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Multivariate modelling of disinfection kinetics: A comparison among three different disinfectants

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ABSTRACT

Disinfection kinetics has been extensively discussed in scientific literature, however, most of the studies refer to batch reactor experiences and mostly to potable water. Only few authors have compared batch kinetics to continuous flow performances and even fewer are the studies where kinetic models are provided with complete regression statistics. Aim of this study was to apply multivariate regression analysis to model the inactivation kinetics of three different disinfectants: sodium hypochlorite (NaClO), peracetic acid (PAA) and ozone (O_3). The inactivation of the three disinfectants has been studied on pilot-scale continuous-flow reactors fed with a secondary effluent of a full scale wastewater treatment plant. *Escherichia coli*, total and faecal coliforms were used as microbial indicators. The accuracy of the most commonly used inactivation models (i.e. Chick–Watson, Selleck, and Hom) was tested and compared. The goodness of fit of each model was evaluated and the inactivation parameters were determined for each disinfectant–indicator combination. The best-fit models for NaClO and O_3 inactivation kinetics were based on Hom's formula whereas PAA inactivation was found to be better modeled by the more recently described "S-model". Regression analysis outlined the dominance of disinfectant dosage over contact time for NaClO and PAA and the lack of such a dominance for O_3. Furthermore, whereas the inactivation kinetics of the three microbial indicators resulted to be comparable for NaClO and O_3, a faster inactivation was shown for *Escherichia coli* with PAA suggesting a inactivation mechanism different from total and faecal coliforms. This result is extremely relevant since Italy in 2000 replaced *Escherichia coli* to total and faecal coliforms as microbial indicator to assess the water quality requirements of surface waters and reused wastewaters and PAA is increasingly preferred as disinfectant agent to hypochlorite and ozone.

Keywords: Disinfection kinetics; Ozone; Peracetic acid; Sodium hypochlorite; Multivariate analysis

1. Introduction

The inactivation kinetics of the most commonly used disinfectant agents (i.e. chlorine based agents, ozone and peracetic acid) has been extensively studied [1]. Disinfection kinetics is generally described with analytical expressions that combine the main process parameters such as disinfectant dosage, contact time, microbial concentration and, depending on the case, temperature, pH, etc. Different mathematical models have been proposed to describe

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Table 1
Most used disinfection models

Chick–Watson	$\ln\frac{N_t}{N_0} = -\Lambda C^n t$
Hom	$\ln\frac{N_t}{N_0} = -kC^n t^m$
Selleck	$\frac{N_t}{N_0} = \left(\frac{C\cdot t}{b}\right)^{-d}$
S-Model	$\ln\frac{N_t}{N_0} = -\frac{kC^n}{1+\left(\frac{h}{C\cdot t}\right)^m}$

the microorganism inactivation of different chemicals. Table 1 shows the most known inactivation models.

The Chick–Watson formula [2] is probably the oldest and is based on the product of disinfectant active concentration (C) and contact time (t). In Chick–Watson formula N_0 and N_t are respectively the initial and the final (i.e. after time t) microbial counts, L is the specific coefficient of lethality, — i.e. the disinfection efficacy when C and t are equal to 1, [3] — n is the dilution coefficient, which depends on the specific disinfectant, pH and temperature, and it is often close to 1. The other models, more recent, are on a broader sense generalizations of the Chick–Watson formula. Among these, Hom's model is probably the most widely used to account for deviations from the first-order kinetics of the Chick-Watson formula [3–6]. Selleck's empirical model [1,4] is also commonly used. In Selleck's formula, the coefficient b represents the $C{\cdot}t$ critical value for disinfection to occur, and d is a coefficient that accounts for the microorganism-disinfectant combination. Some other authors [8,9] proposed an S-model to describe the inactivation kinetics of PAA when resistance to diffusion into the cell membrane or microbial aggregates affects the process. In Fig. 1 the inactivation curve described by the S-model is shown. Three phases can be observed:

1st phase: initial resistance to inactivation (possibly due to the specific characteristics of either disinfectant or microorganisms); the first phase "shoulder" is particularly evident at values higher than 1 of the empirical coefficient m.

2nd phase: exponential inactivation (maximum inactivation rate); in this phase the S-model is very close to the Chick-Watson's formula;

3rd phase: asymptotic inactivation; the inactivation rate decreases.

Even though the theoretical basis for disinfection kinetics has been reported extensively in the literature, the majority of the studies is based on batch reactor experiences and is mostly referred to potable water. Moreover, to date, very few authors [4,10–12] have compared batch kinetic information to continuous flow performances. Even fewer are the studies where the kinetic models are provided with the complete statistics of the regression analysis [1,9,12,13] and very rarely the significance levels of model's coefficients are shown [9,12,13]. In this study multivariate regression analysis has been applied to study the inactivation of three different disinfectants (NaClO, PAA and O_3). Disinfection trials were run on pilot-scale continuous-flow reactors fed with the secondary effluent of a full scale wastewater treatment plant. The inactivation efficiency was evaluated with respect to three different microbial indicators: *Escherichia coli*, total and faecal coliforms.

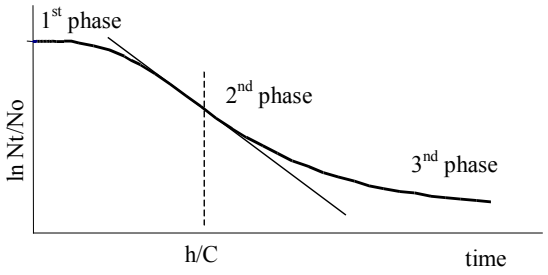


Fig. 1. The inactivation curve according to S-model - $m > 1$ [8].

