, S. Rossi, V. Mezzanotte, C. Nurizzo, Secondary effluent disinfection: PAA long term efficiency, Environ. Sci. Technol. 40 (2006) 4771–4775.
[15] C. Nurizzo, M. Antonelli, M. Profaizer, L. Romele, By-products in surface and reclaimed water disinfected with various agents, Desalination 176 (2005) 241–253.
[16] A. Dell'Erba, D. Falsanisi, L. Liberti, M. Notarnicola, D. Santoro, Disinfection by-products formation during wastewater disinfection with peracetic acid, Desalination 215 (2007) 177–186.
[17] S.D. Richardson, Disinfection by-products and other emerging contaminants in drinking water, TrAC – Trends Anal. Chem. 22 (2003) 666–684.
[18] S. Monarca, C. Zani, S.D. Richardson, A.D. Thruston, M. Moretti, D. Feretti,

M. Villarini, A new approach to evaluating the toxicity and genotoxicity of disinfected drinking water, Water Res. 38 (2004) 3809–3819.
LI. F. Lefevre, J.M. Audic, F. Ferrand, Peracetic acid disinfection of secondary effluents discharged off coastal seawater, Water Sci. Technol. 25 (1992) 155–164.
LII. V. Lazarova, M. Janex, L. Fiksdal, C. Oberg, I. Barcina, M. Pommepuy, Advanced wastewater disinfection technologies: Short and long term efficiency, Water Sci. Technol. 38 (1998) 109–117.
LIII. M. Wagner, D. Brumelis, R. Gehr, Disinfection of wastewater by hydrogen peroxide or peracetic acid: development of procedures for measurement of residual disin-fectant and application to a physicochemically treated municipal effluent, Water Environ. Res. 74 (2002) 33–50.
LIV. D. Liu, C. Steinberg, D.L. Straus, L. Pedersen, T. Meinelt, Salinity, dissolved organic carbon and water hardness affect peracetic acid (PAA) degradation in aqueous solutions, Aquacult. Eng. 60 (2014) 35–40.
LV. L.F. Pedersen, T. Meinelt, D.L. Straus, Peracetic acid degradation in freshwater aquaculture systems and possible practical implications, Aquacult. Eng. 53 (2013) 65–71.
LVI. Z. Yuan, Y. Ni, A.R. van Heiningen, Kinetics of the peracetic acid decomposition: Part II: pH effect and alkaline hydrolysis, Can. J. Chem. Eng. 75 (1997) 42–47.
LVII. P.O. Pedersen, E. Brodersen, D. Cecil, Disinfection of tertiary wastewater effluent prior to river discharge using peracetic acid; treatment efficiency and results on by-products formed in full scale tests, Water Sci. Technol. 68 (2013) 1852–1856.
LVIII. E. Koubek, M.L. Haggett, C.J. Battaglia, K.M. Ibne-Rasa, H.Y. Pyun, J.O. Edwards, Kinetics and mechanism of the spontaneous decompositions of some peroxoacids, hydrogen peroxide and t-butyl hydroperoxide, J. Am. Chem. Soc. 85 (1963) 2263–2268.
LIX. Z. Yuan, Y. Ni, A.R.P. Van Heiningen, Kinetics of peracetic acid decomposition: Part I: spontaneous decomposition at typical pulp bleaching conditions, Can. J. Chem. Eng. 75 (1997) 37–41.
LX. L.F. Pedersen, P.B. Pedersen, J.L. Nielsen, P.H. Nielsen, Peracetic acid degradation and effects on nitrification in recirculating aquaculture systems, Aquaculture 296 (2009) 246–254.
LXI. S. Stampi, G. De Luca, M. Onorato, E. Ambrogiani, F. Zanetti, Peracetic acid as an alternative wastewater disinfectant to chlorine dioxide, J. Appl. Microbiol. 93 (2002) 725–731.
LXII. D. Falsanisi, R. Gehr, L. Liberti, M. Notarnicola, Effect of suspended particles on disinfection of a physicochemical municipal wastewater with peracetic acid, Water Qual. Res. J. Can. 43 (2008) 47–54.
LXIII. M.F. Dignac, P. Ginestet, D. Rybacki, A. Bruchet, V. Urbain, P. Scribe, Fate of wastewater organic pollution during activated sludge treatment: nature of residual organic matter, Water Res. 34 (2000) 4185–4194.
