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Kinetics of PAA Demand and its Implications on Disinfection of Wastewaters

Dario Falsanisi,[1]* Ronald Gehr,[2] Domenico Santoro,[1,3] Adele Dell'Erba,[1] Michele Notarnicola[1] and Lorenzo Liberti[1]

[1]*Technical University of Bari, Department of Environmental Engineering and Sustainable Development, Taranto, Viale del Turismo, 74100, Italy*
[2]*McGill University, Department of Civil Engineering, Montreal, Quebec H3A 2K6*
[3]*Trojan Technologies, London, Ontario N5V 4T7*

Disinfectant demand and microbial inactivation rate are essential issues for assessing disinfection performance and proper design of disinfecting systems. In the United Kingdom and Italy, peracetic acid (PAA) has recently become an accepted disinfectant for treating wastewaters prior to reuse in agriculture, and its use is likely to spread worldwide due to its efficacy as well as the benign nature of the by-products produced. In this paper, overall PAA demand during the advanced disinfection of municipal wastewater for agricultural reuse was evaluated under different experimental conditions. Batch tests were carried out using primary and secondary settled effluents sampled at the City of Taranto municipal wastewater treatment plant. PAA dosages ranged from 1.5 to 8.5 mg/L and from 21 to 40 mg/L for the secondary and primary settled effluents, respectively. Residual PAA was measured after contact times ranging from 1 to 60 min. Results showed that after a strong and almost instantaneous initial disinfectant consumption, the PAA consumption followed first-order kinetics with both effluents. The effluent characteristics affected the values of the parameters in the consumption model. PAA disinfection efficacy was assessed in terms of total coliform and *Escherichia coli* indicator organism reduction; better results were achieved with the latter. The approximate solution of Hom's model established by Haas and Joffe was used to model inactivation kinetics of both microbial targets.

Key words: **wastewater disinfection, peracetic acid (PAA), disinfectant demand, inactivation kinetics, Hom model**

Introduction

During the disinfection process, initial demand-free conditions are unlikely to occur for most chemical disinfectants used in wastewater and natural waters (Hoff 1987). A sharp initial decrease of disinfectant concentration often occurs which can be attributed to particulates, reduced inorganic species such as iron and manganese, microorganisms, volatilization and reaction of the disinfectant with water (Hoff 1987; Sobsey 1989).

Given the difficulty of assessing the impact of each factor, the overall disinfectant-demand kinetics is a key element for proper design of disinfection systems. Further information required includes the rate of inactivation of target (or indicator) microorganism(s). In particular, the effect of disinfectant concentration on the inactivation rate will determine the most efficient combination of the contact time (i.e., basin volume at a given design flow rate) and dose to be employed.

Numerous studies have been reported concerning the disinfectant demand exerted by chemical disinfectants in common use today. For chlorine, Taras (1950) found that in pure solutions of various organic compounds, chlorine demand kinetics can be expressed as $D = kt^n$ where D is the chlorine demand, t is the time, and k and n are empirical constants. Feben and Taras (1951) established that the value of n in waters blended with wastewater is correlated to the residual chlorine concentration after one hour. Lin and Evans (1974) applied the Taras model to secondary settled effluents and found different sets of k and n values according to the contact time considered. Haas and Karra (1984a,b) fitted the data of Lin and Evans (1974) and introduced the following combined first-order decay model to explain the changing chlorine demand exerted over time:

$$D = C_0 \left\{1-\left[x \exp(-k_1 t) + (1-x)\exp(-k_2 t)\right]\right\} \qquad (1)$$

where x ranged from 0.4 to 0.6, k_1 and k_2 were the rate constants (approximately 1.0 min^{-1} and 0.003 min^{-1}, respectively), and C_0 was the chlorine dose in mg/L.

Chlorine dioxide (ClO_2) works as an oxidizing but not as a chlorinating agent. Currently, ClO_2 is used mainly as a pre- and intermediate oxidant and disinfectant (Long et al. 1999). In both cases, the proper way to determine a ClO_2 treatment dose is to perform an oxidant-demand study (Gordon 2001). The oxidant demand typically increases with time and must be defined for a given dose, contact time, temperature and

* Corresponding author; d.falsanisi@poliba.it

pH (Swietlik et al. 2003). These factors make it difficult to extrapolate oxidant demand data from one set of concentrations to another (Gordon 2001). It was previously shown (Swietlik et al. 2002) that in some cases the ClO_2 demand is a highly variable parameter. At mg/L concentrations, ammonia nitrogen, peptone, urea and glucose have insignificant chlorine dioxide demand after 1 h (Sikorowska 1961). In contrast, iron (Fe^{2+}), manganese (Mn^{2+}), nitrites and natural organic matter (NOM) exert a strong oxidant demand. The latter two seem to be the most important since iron and manganese can be efficiently removed by aeration and sand filtration (Swietlik et al. 2003).

Once added, ozone reacts with hydroxide ions to form hydroxyl and organic radicals. These radicals may contribute to additional decomposition of ozone by also reacting with other dissolved components, especially organic materials. Carbonates and possibly other ions affect ozone consumption as they can act as radical scavengers (Hoigne and Bader 1976). Gurol and Singer (1982) determined that ozone decomposition in various aqueous solutions follows second-order kinetics. However, it is very difficult to establish a general expression for ozone decay as water chemistry can heavily affect the rate and the initial ozone demand.

In general, after a given initial disinfectant demand has been satisfied, the rate of disappearance of chlorine, chlorine dioxide and ozone in aqueous solution can be described by first-order kinetics (Haas and Karra 1984a; Hoigne and Bader 1994).