2. Material and methods

2.1. Pilot plant set description

The pilot plant processed the secondary effluent of a full-scale municipal wastewater treatment plant (Pero WWTP), located near Milan in northern Italy. Pero WWTP uses a conventional activated sludge process and consists of preliminary treatments (e.g. screening of coarse and fine solids), a primary clarification, a single sludge biological nitrogen-removal process (i.e. nitrification/denitrification) followed by a final clarification. Pero secondary effluent is quite diluted, due to the high domestic water consumption, and to the considerable contribution of industrial cooling waters and of the groundwater infiltrations into the sewage network, both typical elements of the area around Milan. Only 50% of the treated-effluent samples had COD values higher than 20 mg L^{-1}, while the maximum concentration measured during the test period was 94 mg L^{-1}. TSS concentration and turbidity were also extremely low and respectively comprised within a range of 3–24 mg L^{-1} and 2–9 NTU. The pilot plant was fed with Pero WWTP effluent at a constant flow rate (3 and 4.5 $m^3 h^{-1}$) and consisted of a preliminary rapid sand filtration (maximum hydraulic load: 10.6 m h^{-1}), followed by the disinfection units, as shown in Fig. 2. NaClO (NaClO, 1 N, Merck KGaA, Darmstadt, Germany) and PAA (15% PAA, 23% H2O2 and 17% w/w acetic acid,

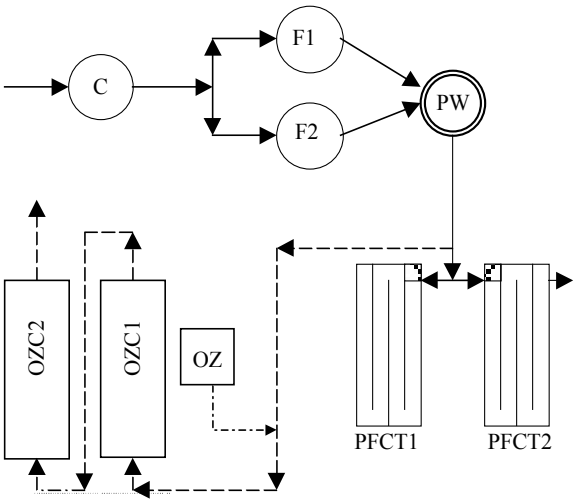


Fig. 2. Scheme of the pilot plant. C: feed tank; F1/2: rapid sand filters; PW: flow partition; PFCT1/2: plug-flow contact tanks; OZ: ozone generator; OZC: ozone contact tanks.

marketed as Oxystrong®, Solvay Italia Spa) were dosed in two in-series 'chicane' contact reactors (volume: 2.23 m^3 each). Each reactor consisted of 5 channels subdivided by 4 partitioning walls. The channel's dimensions were 0.3 m width and 4.5 m length. Water depth was regulated with an adjustable weir at the end of the tank to have hydrodynamic characteristics similar to those of the real scale plant; it was 0.19 m with 3 m^3/h flow rate (theoretic HRT = 25.7 min; Re = 4863) and 0.33 m with 4.5 m^3/h flow rate (theoretic HRT = 29.7 min; Re = 5167). At the inlet the wastewater was uniformly distributed across the section of the first channel thanks to a holey stainless steel plate. Both NaClO and PAA were added by a peristaltic pump and mixed to the effluent respectively in an in-line static mixer and in a rapid mixing tank. To validate the assumptions about the two tank reactors and couple hydraulics with kinetics, tracer tests were carried out by injecting a salinity pulse (i.e. 200 ml of a 2 g/l KI concentrated solution; injection time approximately 2 s) in the system. The best-fit model correlating conductivity values to KI concentrations had *R*-square value higher than 0.99. Tracer tests were conducted under the same flow, temperature and water quality conditions of disinfection trials, and effluent conductivity was recorded against the time elapsed after KI injection (the conductivity values were recorded every minute).

These data were fitted (Fig. 3) with normal curves [Eq. (1)].

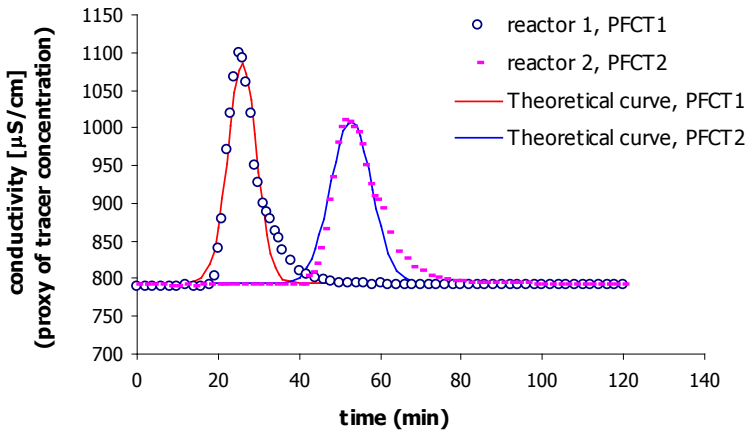
$$\varphi_{\mu,\sigma}(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} \quad (1)$$

and revealed that the retention times of the two reactors were respectively of about 25.4–30.4 min at a flow rate of 4.5 m^3 h^{-1}, increasing up to 52.8–61.3 min when the two reactors were used in series. The tracer response curves fitted quite well the normal curve, being the *R*-square values for every trial higher than 0.90. Axial dispersion (d) was estimated according to Eq. (2) [14]:

$$d = 2\frac{D}{uL} = \frac{\sigma^2}{t_t^2} \quad (2)$$

where D: coefficient of axial dispersion, L^2 T^{-1} (m^2 s^{-1}); U: fluid velocity LT^{-1} (m s^{-1}); L: total length of the reactor (m); σ^2: variance derived from the best-fit response curve of tracer data dispersion, assuming the curve as normal; tr: mean residence time derived from the best-fit response curve of tracer data dispersion, assuming the curve as normal.

The axial dispersion (d) was evaluated for both the reactors (d_1: 0.009; d_2: 0.004) and was found in both cases much lower than 0.01, consistently with the hypothesis of a small deviation from the ideal plug-flow behavior [11].



