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Pilot-plant comparative study of peracetic acid and sodium hypochlorite wastewater disinfection

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Abstract

Peracetic acid (PAA) use in wastewater disinfection was assessed by examining its performances in a pilot plant fed by the effluent from a conventional activated-sludge treatment plant. The influence of PAA initial concentrations (0.5–4.0 mg/l) and contact times (8–38 min) on the presence of seven microorganisms (total coliforms, fecal coliforms, fecal streptococci, *Escherichia coli, Pseudomonas* sp., *Salmonella* sp., and bacteriophages anti-*E. coli*) and on residual biocide and halogenated organic compound (AOXs) concentrations were evaluated. The data so obtained were compared to the corresponding results acquired using sodium hypochlorite (HYP) in the same experimental conditions.

The biocide effect of PAA against total and fecal coliforms, *E. coli, Pseudomonas* sp. and *Salmonella* sp. was similar to that shown by HYP. The former disinfectant was, however, less efficient than the latter in the reduction of fecal streptococci and bacteriophages anti-*E. coli*. In both cases the biocide quantities initially introduced in the sewage resulted in the presence of significant concentrations at the end of the contact time. No significant variation of AOX content was detected in the effluent treated with PAA, whereas a progressive increment of such compounds was found when increasing quantities of HYP were added to the sewage.

Keywords: Peracetic acid; Sodium hypochlorite; Wastewater disinfection; Biocide effect; AOX formation

1. Introduction

Several studies have pointed out that treated and untreated wastewater is a primary contributor of a variety of pathogenic microorganisms to the aquatic ecosystem [1–4]. Their presence in surface waters can denote fecal pollution and may constitute a risk of transmission of waterborne diseases to the human population, especially in bathing zones or shellfish farming areas. The treatment of raw wastewater by adequate processes is essential to avoid this problem. At the moment, the widespread depurative process based on primary treatments and biological oxidation allows a good reduction of the pathogen load, but it is not sufficient to obtain quality levels compatible with public health and environmental protection. In order to minimize human exposure to waterborne pathogens, effluents from the secondary settler are treated with a disinfectant before they are discharged in surface waters. An ideal disinfection system should guarantee the maximum efficiency in pathogenic microorganism removal without generating toxic and undesirable by-products. Moreover, it should be inexpensive and technologically compatible with other treatment processes. At the present time, effluents are mainly disinfected by chlorine, as gas or hypochlorite, and chlorine dioxide because of their high biocide power. However, their use has provoked worries for toxic, mutagenic and carcinogenic properties of their by-products [5–9]. Other alternative techniques, such as

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ozonization, UV irradiation, microfiltration, etc., have shown sanitary and technologic limits not entirely well known.

In the last years, peracetic acid has been introduced as disinfectant in agronomical and alimentary industries as well as in hospital structures. Further applications have also been developed in German industrial laundries and in English zootechnics [10]. Only recently wastewater disinfection has been carried out using peracetic acid alone or in combination with other reagents [11–13]. Consequently, there are not enough data on the efficiency of environmental matrix treatment and on the nature of its potential by-products.

In this research we have studied the disinfectant action of peracetic acid against the usual indicators of fecal contamination (total and fecal coliforms, fecal streptococci, and *E. coli*), an environmental microorganism and opportunistic pathogen (*Pseudomonas* sp.), a bacterial pathogen (*Salmonella* sp.) and a viral indicator (bacteriophages anti-*E. coli*). The biocide was added to the sewage effluent coming from the secondary settler of an urban treatment plant. All the results obtained have been compared with the corresponding removal efficiencies determined using sodium hypochlorite in the same experimental conditions. Disinfectant residues and halogenated by-products (AOXs) in treated wastewater have also been examined as a function of the controlled variables (contact time and reagent concentration).

2. Materials and methods

2.1. Description of the pilot plant

The experimentation, organized by Istituto Superiore di Sanità (ISS) and ACEA S.p.A., was carried out in a pilot plant installed in a municipal wastewater-treatment plant located in Rome (Italy) and administered by ACEA S.p.A.

The municipal plant uses a conventional sewage-treatment system based on screening, primary clarification, aeration and biological oxidation through activated sludge, secondary clarification, and chlorination.