LXIV. S. Stampi, G. De Luca, F. Zanetti, Evaluation of the efficiency of peracetic acid in the disinfection of sewage effluents, J. Appl. Microbiol. 91 (2001) 833–838.
LXV. H.K. Shon, S. Vigneswaran, S.A. Synder, Effluent organic matter (EfOM) in waste-water: constituents, effects, and treatment, Crit. Rev. Environ. Sci. Technol. 36 (2006) 327–374.
LXVI. D. Falsanisi, R. Gehr, D. Santoro, A. Dell'Erba, M. Notarnicola, L. Liberti, Kinetics of PAA demand and its implications on disinfection of wastewaters, Water Qual. Res. J. Can. 41 (2006) 398–409.
[35] APHA/AWA/WEF, Standard Methods for the Examination of Water and Wastewater, 22nd ed., Washington, DC., 2012.
[36] J.R. Baker, M.W. Milke, J.R. Mihelcic, Relationship between chemical and theoretical oxygen demand for specific classes of organic chemicals, Water Res. 33 (1999) 327–334.
[37] M. Deborde, U. von Gunten, Reactions of chlorine with inorganic and organic compounds during water treatment-Kinetics and mechanisms: a critical review, Water Res. 42 (2008) 13–51.
[38] G.E.P. Box, J.S. Hunter, W.G. Hunter, Statistics for Experimenters: Design, Innovation, and Discovery, Wiley-Interscience, 2005.
[39] C.N. Haas, G.R. Finch, Methodologies for the Determination of Disinfection Effectiveness, AWWA Research Foundation and American Water Works Association, 2001.
[40] R.R. Irani, W.W. Morgenthaler, Iron sequestration by polyphosphates, J. Am. Oil Chem. Soc. 40 (1963) 283–285.
[41] K.G. Klueh, R.B. Robinson, Sequestration of Iron in Groundwater by Polyphosphates, J. Environ. Eng. 114 (1988) 1192–1199.
[42] A. Aklil, M. Mouflih, S. Sebti, Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent, J. Hazard. Mater. 112 (2004) 183–190.
[43] D.L. Varner, S. Skipton, D. Hay, P.J. Jasa, G96-1280 Drinking Water: Iron and Manganese, Hist. Mater. from Univ. Nebraska-Lincoln, 1996.
[44] Z. Elouear, J. Bouzid, N. Boujelben, M. Feki, F. Jamoussi, A. Montiel, Heavy metal removal from aqueous solutions by activated phosphate rock, J. Hazard. Mater. 156 (2008) 412–420.
[45] T.E. Larson, Evaluation of use of polyphosphates in water industry, J. Am. Water Work. Assoc. 49 (1957).
[46] B. Kerkaert, F. Mestdagh, T. Cucu, P.R. Aedo, S.Y. Ling, B. De Meulenaer, Hypochlorous and peracetic acid induced oxidation of dairy proteins, J. Agric. Food Chem. 59 (2011) 907–914.
[47] C.C. Winterbourn, M.B. Hampton, Thiol chemistry and specificity in redox signaling, Free Radical Biol. Med. 45 (2008) 549–561.
[48] E. Cabiscol, J. Tamarit, J. Ros, Oxidative stress in bacteria and protein damage by reactive oxygen species, Int. Microbiol. 3 (2000) 3–8.
[49] S.P. Denyer, G.S.A.B. Stewart, Mechanisms of action of disinfectants, Int. Biodeterior. Biodegrad. 41 (1998) 261–268.
[50] G. Storz, J.A. Imlayt, Oxidative stress, Curr. Opin. Microbiol. 2 (1999) 188–194.
[51] M. Finnegan, E. Linley, S.P. Denyer, G. McDonnell, C. Simons, J.Y. Maillard, Mode of action of hydrogen peroxide and other oxidizing agents: differences between liquid and gas forms, J. Antimicrob. Chemother. 65 (2010) 2108–2115.
[52] P.J. Westgate, C. Park, Evaluation of proteins and organic nitrogen in wastewater treatment effluents, Environ. Sci. Technol. 44 (2010) 5352–5357.
[53] E. Pehlivanoglu-Mantas, D.L. Sedlak, Measurement of dissolved organic nitrogen forms in wastewater effluents: concentrations, size distribution and NDMA formation potential, Water Res. 42 (2008) 3890–3898.