	Reactor 1	Reactor 2
t_r	26 min	53 min
d	0.009	0.004

Fig. 3. Tracer tests: actual conductivity data (dots) and theoretical curves are shown for the two reactors PFCT1 and PFCT2. Residence time (t_r) and the axial dispersion (d) are also shown.

The ozone contact reactor consisted of two columns in-series (diameter: 350 mm; height: 5 m; volume: 0.48 m^3, made of AISI 304 L, Air Liquide®). Ozone was generated from pure oxygen with an OZAT CFS1 compact ozone generator (Ozonia®; nominal production rates: 80 gO_3/h at 6 wt% from oxygen) and the ozonated gas stream was introduced into the contactor through fine ceramic diffusers at the bottom of each column.

2.2. Disinfection trials set up and analytical methods used

Table 2 and Table 3 show respectively the characteristics of the treated influent and the main operational parameters of the disinfection trials.

COD, TSS, turbidity, pH and temperature of the influent were measured for every disinfection trial.

Analyses were performed according to American Standard Methods ([16], Table 2).

The same parameters were also measured in the sand filters effluent and after disinfection. Residual disinfectant and microbial concentrations (i.e. Escherichia coli, total and faecal coliforms) were evaluated for varying dosage and contact time (Table 3).

Sodium thiosulfate ($Na_2S_2O_3$) was used to quench free chlorine residuals of disinfected effluent samples. For the same purpose, drops of catalase (crystalline water suspension, Merck) were added to neutralize further disinfection due to PAA residues.

The samples (stored at 4°C) were carried to the laboratory where microbiological indicators were determined within 24 h on replicated samples (i.e. 3 replicas for each sample) by means of standard plate count techniques (PCA) using a membrane filtration procedure (Millipore, Bedford, MA, USA).

Total coliform (*T. coli*) colonies were enumerated after 24 h incubation at 36°C on M-Endo Agar culture media; Faecal coliforms (*F. coli*) were enumerated after 20 h incubation at 44°C on C-EC Agar; *Escherichia coli* (*E. coli*) colonies were evidenced through the Wood lamp light (365 nm), because fluorescent.

2.3. Statistical methods

The inactivation kinetics of the different disinfectant agents was studied by means of a non linear multivariate regression analysis with respect of the three microbial indicators. The log-survival ratio was chosen as dependent variable, whereas both dosage and contact time were used as predictors.

Although it was acknowledged these chemicals being highly reactive in the investigated conditions [17–21], the disinfectant decay was not included in the kinetic models for the sake of the comparison among disinfectant kinetics.

Least square methods were used where the loss

Table 2
Characteristics of the WWTP secondary effluent fed to the pilot plant

Parameter	Analytical method	Mean ± SD	Range
pH	4500-H+ B electrometric method.	7.68±0.42	7.1–7.7
COD, mg L^{-1}	5220 B b. open reflux method	27.5±13.5	4–94
BOD5, mg L^{-1}	5210 B 5-day BOD test	17.4±29.9	2–24
TSS, mg L^{-1}	2540 D total suspended solids	6.4±2.9	3–24
Electrical conductivity (E_{cw}), μS cm^{-1}	2510B electrical conductivity	708.6±241.1	447–944
Ammonia-nitrogen, mg NH3–N L^{-1}	4500-NH3 D. ammonia selective electrode method	1.25±3.44	0.3–4.8
Escherichia coli, CFU/100 ml	9222 G MF partition method	$1.56\times10^4\pm1.46\times10^4$	1.58×10^3–6.05×10^4
Total coliforms, CFU/100 ml	9222 B standard total coliform MF	$1.04\times10^5\pm13.5\times10^5$	10^2–1.04×10^6
Faecal coliforms, CFU /100 ml	9222 D fecal coliform MF	$2.17\times10^3\pm6.8\times10^4$	1.96×10^4–8×10^4

Table 3
Disinfection trials: set up of the main operational parameters

Disinfectant	Flow rate	Dosage	Number of trials			Contact time (min)
	m^3/h	mg/L	*E. coli*	*F. coli*	*T. coli*	
NaClO	3 and 4.5	0.5, 1, 2, 3, 4, 5, 7.5	64	74	71	5, 10, 18, 35, 42, 54
O3	4.5	1.08, 1.80, 2.36, 2.56, 3.02, 3.46, 4.07, 4.74	17	20	19	6.4, 12.8
PAA	4.5	2, 5, 15, 25	91	118	114	6, 12, 18, 36, 42, 54

function was minimized through the Quasi-Newton algorithm[1].

The significance level of the regression coefficient estimates was assessed by means of Student's t-tests [22] where the null hypothesis was the independence of the response variable (log-survival ratio) from the predictors and the test statistic was:

$$t_{df} = \frac{B_i - 0}{SE(B_i)} \tag{3}$$

where B_i: coefficient estimate; $SE(B_i)$: standard error of the B_i estimate.

On the other hand, to compare the removal efficiency of a disinfection treatment with respect to the different microbiological indicators, One-Way ANOVA tests [23,24] were applied according to Eq. (4).

$$y_{ij} = \mu + \alpha_i + \varepsilon_{ij} \tag{4}$$

where y_{ij}: j_{th} log-inactivation observation of the i_{th} level of factor A (type of indicator: *E. coli*, *T. coli*, *F. coli*); μ: true overall mean; α_i: incremental effect of treatment i, such that $\alpha_i = \mu_i - \mu$; μ_i: true population mean for the i_{th} level of factor A (i.e. type of indicator: *E. coli*, *T. coli*, *F. coli*); ε_{ij}: error for the j_{th} observation of the i_{th} level of factor A.