The pilot plant (Fig. 1) consisted of a metallic structure (3.5 m long, 2.5 m wide and 2.2 m high) subdivided lengthwise in two parallel tanks. Every tank employed for the contact between sewage and a disinfectant was internally coated by a stainless steel plate (AISI 316 L), at least 1 mm thick. Four septa were installed crosswise into each tank. The septa had staggered openings (0.4 m wide and 0.3 m high) at the bottom in order to set the fluid in a zigzag motion.

Both tanks were fed by the effluent from the secondary settler placed after the activated-sludge biological tank of the municipal plant. Table 1 lists physico-chemical, chemical and microbiological composition of the sewage employed during the experimentation.

The effluent sucked by a submersible pump was introduced in the tanks by means of a pipe divided in two branches by a tee joint. A magnetic volume meter and a throttle valve were installed along each branch. Before the tee joint, a by-pass was used to set flow rates much lower than the nominal value of the charging pump. The flow rate in the by-pass was regulated by a throttle valve. A weir at the exit of every tank set liquid level in the pilot plant.

Residence times (t_R) of each tank were determined by injecting rapidly a tracer (61 of a saturated solution of sodium chloride) into the sewage stream at the inlet of the pilot plant and by measuring the electrical conductivity at the exit of the tanks. Instantaneous flow

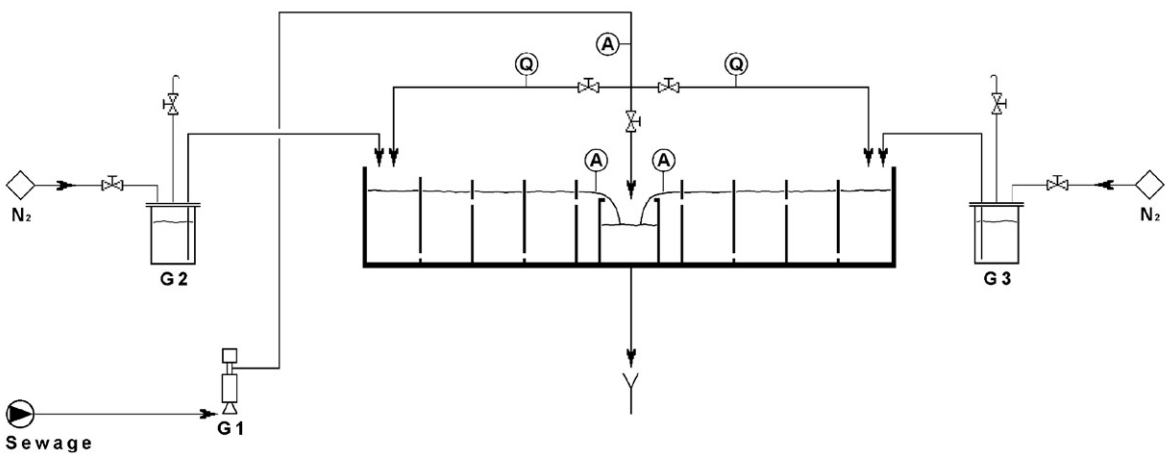

Fig. 1. Simplified scheme of the pilot plant. (G1: submersible pump; G2: pneumatic pump containing concentrated HYP; G3: pneumatic pump containing concentrated PAA; A: sampling site; Q: magnetic volume meter).

Table 1
Physico-chemical, chemical and microbiological characteristics of the sewage before the disinfection

Parameter		Min	Max	Data no.	Mean	Standard error	95% confidence interval
Temperature	°C	13.9	29.5	30	19.3	0.8	17.6; 20.9
pH		6.58	8.05	30	7.63	0.06	7.51; 7.74
Electrical conductivity	mS/cm	0.63	0.88	10	0.81	0.03	0.75; 0.86
Dissolved oxygen	mg/l	4.4	5.9	10	5.0	0.1	4.6; 5.3
E_h	mV	282	416	30	351	7	336; 366
Turbidity	NTU	1.6	26.9	30	6.6	0.9	4.7; 8.5
TSS	mg/l	2	24	29	8	1	6; 10
TOC	mg/l C	5	60	29	22	3	15; 28
AOX	μg/l Cl	9	53	29	23	2	20; 27
NH_4^+	mg/l	0.2	7.3	29	2.0	0.4	1.2; 2.7
NO_2^-	mg/l N	0.03	0.42	30	0.18	0.02	0.13; 0.22
NO_3^-	mg/l N	3.0	15.4	30	9.1	0.7	7.7; 10.5
Total coliforms	Log (CFU/100 ml)	4.4	6.4	29	5.3	0.1	5.1; 5.5
Fecal coliforms	Log (CFU/100 ml)	4.0	5.9	29	4.9	0.1	4.7; 5.1
Fecal streptococci	Log (CFU/100 ml)	3.6	5.6	29	4.4	0.1	4.2; 4.6
Escherichia coli	Log (CFU/100 ml)	4.0	5.9	29	4.8	0.1	4.7; 5.0
Salmonella species	Log (MPN/100 ml)	1.5	4.7	20	3.8	0.2	3.4; 4.2
Pseudomonas species	Log (CFU/100 ml)	3.1	7.0	20	5.1	0.3	4.6; 5.7
Bacteriophages anti-*E. coli*	Log (PFU/100 ml)	0.9	3.9	20	1.8	0.1	1.5; 2.1