Recently, there has been growing interest in the use of peracetic acid (PAA) as an alternative wastewater disinfectant. This is based on the main consideration that the formation of disinfection by-products (DBPs) and the overall toxicity during its use is much lower than with chlorine or ozone (Booth and Lester 1995; Monarca et al. 2002; Crebelli et al. 2005). PAA is generated by reaction between acetic acid and hydrogen peroxide, and it is commercially available in the following quaternary equilibrium solution:

$$CH_3CO_2H + H_2O_2 \leftrightarrow CH_3CO_3H + H_2O \quad (2)$$

Due to safety considerations during product handling, transport and storage, the commercial solution commonly used in wastewater disinfection has 15% (w/w) active PAA, 25% hydrogen peroxide, 35% acetic acid and 25% water. The principal PAA end products are acetic acid, hydrogen peroxide, oxygen and water (Lefevre et al. 1992).

Preliminary studies conducted in distilled water have highlighted the effectiveness of PAA against bacteria and, to a lesser extent, viruses (Baldry and Fraser 1988). The use of PAA in various wastewater treatment plants has confirmed that PAA dosages between 1 and 10 mg/L and contact times from 5 to 60 min can achieve 2 to 4 log reductions of total coliforms, fecal coliforms and *Streptococcus fecalis* (Arturo-Schaan et al. 1996; Lazarova et al. 1998; Liberti et al. 1999; Gehr et al. 2002; Santoro et al. 2005). Under the same conditions, *Escherichia coli* appears to be more sensitive to PAA, and up to 3 to 4 log reductions were achieved (Antonelli et al. 2004; Dell'Erba et al. 2004; Santoro et al. 2005). Higher PAA concentrations and contact times are necessary to inactivate viruses (Lazarova et al. 1998). PAA maintains its efficacy for pH values ranging from 5 to 7, while suspended solids concentrations less than 100 mg/L have a negligible effect (Sanchez-Ruiz 1995; Liberti et al. 1999; Gehr et al. 2002).

Since the literature on PAA disinfection kinetics is sparse, furthermore since these kinetics are complicated by the interactions of PAA with dissolved chemicals as well as with the target microorganisms, the goal of this paper is to elucidate PAA reaction rates when disinfecting treated municipal wastewaters. The overall effect of wastewater characteristics on PAA decay was investigated during batch disinfection tests carried out on primary settled effluents (PSE) or secondary settled effluents (SSE) in order to account for widely different operating conditions. Moreover, the disinfection efficacy against two common microbiological indicators (total coliforms and *Escherichia coli*) was evaluated. The suitability of modelling inactivation kinetics using a modified Hom model was explored.

Materials and Methods

Experimental Procedure

Wastewater was sampled from the city of Taranto (South Italy) Wastewater Treatment Plant (TWWTP), which includes primary treatment (mechanical screening and sedimentation) followed by activated sludge oxidation (90–95% BOD removal) and final disinfection with sodium hypochlorite. In order to ensure that there would be a broad range of feed characteristics during PAA disinfection, wastewater samples were spiked either at the outlet of the primary settling tank (primary settled effluent, PSE) or immediately upstream of final disinfection (secondary settled effluent, SSE).

Samples, collected between 9 a.m. and 2 p.m., were transferred to the Environmental Chemistry Laboratory in the Technical University of Taranto in a cooler, stored at 4°C, then analyzed before undergoing PAA disinfection experiments through batch tests. The physico-chemical parameters routinely analyzed (Standard Methods; APHA-AWWA-WEF 1998) for both effluents are reported in Table 1. Differences between SSE and PSE characteristics clearly emerge especially for those parameters, such as TSS and COD, able to potentially affect the disinfection process.

PAA consumption was investigated under widely different substrate characteristics, i.e., using SSE and PSE,

respectively. PAA dosages were chosen according to the strength of the wastewater with each dosage applied four times for both effluents: 1.5, 2.5, 3.5, 4.5, 5.5, 6.5, 7.5 and 8.5 mg/L to SSE and 21, 24 and 28 mg/L to PSE. In both cases, tests for residual concentrations were carried out after 1, 5, 10, 15, 20, 30, 40 and 60 min contact times.

The disinfectant action of PAA was analyzed by measuring the *E. coli* and total coliform concentrations. PAA dosages of 4, 6 and 8 mg/L for SSE and 31, 34, 37 and 40 mg/L for PSE were applied and 5, 10, 20 and 40 min contact times were investigated. The PSE dosages were substantially different from SSE to account for the higher initial demand exerted by the PSE effluent (this point is discussed further in the Results and Discussion section) and a narrow dosage range was chosen to better model the microbial inactivation with increasing PAA concentrations.

The experiments were conducted in 5-L glass tanks filled with the selected wastewater (PSE or SSE) and the samples were magnetically stirred to avoid sedimentation.

For characterizing the PAA consumption, after dosing with PAA, the residual PAA concentration was measured at the specified contact times by withdrawing an aliquot of the sample and performing the residual PAA analysis.

To assess the disinfecting action of PAA, in addition to the PAA residual analysis, 500-mL samples were taken and stored in Sterilin bottles containing $Na_2S_2O_3$ (0.01% w/w) in order to quench any PAA residual. Moreover, 0.5 mL of catalase were added to neutralize any further disinfection action due to the presence of H_2O_2 in the disinfectant mixture. The Sterilin bottles were stored in the refrigerator (4°C) for subsequent microbial analyses.