[1] The Quasi-Newton algorithm uses the first-order and second-order derivatives to follow a path towards the minimum of the least square loss function

Moreover, only for peracetic acid trials, a two-way ANOVA was applied to test whether the removal efficiency for *E. coli* was higher at the lower PAA doses with respect to the removal efficiency of the other indicators. The two-way ANOVA design according to Eq. (5).

$$y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \varepsilon_{ijk} \tag{5}$$

where y_{ijk}: k_{th} log-inactivation observation of the i_{th} level of factor A (type of indicator: *E. coli*, *T. coli*, *F. coli*) and the j_{th} level of factor B (PAA dosage: 2–5–15–25 mg/l); μ: true overall mean; α_i: incremental effect of treatment i, such that $\alpha_i = \mu_i - \mu$; β_j: incremental effect of treatment j, such that $\beta_j = \mu_i - \mu$; μ_i: true population mean for the i_{th} level of factor A (i.e. type of indicator: *E .coli*, *T. coli*, *F. coli*); μ_j: true population mean for the j_{th} level of factor B (i.e. PAA dosage: 2–5–15–25 mg/l); $(\alpha\beta)_{ij}$: interaction effect for the i_{th} level of factor A and the j_{th} level of factor B, (i.e. type of indicator* PAA dosage); ε_{ijk}: error for the k_{th} observation of the i_{th} level of factor A and the j_{th} level of factor B.

The StatSoft STATISTICA package was used for all the statistical analyses.

3. Results and discussion

3.1. Removal efficiency of microbiological indicators

The main experimental results for the three disinfection agents at different contact times are summarized in Figs. 4, 5 and 6 respectively for chlorination, ozone and

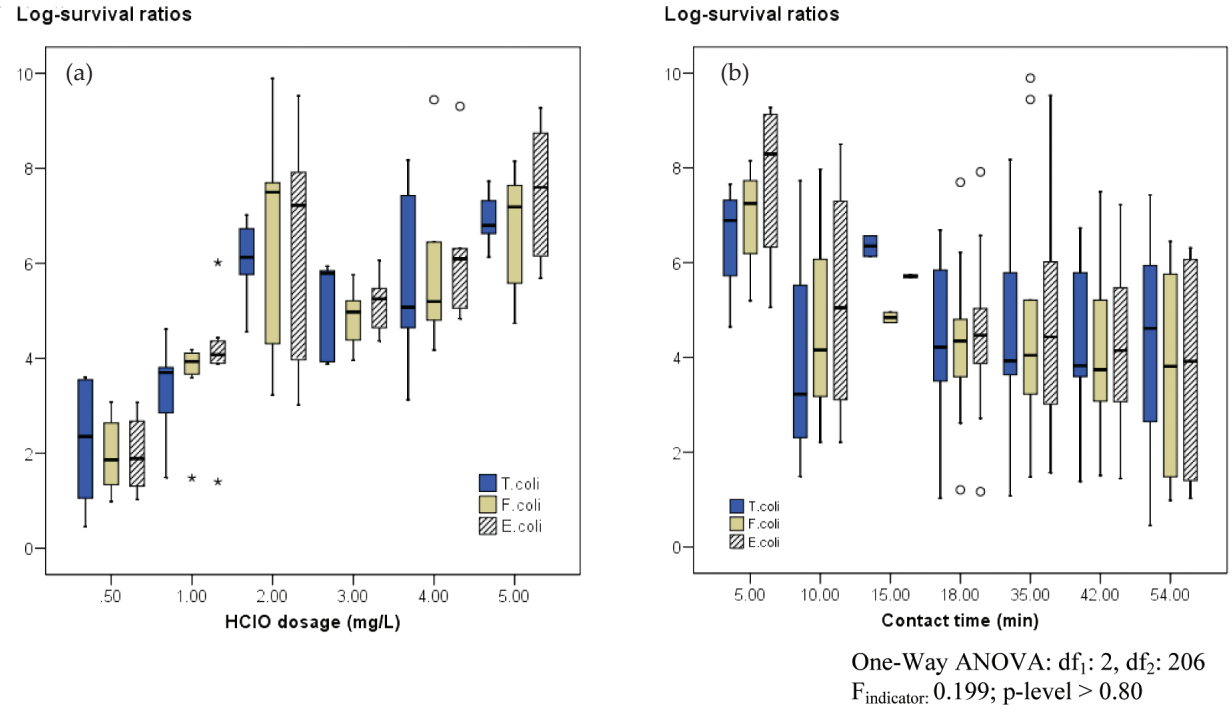


Fig. 4. Hypochlorite: the inactivation of each disinfectant-indicator combination is shown as a function of either dosage (a) or contact time (b). Box plots show the first, the second (median) and third quartile, the extreme values not considered outliers (whiskers) and the outliers (dots and stars) according to Tukey [17]. ANOVA results allow to conclude that the removal efficiency is the same for all the indicators.