Analytical Methods

Peracetic acid. An equilibrium mixture (Oxymaster) containing approximately 15% PAA and 23% H_2O_2, produced and marketed by Solvay, Italy, was used.

The actual PAA concentration in the Oxymaster solution was determined daily by iodometric titration according to a two-step procedure developed for PAA determination (Greenspan and McKellar 1948; Sully and Williams 1962; Pinkenell et al. 1994). First, hydrogen peroxide is consumed by addition of catalase ($15 \cdot 10^6$ unit/vial, Merck 105186) and then PAA is titrated by thiosulfate addition.

Details of the method are as follows: 25 mL of a diluted solution of Oxymaster stock solution were added into 50 mL of double-distilled water previously kept for 10 min at 4°C. After addition of 10 mL of phosphate buffer solution at pH 5.5 (0.34 mM of potassium phosphate monobasic [KH_2PO_4, 99.5% J.T. Baker 4008], 0.14 mM of sodium phosphate dibasic dodecahydrate [$Na_2HPO_4{\cdot}12H_2O$, 99% J.T. Baker 0304] and 0.0021 mM of EDTA disodium salt [99.5%, J.T. Baker 4040]), 0.2 mL of catalase ($15 \cdot 10^6$ unit/vial, Merck 105186) were introduced and the solution was homogenized for 60 s. Then, 15 mL of a 12 N sulphuric acid solution (H_2SO_4, 95–97%, Merck 100731) containing 0.15 mM ammonium molybdate were added, immediately followed by 15 mL of 166 g/L KI solution [99.8% J.T. Baker 0227]. The solution was covered and stored in the dark for 20 min. The solution was then titrated by 0.1 N sodium thiosulphate solution ($Na_2S_2O_3$, 97%, Merck 106512) using a starch indicator to show the end of the titration by bleaching of the solution. The PAA concentration in the diluted solution was found by the following equation:

$$[PAA] = \frac{V_{Na_2SO_3} \cdot N_{Na_2SO_3} \cdot EW_{PAA} \cdot 1000}{V_{Oxymaster}} \quad (3)$$

where [PAA] is the PAA concentration in the Oxymaster diluted sample (expressed as mg/L); $V_{Na_2SO_3}$ is the diluted titration volume of thiosulphate solution added (expressed as mL); $N_{Na_2SO_3}$is the normality of the thiosulphate solution (i.e., 0.1 N); EW_{PAA} is the PAA equivalent weight; and $V_{Oxymaster}$ is the volume of Oxymaster diluted solution initially added (i.e., 25 mL).

The residual PAA during the batch tests was analyzed using a spectrophotometer (HACH DR 2010) at 530 nm. The 11 mL colorimetric assay comprised the following components: 10 mL of sample, 0.5 mL of a chemical solution (containing the following concentrations: 0.037 mM of H_2SO_4, 0.54 mM EDTA and 0.061 mM of DPD [DPD, 99%, Carlo Erba 443341]), 0.5 mL of sodium phosphate buffer solution at pH 6.5 (0.18 mM of disodium hydrogen phosphate dihydrate [$Na_2HPO_4{\cdot}2H_2O$, 99% J.T. Baker 1772], 0.34 mM KH_2PO_4, 0.074 µM $HgCI_2$ [99%, Rudi Pont 18650-10] and 0.0060 mM KI). The interaction between DPD and PAA produces a red colour in the sample and the reaction is catalyzed by adding phosphate buffer solution containing KI. According to the Beer-Lambert law, the PAA concentration is proportional to the absorbance of the sample measured and the calibration line was determined as:

$$C = 2.91 \cdot Abs_{530} \quad (4)$$

where C is the PAA concentration in mg/L, and Abs_{530} is the absorbance of the sample at 530 nm.

The mean standard deviation, calculated on seven standard solution absorbance values, each absorbance measurement replicated six times, was ±0.009 absorbance units. As a consequence, from equation 4, the estimated mean experimental error on PAA residual measurements was ±0.026 mg/L.

Microbial tests. Because they are standard indicator organisms in Italy and elsewhere, total coliforms and *E. coli* were analyzed according to membrane-filtration-based procedure no. 9222D from Standard Methods (APHA-AWWA-WEF 1998) within four hours of collection.

Modelling and Statistical Analyses

PAA Consumption. The PAA residual and inactivation data were fitted with different models to characterize the disinfectant consumption and to describe the kinetics of disinfection of the target organisms.

For PAA consumption, the following differential equation was applied:

$$\frac{dC}{dt} = -k_\alpha \cdot C^a \tag{5}$$

where t is the contact time; k_α is a constant; α is the overall reaction order of PAA decay, in the range of 0 to 2.

If disinfectant demand is minor ($D \approx 0$), equation 5 can be integrated as follows:

$$\int_{C_0}^{C} \frac{dC}{C^\alpha} = -k_\alpha \cdot \int_0^t dt \tag{6}$$

For 0, 1st or 2nd orders of PAA decay, one can obtain the following expressions, respectively:

$$C(t) = C_0 - k_0 \cdot t \tag{7}$$

$$C(t) = C_0 \cdot \exp^{-k_1 \cdot t} \tag{8}$$

$$C(t) = \frac{C_0}{1 + k_2 \cdot C_0 \cdot t} \tag{9}$$

By analogy, equation 5 can be integrated in the case of $D \neq 0$ with the initial condition C_0 - D:

$$\int_{C_0-D}^{C} \frac{dC}{C^\alpha} = -k_\alpha^* \cdot \int_0^t dt \tag{10}$$

and the respective 0, 1st or 2nd orders of PAA decay yield:

$$C(t) = (C_0 - D) - k_0^* \cdot t \tag{11}$$

$$C(t) = (C_0 - D) \cdot \exp^{-k_1^* \cdot t} \tag{12}$$

$$C(t) = \frac{C_0 - D}{1 + k_2^* \cdot (C_0 - D) \cdot t} \tag{13}$$

PAA residual data were test-fitted with equations 7 to 9 and subsequently with equations 11 to 13. Then, the curve-fitting global results were analyzed as follows to assess the suitability of the models. Firstly, the width of the 95% confidence interval was evaluated. If the confidence intervals were extremely wide, the fit was not likely to be very helpful. Secondly, the comparison of the goodness of fit coefficients (i.e., R^2, absolute sum of squares [SS], and standard deviation of the vertical distances [$S_{y.x}$]) was performed and the solution reporting the highest value for R^2 and the lowest values for SS and $S_{y.x}$ was chosen. As a consequence, the model best able to describe the PAA decay was established, respectively, for the equation with $D = 0$ and for the equation with $D \neq 0$.

Moreover, F-tests were performed to determine whether the more highly parameterized model provided statistically better fit to the experimental data than the simpler model. The F-test evaluates the fits of two models by comparing two hypotheses. If the simpler model (the null hypothesis) is correct, one expects the relative increase of the sum of squares (SS) to be approximately equal to the relative increase in degrees of freedom (DF). If the more complicated model (alternative hypothesis) is correct, then one expects the relative increase in SS to be greater than the relative increase in DF. Mathematically, if model 1 has more parameters than model 2, then the more complex model provides a statistically significant better fit when:

$$\frac{SS_1 - SS_2}{SS_2} > \frac{DF_1 - DF_2}{DF_2} \tag{14}$$

The F ratio is therefore defined as follows:

$$F = \frac{(SS_1 - SS_2) / (DF_1 - DF_2)}{SS_2 / DF_2} \tag{15}$$

From the F ratio, a P value is calculated. Usually the threshold P value is set at its traditional value of 0.05, then if the calculated P value is less than 0.05 the null hypothesis is rejected and the more complicated model 1 fits the data significantly better.

Microbial inactivation

The Chick-Watson law is known to be inadequate to describe microbial inactivation with tailing or shoulder behaviour. More sophisticated models were introduced to account for the aforementioned complex phenomena, such as the one advanced by Hom (1972). He proposed the following differential rate law:

$$\frac{dN}{dt} = -mk'C^n t^{m-1} N \tag{16}$$

where N is the number of viable microorganisms at contact time, t; k' is the inactivation rate constant; m and n are empirical constants. Hom's model is the three-parameter model which has shown the best fitting results in several disinfection studies (Gyurek and Finch 1998; Wagner at al. 2002; Santoro et al. 2005).

If the disinfectant decay follows a first-order model and disinfectant demand is negligible, the following integral expression can be derived:

$$\ln \frac{N}{N_0} = -mk'C_0^{\,n} \int_0^t \exp(-nk_1 t) t^{m-1} dt \tag{17}$$

where N_0 is the initial microbial concentration.

In order to obtain an analytical solution to equation 17, Haas and Joffe (1994) proposed the following approximate expression:

$$\ln \frac{N}{N_0} = -k'C_0^n t^m \left[\frac{1 - \exp\left(-\frac{\psi}{m}\right)}{\left(\frac{\psi}{m}\right)} \right]^m \tag{18}$$

where $\psi = n \cdot k_1 \cdot t$.

TABLE 1. Key characteristics of SSE and PSE for Taranto's wastewater treatment plant

	SSE[a]			*PSE*[b]		
Parameter	*min.*	*max.*	*ave.*	*min.*	*max.*	*ave.*
pH	7.4	8.0	7.7	4.4	7.9	6.2
EC (mS/cm)	1.34	2.63	1.99	1.40	1.68	1.54
RedOx (mV)	165	273	219	–226	112	–57
COD (mg/L)	10	79	45	335	394	365
Cl^- (mg/L)	264	630	447	284	420	352
DO (mg/L)	9.5	10.9	10.2	2.4	7.0	4.7
TSS (mg/L)	2	10	6	12	31	22
$P\text{-}PO_4^{3-}$ (mg/L)	1.2	1.7	1.5	4.5	5.1	4.8
$N\text{-}NO_3^-$ (mg/L)	7.9	9.9	8.9	0.2	0.7	0.4
$N\text{-}NH_4^+$ (mg/L)	1.6	4.1	2.1	10.1	30.5	24.8
E. coli (CFU/100 mL)	924	1044	987	380,000	389,000	384,000
Total coliforms (CFU/100 mL)	7250	8500	7880	3,050,000	3,174,000	3,112,000

[a]Collected immediately upstream of final disinfection.
[b]Collected at the outlet of the primary settling tank.

Once the parameters (k', n, m) of the model are determined, Haas and Joffe (1994) provided a contour plot of the error in a two-dimensional space (m and ψ, in the range frequently encountered by the authors) to evaluate the goodness of the approximation.

In this study, equation 18 was used to model the inactivation of the PSE experimental data after preliminary identification of the best PAA consumption model as described above. The goodness of the approximation of Haas and Joffe's model was investigated by analyzing the 95% confidence interval and the goodness of fit coefficients (i.e., R^2, SS and $S_{y.x}$).

Fitting of the experimental data and the F-tests was carried out by the Graph Pad Prism software (v. 4.02, Graph Pad Software, Inc.) which determines the statistical errors of the unknown parameters and assesses the goodness of the fit of the tested equation.

Results and Discussion

PAA Consumption

Tables 2 and 3 report the curve-fitting results of the 0, 1st and 2nd order models with the two different hypothesized initial conditions ($D = 0$ and $D \neq 0$, respectively). The 95% confidence intervals are quite narrow for all the models, underlining the suitability of the decay model tested. However, a closer look at the goodness of fit values reveals the 1st order model as the best one to represent the PAA decay in SSE even if, under the $D \neq 0$ hypothesis, the goodness of fit results obtained with the 2nd order model are also close. If one compares the 1st order models for both conditions, the statistical improvement of the $D \neq 0$ hypothesis emerges for all the coefficients, as the R^2 coefficient increases (0.96 for $D = 0$ ver-

TABLE 2. PAA consumption in SSE: global fitting parameter results of the models with $D = 0$ hypothesis

	0 order	*1st order*	*2nd order*
	$C(t) = C_0 - k_0 \cdot t$	$C(t) = C_0 \cdot exp(-k_1 \cdot t)$	$C(t) = C_0/(1 + k_2 \cdot C_0 \cdot t)$
	k_0 [$mg \cdot L^{-1} \cdot min^{-1}$]	k_1 [min^{-1}]	k_2 [$mg^{-1} \cdot L \cdot min^{-1}$]
Best fit values	0.0222	0.00514	0.00085
Standard error	0.00087	0.000194	0.0000042
95% Confidence interval	0.0205 to 0.0239	0.00476 to 0.00552	0.00077 to 0.00093
Goodness of fit			
R^2	0.95	0.96	0.95
SS	58.0	47.8	61.7
Sy.x	0.44	0.40	0.45
Data number		375	

TABLE 3. PAA consumption in SSE: global fitting parameter results of the models with $D \neq 0$ hypothesis

	0 order	*1st order*	*2nd order*
	$C(t) = (C_0 - D_0) - k^*_0 \cdot t$	$C(t) = (C_0 - D_1) \cdot exp(-k^*_1 \cdot t)$	$C(t) = (C_0 - D_2)/[1 + k^*_2 \cdot (C_0 - D_2) \cdot t]$
	D_0 [mg/L] k^*_0 [mg·L^{-1}·min^{-1}]	D_1 [mg/L] k^*_1 [min^{-1}]	D_2 [mg/L] K^*_2 [mg^{-1}·L·min^{-1}]
Best fit values			
D_i	0.47	0.44	0.50
k^*_α	0.00982	0.0028	0.00043
Standard error			
D_i	0.029	0.022	0.019
k^*_α	0.001004	0.00017	0.000027
95% Confidence interval			
D_i	0.41 to 0.53	0.40 to 0.48	0.46 to 0.54
k^*_α	0.00786 to 0.01179	0.0025 to 0.0031	0.00038 to 0.00048
Goodness of fit			
R^2	0.97	0.98	0.98
SS	31.3	21.0	21.2
Sy.x	0.32	0.26	0.27
Data number		375	

sus 0.98 for $D \neq 0$) whilst the values of SS (47.8 versus 21.0) and $S_{y.x}$ (0.40 versus 0.26) decrease substantially.

Figures 1 and 2 show the curve-fitting plots of the 1st order model from the above statistical data analysis, with $D = 0$ and $D \neq 0$, respectively. For the model which assumes D = 0 (Fig. 1), there is a very low correspondence between the experimental data and the model at each dosage tested. In contrast, the model with $D \neq 0$ (Fig. 2) better reproduces the experimental values even if at the highest dosage the model overestimates the PAA residual at short contact times while after 30 min it underestimates the experimental values. However, it is evident that including the initial demand, *D*, in the model improves both the statistics and the curve fit. Application of the F-test confirms that including the initial demand in the kinetic equations yields a better representation of PAA consumption. In fact, the calculated P value from equation 15 was less than the fixed threshold (P = 0.0001 < 0.05) highlighting the fact that the *D* parameter effectively provides a statistically better fit to the experimental data.

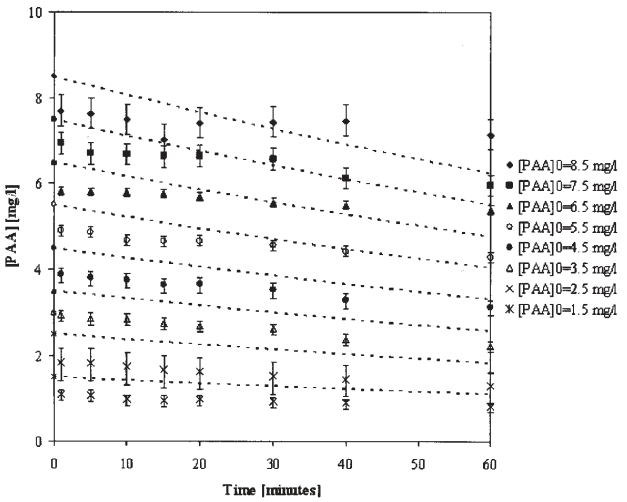

Fig. 1. SSE: PAA consumption. Dotted lines refer to the 1st order model with $D = 0$ (bars indicate minimum and maximum PAA concentration values).