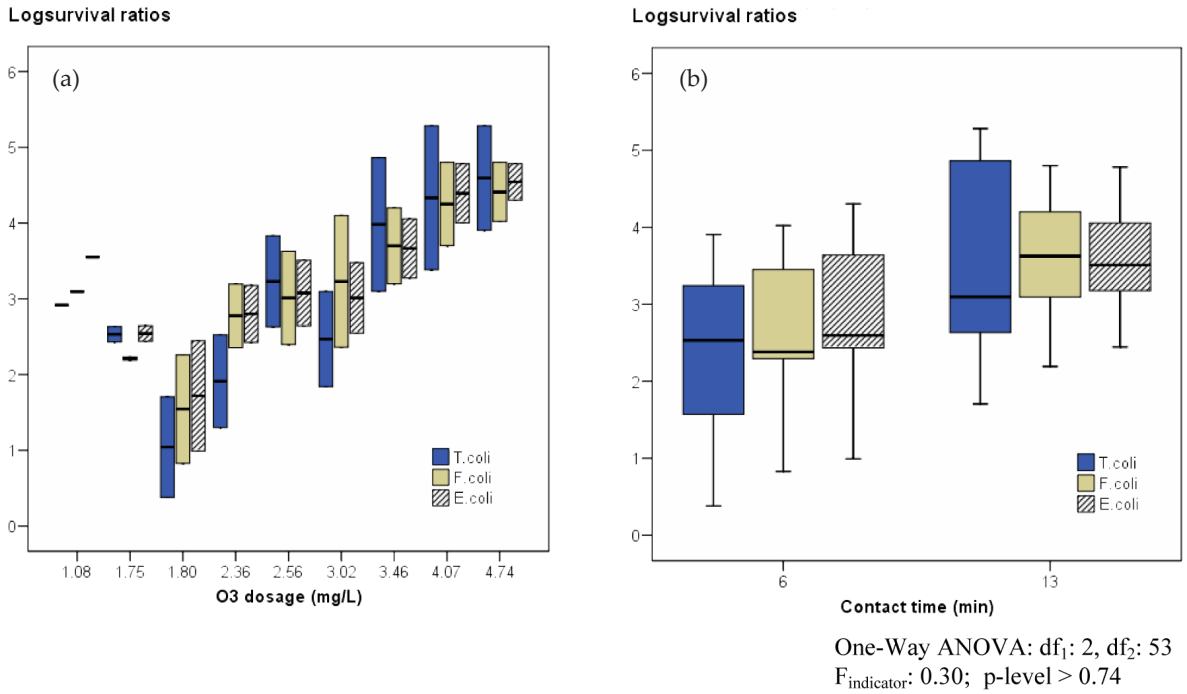


Fig. 5. Ozone: the inactivation of each disinfectant–indicator combination is shown as function of either dosage (a) or contact time (b). Box plots show the first, the second (median) and third quartile, the extreme values not considered outliers (whiskers) according to Tukey [17]. ANOVA results allow concluding that the removal efficiency is the same for all the indicators.

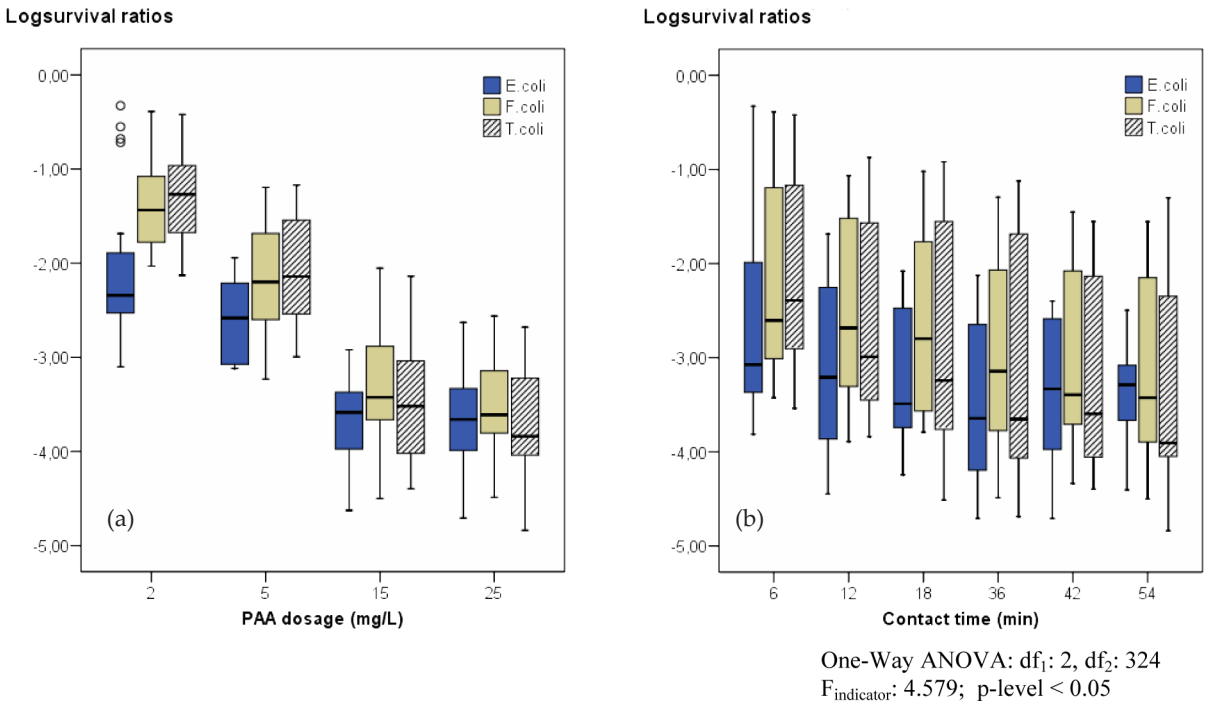


Fig. 6. Peracetic acid: the inactivation of each disinfectant–indicator combination is shown as function of either dosage (a) or contact time (b). Box plots show the first, the second (median) and third quartile, the extreme values not considered outliers (whiskers) and the outliers (dots) according to Tukey [17]. ANOVA results shown allow to conclude that the removal efficiency is not the same for all the indicators.

peracetic acid. As the box plots clearly show all the trials were affected by a certain amount of variability. It must be pointed out that the pilot-plant influent also had a large variation in BOD_5/COD, and microbial count values. These variations were found to influence the disinfection performances of hypochlorite (see supplemental material). No correlation was found instead with the influent characteristics for ozone and peracetic acid. However, it should be pointed out that during the experiments with hypochlorite, the variability of the organic and suspended solid loads was always correlated with microbial counts. Moreover ammonia concentrations were always below detection limits, so it could be concluded that the highest performances corresponded always to the highest microbial loads. To test whether the three disinfection treatments were characterized by the same removal efficiency with respect to the three microbial indicators One-Way ANOVA tests were applied. On this respect, while chlorination and ozone provided very similar removal efficiencies for all the indicators (One-Way ANOVA: p-level > 0.70, Figs, 4 and 5), PAA showed a more complex pattern (Fig. 6). At the lowest PAA doses (2 and 5 mg/L, as pure PAA), in fact the removal efficiency for *E. coli* was apparently higher than the efficiency evaluated on the other indicators; on the contrary, at the higher doses such difference was not appreciable. In order to test such a pattern, two-way ANOVA was applied to the data subsets corresponding to contact times of 18 min and 54 min runs. ANOVA tests showed significant results (p-level < 0.05) for both data subsets however different with respect to the type of indicator and their interaction with PAA dosage. In the "18 min" subset, in fact the type of indicator turned out to be significant, showing a higher inactivation of *E. coli* with respect to total and faecal coliforms independently from dosage. Moreover, being the interaction term type of indicator* PAA dosage not significant the pattern of the higher removal of *E. coli* is confirmed for all the PAA dosages (Table 4). On the contrary, in the 54 min subset the type of indicator was not significant but the interaction term PAA-indicators was significant (Table 4) showing that with a contact time of 54 min the removal efficiency with respect to the three microorganisms is not significantly different, although the inactivation for *E. coli* is higher at the lower dosages.

So these results allow concluding that:

a at 18 min of contact time, at all the tested PAA dosages, the *E. coli* removal is significantly higher than the removal of the other microbial indicators. However the effect was more evident at the low PAA dosages (Fig. 7);

b at the higher contact time (i.e. 54 min) the removal efficiency of the three microbial indicators obtained by pooling all the PAA dosages, is not statistically different, however, the fact that the interaction term PAA-type of indicator is significant confirms the higher removal of *E. coli* at the lower PAA dosages. Although, disinfectants are routinely used, very rarely the mechanisms by which these disinfectants kill and the extent to which bacteria are resistant is completely understood [25]. This study findings suggest that PAA may have a different inactivation mechanism with respect to *Escherichia coli*, and total and faecal

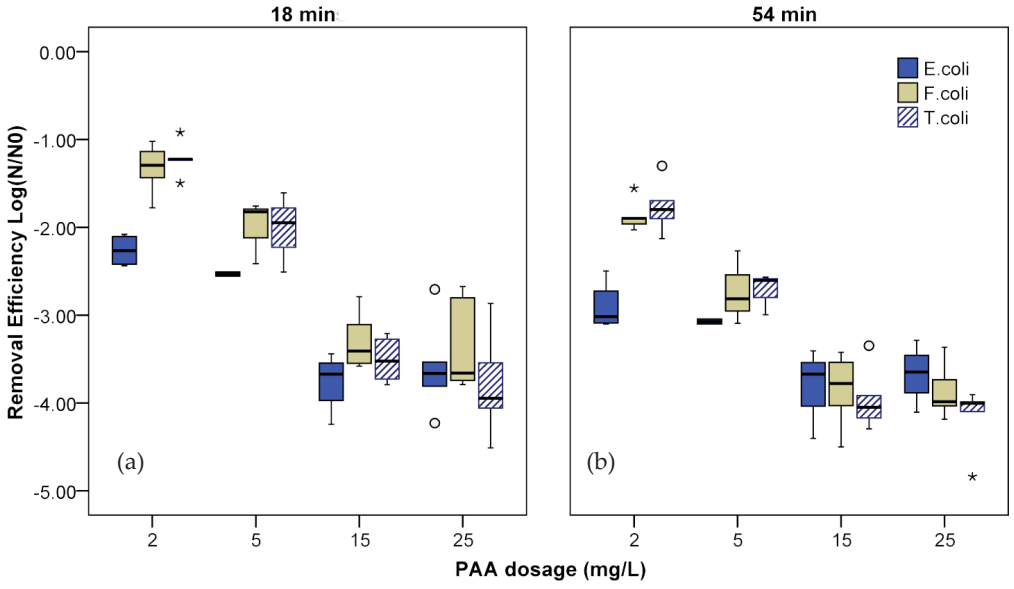


Fig. 7. Peracetic acid: the inactivation is shown for the three microbial indicators as function of dosage for the two data subsets: the 18 min and 54 min runs. Box plots show the first, the second (median) and third quartile, the extreme values not considered outliers (whiskers) and the outliers (dots) according to Tukey [18]. As ANOVA results showed, the removal efficiency is higher for *E. coli* at the lower contact time.

Table 4
Two-way ANOVA table of statistics of the removal efficiency - log(N/N0). Not significant p-levels (higher than 5%) are outlined in italics

	Source	Sum of squares	*df*	Mean square	*F*	p-level
18 min	DosePAA	42.037	3	14.012	93.970	0.000
	type_indicator	2.361	2	1.181	7.918	0.001
	DosePAA * type_indicator	2.028	6	0.338	2.266	0.054
	Error	6.561	44	0.149		
	Total	511.925	56			
54 min	DosePAA	28.367	3	9.456	84.308	0.000
	type_indicator	0.643	2	0.322	2.868	0.069
	DosePAA * type_indicator	3.528	6	0.588	5.243	0.000
	Error	4.374	39	0.112		
	Total	577.224	51			

coliforms. Modelling PAA kinetics will clarify further such a difference.

3.2. Disinfection kinetics

Disinfection kinetics was compared by means of non-linear regression multivariate analysis. The goodness of fit of the different models (i.e. Chick–Watson, Selleck, Hom and 'S') was compared and, for each disinfectant–indicator combination, the inactivation parameters were determined. The log-transformed survival ratio was used as dependent variable.

3.2.1. Chlorination

Among the different models analysed through regression analysis, the best-fit turned out to be the Hom's formula. Table 5 shows the summary statistics and the least squares estimates of the best-fit models. It should be pointed out that the coefficient of contact time (i.e. 'm' in the original Hom's formula), only occasionally was significantly different from zero. To better investigate the effect of contact time, the same regression analysis was carried out on logsurvival data corresponding to contact times shorter than 15 min. The regression coefficients for this subset were quite similar to those derived by all the data pooled together (Table 5).

Contact time level of significance was lower than 10% only in total coliforms whereas it was always very far from the 5% threshold for the other two indicators. Only modifying the original Hom's formula and excluding the '*k*' parameter, the results for contact time changed. However these "Hom-modified" models had lower goodness of fit than the previous. These results confirm that hypochlorite disinfection kinetics is extremely fast for all the indicators.