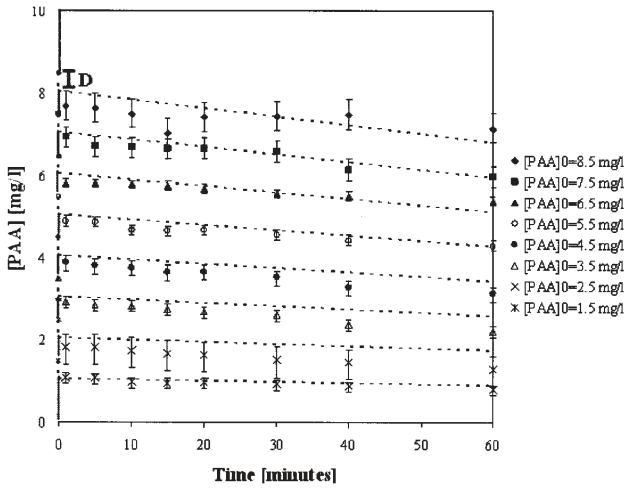

Fig. 2. SSE: PAA consumption. Dotted lines refer to the 1st order model with $D \neq 0$ (bars indicate minimum and maximum PAA concentration values).

It must be noted that equation 12 results in an almost linear correlation of PAA consumption over time because the k_1^* parameter of the model is very small (k_1^* = 0.0028 min^{-1}). This confirms the choice adopted in previous works, when analyzing a smaller residual data set and in the absence of a detailed study of the PAA demand (Dell'Erba et al. 2004; Santoro et al. 2005), that a linear model for the disinfectant decay was appropriate.

The high initial disinfectant demand exerted by the PSE shows the error of using a consumption model with D = 0. This conclusion is highlighted by the negative value of R^2 and the high values of SS and $S_{y.x}$ (Table 4). Therefore further plotting and statistical analysis were abandoned in this case.

Regarding models with $D \neq 0$ (Table 5), all fitting results confirm clearly that the 1st order kinetic model is also suitable for reproducing PAA consumption when PSE is being disinfected. The R^2 value indicates a better correlation of the data whilst *SS* and $S_{y.x}$ are considerably lower compared to the 0 and 2nd order models. The parameters of the model are indeed appropriate as shown by the narrow range of the 95% confidence interval.

Therefore, the global fitting parameter results in Table 5 suggested that the 1st order model with $D \neq 0$ be used to model the PAA consumption and Fig. 3 shows

TABLE 4. PAA consumption in PSE: global fitting parameter results of the models with D = 0 hypothesis

	0 order	*1st order*	*2nd order*
	$C(t) = C_0 - k_0 \cdot t$	$C(t) = C_0 \cdot exp(-k_1 \cdot t)$	$C(t) = C_0/(1 + k_2 \cdot C_0 \cdot t)$
	k_0 [mg·L^{-1}·min^{-1}]	k_1 [min^{-1}]	k_2 [mg^{-1}·L·min^{-1}]
Best fit values	0.66	1.50	0.42
Standard error	0.05	0.16	0.18
95% Confidence interval	0.55 to 0.76	1.18 to 1.82	0.05 to 0.79
Goodness of fit			
R^2	–29.63	–0.62	–0.75
SS	15,140	803	863
Sy.x	13.27	3.06	3.17
Data number		98	

TABLE 5. PAA consumption in PSE: global fitting parameter results of the models with $D \neq 0$ hypothesis

	0 order	*1st order*	*2nd order*
	$C(t) = (C_0 - D_0) - k^*_0 \cdot t$	$C(t) = (C_0 - D_1) \cdot exp(-k^*_1 \cdot t)$	$C(t) = (C_0 - D_2)/[1 + k^*_2 \cdot (C_0 - D_2) \cdot t]$
	D_0 [mg/L]	D_1 [mg/L]	D_2 [mg/L]
	k^*_0 [mg·L^{-1}·min^{-1}]	k^*_1 [min^{-1}]	k^*_2 [mg^{-1}·L·min^{-1}]
Best fit values			
D_i	20.03	19.41	19.70
k^*_α	0.0997	0.0396	0.0082
Standard error			
D_i	0.232	0.145	0.199
k^*_α	0.00857	0.00207	0.00077
95% Confidence interval			
D_i	19.57 to 20.49	19.12 to 19.70	19.30 to 20.09
k^*_α	0.0826 to 0.1167	0.0354 to 0.0437	0.00663 to 0.00970
Goodness of fit			
R^2	0.65	0.93	0.85
SS	171.3	36.5	73.9
Sy.x	1.42	0.65	0.93
Data number		98	

the related curve-fitting plot. The model is consistent with the data and provides a good prediction of the PAA concentration values.

Table 6 summarizes the parameter values of the 1st order model with $D \neq 0$ for both effluents investigated. Although expressible with a common equation, the different values of D_1 and k^*_1 underline the influence that the quality of the wastewater has on the PAA consumption. From Table 1 one notes that the main differences between SSE and PSE are the lower oxygen content of PSE (expressed by the DO value) and the consequently strong oxygen demand in PSE overall, which is manifested by the negative value of the RedOx parameter and is specifically attributable to the higher organic content (one order higher for both COD and TSS values). PAA, being a strong oxidant, was very sensitive to the changed influent conditions and it reacted by satisfying the increased initial demand of the effluent, as denoted by faster kinetics of consumption. In particular, both the parameter values increased by more than one order of magnitude when PSE was disinfected.

As a consequence, the above analysis underlines the importance to properly assess the PAA consumption as it is strongly dependent on the characteristics of the effluent which is being disinfected.

Microbial Inactivation

The disinfection process was also assessed by monitoring total coliforms and *E. coli*. Tables 7 and 8 report the average experimental results obtained during disinfection tests on SSE and PSE, respectively.