3.2.2. Ozone

Also for ozone the Hom's formula had the best fit. Table 6 shows the summary statistics and the least squares estimates for the best-fit models. Ozone kinetics turned out to be completely different from chlorination. Although concentration was still the most important parameter, contact time was also highly significant (p-level < 0.01) as far as total and faecal coliforms were concerned and significant (p-level < 0.05) as for *Escherichia coli*. Some authors [17,26] have underlined the importance of the hydraulic characterization for ozone reactors even at pilot scale, so these results sound coherent with their findings and confirm the relevance of contact time for ozone disinfection.

3.2.3. Peracetic acid

Although Hom's model had a very good fit also for PAA inactivation data, the best-fit in this case was achieved using the S-model. Tables 7 and 8 show the results for both models.

Since PAA disinfection depends more on concentration than on contact time, the S-model, where concentration is even more important than in the Hom's model, showed a better fit. The S-model allowed also demonstrating the faster inactivation of *E. coli* with respect to the other indicators. In fact, as Fig. 8 clearly shows, *E. coli* inactivation curves have a faster ascent than *T. coli*, independently from dosages. The observed difference may be misleading when *E. coli* is the only microbial indicator used to evaluate the efficiency of PAA disinfection. However, as our results showed, to achieve the same removal efficiency for total and faecal coliforms higher dosages and contact times are required. Such a difference in kinetics is relevant since the Italian legislation about surface waters protection and wastewater reuse since 1999 substituted *Escherichia coli* to total and faecal coliforms as microbial indicator, and PAA is now increasingly preferred to hypochlorite as disinfectant due to its lower potential for DBPs formation [28,29].

Table 5
NaClO: summary statistics and regression estimates for the best-fit Hom's models. Not significant p-levels (higher than 5%) are outlined in italics

All data									
	T. coli			*F. coli*			*E. coli*		
	k	*n*	*m*	*k*	*n*	*m*	*k*	*n*	*m*
Estimates	2.132	0.715	0.100	2.927	0.539	0.050	3.224	0.532	0.028
Std. err. (S.E.)	2.071	0.271	0.168	1.000	0.088	0.071	1.069	0.091	0.067
t (*df*)	1.029	2.635	0.596	2.926	6.102	0.707	3.016	5.823	0.419
p-level	*0.307*	0.010	*0.553*	0.005	4.97E–08	*0.482*	0.004	2.3E–07	*0.676*
R^2	0.827			0.761			0.78		
N	69			74			61		
Contact time less than 15 min									
	T. coli			*F. coli*			*E. coli*		
	k	*n*	*m*	*k*	*n*	*m*	*k*	*n*	*m*
Estimates	1.511	0.868	0.142	2.625	0.587	0.063	3.062	0.580	0.015
Std. err. (S.E.)	0.511	0.132	0.083	0.703	0.095	0.074	0.783	0.092	0.070
t (*df*)	2.958	6.598	1.713	3.734	6.191	0.850	3.911	6.290	0.208
p-level	0.006	3.13E–07	*0.097*	0.001	6.25E–07	*0.402*	0.001	7.2E–07	*0.836*
R^2	0.78			0.709			0.747		
N	32			35			32		
Without '*k*' parameter									
	T. coli			*F. coli*			*E. coli*		
	k	*n*	*m*	*k*	*n*	*m*	*k*	*n*	*m*
Estimates	—	1.003	0.217	—	0.865	0.259	—	0.922	0.230
Std. err. (S.E.)		0.082	0.059		0.092	0.066		0.096	0.071
t (*df*)		12.295	3.695		9.403	3.906		9.563	3.253
p-level		3.0×10^{-13}	0.001		7.4×10^{-11}	4.4×10^{-4}		1.3×10^{-10}	0.003
R^2	0.766			0.577			0.565		
N	32			35			32		

Table 6
Ozone: summary statistics and regression best-fit estimates (Hom's kinetics). Not significant p-levels (higher than 5%) are outlined in italics

	T. coli			*F. coli*			*E. coli*		
	k	*n*	*m*	*k*	*n*	*m*	*k*	*n*	*m*
Estimates	0.331	0.721	0.662	0.467	0.669	0.544	0.786	0.585	0.366
Std. err. (S.E.)	0.182	0.165	0.208	0.167	0.110	0.142	0.290	0.127	0.140
t (*df*)	1.824	4.377	3.188	2.797	6.101	3.815	2.713	4.616	2.606
p-level	*0.087*	4.7×10^{-4}	0.006	0.012	1.2×10^{-5}	0.001	0.017	4.0×10^{-4}	0.021
R^2	0.688			0.798			0.699		
N	19			20			19		

Table 7
PAA: summary statistics and regression estimates of the Hom's model

	T. coli			*F. coli*			*E. coli*		
	k	*n*	*m*	*k*	*n*	*m*	*k*	*n*	*m*
Estimates	0.617	0.392	0.189	0.708	0.348	0.170	1.302	0.223	0.120
Std. err. (S.E.)	0.051	0.019	0.018	0.061	0.019	0.020	0.116	0.019	0.022
t (*df*)	12.162	20.745	10.515	11.685	18.307	8.635	11.218	11.470	5.409
p-level	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$
R^2	0.879			0.836			0.682		
N	114			118			95		

Table 8
PAA: summary statistics and regression estimates of the S-model

	T. coli				*F. coli*				*E. coli*			
	k	*n*	*h*	*m*	*k*	*n*	*h*	*m*	*k*	*n*	*h*	*m*
Estimates	2.830	0.146	65.326	0.916	2.695	0.133	50.583	0.909	3.182	0.069	26.173	1.128
Std. err. (S.E.)	0.235	0.023	8.474	0.096	0.255	0.025	8.250	0.116	0.298	0.025	4.430	0.176
t (*df*)	12.049	6.486	7.709	9.543	10.559	5.322	6.131	7.841	10.694	2.724	5.908	6.416
p-level	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	0.008	$< 10^{-7}$	$< 10^{-7}$
R^2	0.923				0.882				0.798			
N	114				118				95			