Based on these data, for SSE the PAA dosage range of 4 to 8 mg/L achieved almost complete disinfection (≥3 to 4 log inactivation) after 5 min with both microbial indicators. If this effluent was to be reused for agricultural purposes, 4 mg/L PAA and 10 min contact time are necessary to respect the microbiological maximum allowable concentration (MAC) regulated by the Italian Technical Guidelines for Wastewater Reuse, which is 10 CFU of *E. coli*/100 mL for 80% of samples. Therefore, the SSE could be directly reused in agriculture after the disinfection treatment as the other monitored parameters are in compliance with the fixed standards (Table 9).

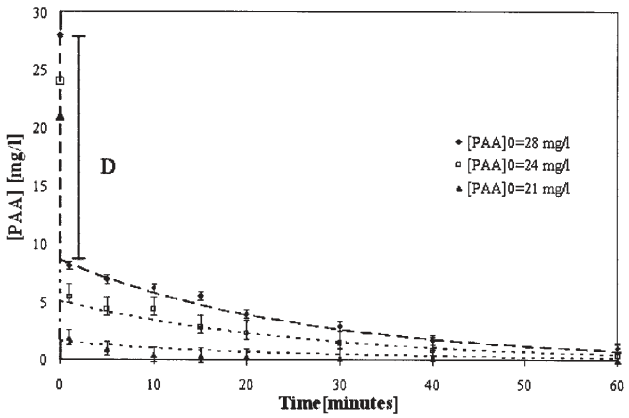

Fig. 3. PSE: PAA consumption. Dotted lines refer to the 1st order model with $D \neq 0$ (bars indicate minimum and maximum PAA concentration values).

TABLE 6. Parameter values of the 1st order model with $D \neq 0$ for SSE and PSE

$C(t) = (C_0 - D_1)\cdot exp(-k^*_1\cdot t)$	*SSE*	*PSE*
D_1 [mg/L]	0.44	19.41
k^*_1 [min^{-1}]	0.0028	0.0396

Much higher PAA dosages (30 to 40 mg/L) and contact times (up to 40 min) were tested for PSE disinfection. After 40 min and at the highest dosage, up to 5 log inactivation was obtained for total coliforms while almost complete *E. coli* disinfection was achieved at this dose. For PSE, 31 mg/L and 40 min were effective to meet the microbial standard for agriculture reuse.

Hom's equation was used to model the inactivation kinetics, and the differential rate law (equation 16) was applied.

The first step was to include the PAA consumption kinetics into the Hom inactivation model. As described previously, the best model is represented by equation 12.

The combination of equations 12 and 16 gives the following expression:

$$\ln \frac{N}{N_0} = -mk'(C_0 - D)^n \int_0^t \exp(-nk_1^* t) t^{m-1} dt \qquad (19)$$

It can be noted that equation 19 is equal to equation 17 except for the initial demand, D, that is a constant; hence the modified Haas and Joffe's approximate expression was applied in the fitting of the experimental data:

$$\ln \frac{N}{N_0} = -k'(C_0 - D)^n t^m \left[\frac{1 - \exp\left(-\frac{nkt}{m}\right)}{\left(\frac{nkt}{m}\right)} \right]^m \qquad (20)$$

Table 10 reports the best fit values of the parameters (k', m, n), the standard error, 95% confidence interval and the goodness of fit coefficients for the target organisms.

Notwithstanding the high initial demand exerted by the PSE, there is good fit of the model for the experimental inactivation ($\ln \frac{N}{N_0}$) data for total coliforms and *E. coli* values, as shown in Fig. 4 and 5, respectively. The goodness of the approximation was evaluated at the longest contact time (40 min) because there is a tendency for the error to increase with time. For the data sets investigated, m and ψ values (0.242 and 0.264 for total coliforms, and

TABLE 7. Microbiology results for total coliforms and *E. coli* in SSE disinfection

	PAA					
	4 mg/L		*6 mg/L*		*8 mg/L*	
Contact time (min)	*T. coliforms (CFU/100 mL)*	*E. coli (CFU/100 mL)*	*T. coliforms (CFU/100 mL)*	*E. coli (CFU/100 mL)*	*T. coliforms (CFU/100 mL)*	*E. coli (CFU/100 mL)*
0	7875	987	7875	987	7875	987
5	12	3	42	1	0	0
10	1	0	1	0	0	0
20	1	0	0	0	0	0
40	0	0	0	0	0	0

TABLE 8. Microbiology results for total coliforms and *E. coli* in PSE disinfection

	PAA							
	31 mg/L		*34 mg/L*		*37 mg/L*		*40 mg/L*	
Contact time (min)	*T. coliforms (CFU/ 100 mL)*	*E. coli (CFU/ 100 mL)*	*T. coliforms (CFU/ 100 mL)*	*E. coli (CFU/ 100 mL)*	*T. coliforms (CFU/ 100 mL)*	*E. coli (CFU/ 100 mL)*	*T. coliforms (CFU/ 100 mL)*	*E. coli (CFU/ 100 mL)*
0	3,110,000	384,000	3,110,000	384,000	3,110,000	384,000	3,110,000	384,000
5	6900	19	2570	10	2380	10	2350	4
10	5800	15	1520	4	800	6	622	3
20	3000	13	1360	2	483	2	118	1
40	800	9	456	1	74	1	18	1

0.100 and 0.134 for *E. coli*, respectively) correspond to an error of less than 10% for both target organisms.

The higher sensitivity of *E. coli* is confirmed by the *k'* value that is much higher than that for total coliforms whereas the *m* value, being considerably less than 1.0, highlights the limited importance that the contact time parameter has on the overall inactivation kinetics, especially for *E. coli*.

The kinetics are affected by a tailing behaviour that may be attributed to the presence of clumping organisms and/or to the presence of subpopulations with varying resistance, especially for total coliforms (Cerf 1977). Moreover, the high initial disinfecting action of PAA may be related to the simultaneous action of other chemicals (such as hydroxyl radicals, *OH, produced by

TABLE 9. Main characteristics of SSE after disinfection with PAA

Parameter	*PAA effluent*[a]	*MAC*[b]
pH	7.7	6–9.5
TSS (mg/L)	6	10
COD (mg/L)	45	100
Cl^- (mg/L)	447	500[c]
E. coli (CFU/100 mL)	3	10

[a]PAA: 4 mg/L, 5 min.
[b]MAC for WW reuse (Italian Technical Guidelines, D.M.I. No. 185/2003).
[c]Apulia Region MAC.

TABLE 10. Fitting parameter results of Haas and Joffe's model for total coliforms and *E. coli* in PSE

	Total coliforms	*E. coli*
Best fit values		
k'	3.51	7.93
n	0.167	0.085
m	0.242	0.100
Standard error		
k'	0.27	0.27
n	0.0218	0.0098
m	0.0215	0.0099
95% Confidence interval		
k'	2.94 to 4.08	7.37 to 8.49
n	0.121 to 0.213	0.064 to 0.105
m	0.196 to 0.287	0.079 to 0.121
Goodness of fit		
R^2	0.98	0.99
SS	4.1	1.7
Sy.x	0.49	0.32
Data number	17	17

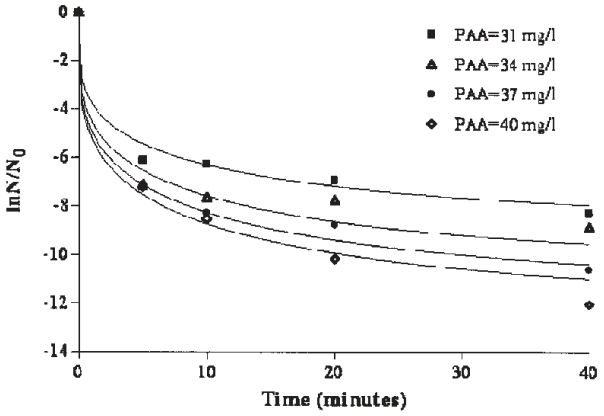

Fig. 4. PSE: application of Hom's model for total coliforms.

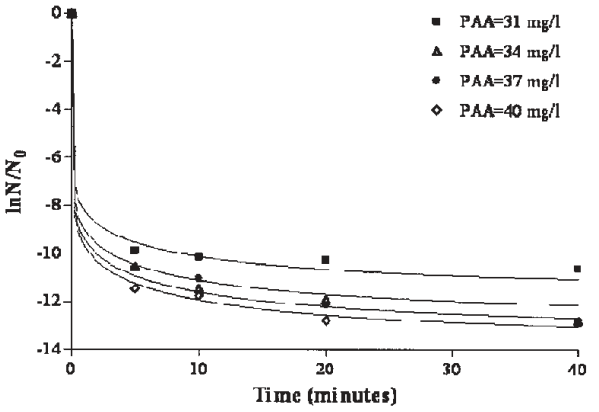

Fig. 5. PSE: application of Hom's model for *E. coli*.

homolytic breakdown of the PAA peroxidic bond) that may also be responsible for microbial inactivation (Bianchini et al. 2002). Future work will entail further investigations into PAA inactivation mechanisms and the impact of hydroxyl radicals on PAA effectiveness.

Conclusions

Peracetic acid (PAA) is a relatively new disinfectant which has only recently been employed at full-scale wastewater treatment plants. In general, the consumption of disinfectant and the inactivation rates are the two most important items of information required to properly design a disinfection unit. The results of this study showed that peracetic acid consumption is heavily influenced by the initial quality of the effluent as demonstrated by the results obtained in secondary settled effluent samples compared to those in primary settled effluent samples.

The initial PAA demand exerted by the effluent has to be considered when the disinfectant dosage is chosen. The PAA demand increases heavily when primary settled effluent samples were disinfected, suggesting that factors such as suspended solids content, COD and/or metals play a key role in the demand.

The importance of considering the initial demand in the overall PAA consumption is confirmed by the comparison of kinetic models (zero, 1st, 2nd order consumption models) applied under two different initial conditions, i.e., presence versus absence of PAA demand. Once the disinfectant demand is satisfied, the residual data were best fit by first-order kinetics in both effluents investigated, but in the primary settled effluent samples a ten times higher consumption rate was found.

The importance of choosing the correct model for microbial inactivation was highlighted as an optimizing criterion in the design of disinfection units (Santoro et al. 2005). In the current study, the inactivation rate was modelled by the approximate solution (established by Haas and Joffe) of Hom's model, and modified to account for the initial PAA demand. The model fits the experimental data well for both of the target organisms investigated (i.e., total coliforms and *E. coli*) and accounts for the tailing behaviour affecting the kinetics. This finding confirms the flexibility of the tested model to describe the inactivation kinetics under a variety of conditions.

Finally, the disinfection tests revealed that PAA was especially effective for *E. coli* disinfection. For the secondary settled effluent, a PAA dose of 4 mg/L and 10 min contact time were required to achieve the Italian microbial national limit (10 CFU *E. coli*/100 mL) for the agricultural reuse of treated wastewater. For the primary settled effluent, much higher dose and contact time (31 mg/L and 40 min, respectively) were needed to meet the same limit.

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