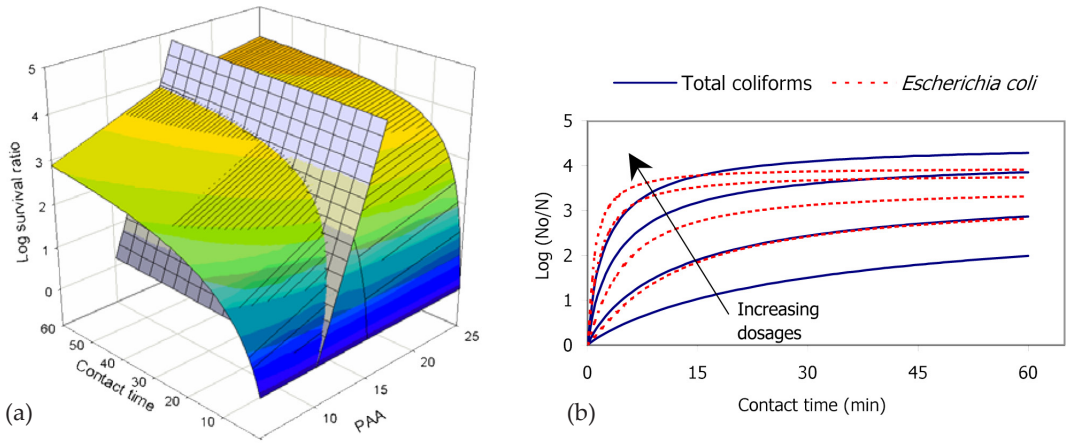


Fig. 8. a) the S-model response surface intersected by a fixed-dosage plane; b) B_i-dimensional plot of different fixed-dosage plane intersections according to the S-model: log-survival predicted values are shown for *E. coli* (dashed line) and *T. coli* (full line) as function of contact time. *E. coli* inactivation kinetics appears to be faster than *T. coli*.

This study results are coherent with the majority of the literature about PAA performance and effectiveness [12,13,20]. Some authors have [11,13] also reported the higher sensitivity of Escherichia coli although kinetics was not specifically recognized in these studies as the cause of the higher sensitivity. Also some conflicting evidence exists in the literature about PAA kinetics [30–32], mostly explainable by scale effects, influent characteristics, and batch rather than continuous flow experimental conditions. Particularly, concerning kinetics Dell'Erba et

al. [11] suggested that PAA inactivation may be described by a zero-order Monod-type equation:

$$\log \frac{N_0}{N_t} = I_{\max} \cdot \frac{t}{k+t} \quad (6)$$

where N_0 and N_t are total coliforms concentration at the initial time (N_0) and t (N_t), respectively; I_{max} is the maximum log inactivation value achievable at equilibrium; k is the semi-saturation time constant corresponding to $I_{max}/2$; t is contact time.

According to these authors, in fact, PAA inactivation is independent from the dosage. In order to test such kinetics on our data, the same regression analysis that was used before was applied. Table 9 summarizes the statistics of the zero-order Monod-type model. As it could be expected from the results obtained by Hom and S-model curve-fitting, even though contact time was confirmed in this analysis as a significant predictor, the zero-order kinetics had a very poor fit on our data. PAA dosage is, in fact, a far more important predictor than contact time, and its absence within the Monod's formula determines a very poor fit ($R^2 < 0.14$).

A possible explanation of such a discrepancy with the findings of Dell'Erba and colleagues [11] could be the very low microbial count levels in their experiment. In the experiment presented here, in fact, the count levels of total coliforms and *Escherichia coli* were 1–2 log higher than those reported in Dell'Erba et al. work [11]. Therefore it seems reasonable to conclude that PAA microbial inactivation may be described by a zero-order kinetics when the microbial count levels are very low (i.e. total coliforms lower than 104 CFU/100 ml, *Escherichia coli* lower than 2×10^2 CFU/100 ml) and the dosage is higher than 4 mg L^{-1}.

4. Conclusions

In summary, the following considerations can be drawn:

- Regression analysis applied to the inactivation data of hypochlorite, ozone and peracetic acid outlined the dominance of disinfectant dosage over contact time for NaClO and PAA and the lack of such dominance for O_3.
- Hom's formula was found the best-fit model for NaClO and O_3 inactivation kinetics whereas PAA kinetics was found to be better modelled by the "S-model".
- The inactivation of NaClO and O_3 with respect to the three microbial indicators, total, faecal coliforms and *Eschericha coli*, was found to be comparable. On the other hand, a faster inactivation was shown for *Escherichia coli* as far as PAA was concerned.
- Disinfectants are routinely used, however the mechanisms by which these disinfectants kill and the extent to which bacteria are resistant remains unclear. This study findings suggest that PAA may have a different inactivation mechanism with respect to *Escherichia coli*, total and faecal coliforms.
- When evaluating the efficiency of PAA disinfection it should be reminded that the inactivation of *E.coli* is faster with respect to total and faecal coliforms so that to achieve the same removal efficiency for coliforms higher dosages and longer contact times are required.

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Table 9
PAA: summary statistics of the regression analysis of the zero-order Monod type model

	T. coli		*F. coli*		*E. coli*	
	I_{max}	k	I_{max}	k	I_{max}	k
Estimates	–3.505	4.287	–3.294	3.648	–3.603	2.280
Std. err. (S.E.)	0.233	1.467	0.197	1.250	0.175	0.819
t (df)	–15.005	2.921	–16.738	2.917	–20.561	2.784
p-level	$< 10^{-7}$	0.00421	$< 10^{-8}$	0.00424	$< 10^{-7}$	0.0065
R^2	0.137		0.121		0.117	
N	114		118		95	

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