rates of the tracer added to the sewage were also recorded during the determination of the conductivity profiles.

2.2. Disinfection

Two different disinfectants, sodium hypochlorite (HYP) and peracetic acid (PAA), were tested in parallel as experimental conditions varied. Their introduction in the respective tanks was carried out by two laboratory-made pneumatic pumps operating with nitrogen. All reagent flow lines were made in Teflon (PTFE).

In this research we have studied the effect of disinfectant concentrations (0.5, 1.0, 2.0, and 4.0 mg/l on average) and reaction times (8, 12, 20, 26, and 38 min on average) on microorganism reduction. The contact time between sewage and each disinfectant was varied acting on the feeding flow of the sewage in the range 2.0–8.0 l/s.

2.3. Chemical analyses

Chemicals were reagent grade (Fluka, Buchs, Switzerland), except in those cases indicated. Sodium-hypochlorite and peracetic-acid solutions containing 5% or 15% of technical-grade disinfectant were supplied by Zarrelli (Rome, Italy) and Solvay Interox (Brussels, Belgium), respectively. Their actual concentration was determined daily by iodometric analyses before starting tests. Free iodine liberated from KI by HYP or PAA was titrated against a standardized $Na_2S_2O_3$ solution (0.1 N) in the presence of a starch indicator. The interference caused by H_2O_2 in the determination of PAA titer was eliminated by adding some drops of catalase from bovine liver (molecular weight: 240,000 amu) to the aliquot of the disinfectant. Total concentration of peroxides ($PAA + H_2O_2$) in peracetic-acid solutions was measured spectrophotometrically at 512 nm after adding a phosphate buffer solution (pH = 6.5), KI and *N*,*N*-diethyl-*p*-phenylenediamine (DPD) to an aliquot of the diluted disinfectant. The reagents were dosed as described in literature for total chlorine determination [14]. The slow reaction between hydrogen peroxide and iodide was catalyzed by a few drops of ammonium molybdate 1 mg/l, which reduced the reaction time to 14 min. The concentration of H_2O_2 in peracetic acid solutions was subsequently calculated by subtracting the peroxiacid titers to the corresponding total peroxide concentrations.

Free and total chlorine in the effluent treated with HYP and residual peracetic acid in wastewater disinfected with PAA were periodically determined by automated flow-injection analyzers located at the exit of the pilot plant. Such disinfectant residues were all dosed by applying the DPD colorimetric method [14] after decomposing H_2O_2 in PAA by means of the enzyme catalase. Hydrogen-peroxide residue in wastewater treated with PAA was determined spectrophotometrically in sample aliquots as described above.

Two samples per site were collected in 500-ml glass bottles at the inlet and outlets of the pilot plant.

Sampling operations were repeated three times at each programmed experimental condition to determine the reproducibility of the obtained results. 0.50 g of sodium sulfite were introduced in all bottles containing the disinfected wastewater in order to reduce the residues of the oxidizing agents. Only a sample per site was acidified with 2 ml of concentrated sulfuric acid (96%). Collected samples were stored at approximately 4°C and subsequently analyzed in laboratory.

Total organic carbon (TOC), adsorbable organic halogens (AOX) and ammonia were determined in the acidified samples, while nitrite, nitrate and total suspended solids (TSS) were dosed in the remaining samples. All these determinations were carried out as indicated in literature [14]. In particular, a Shimadzu TOC-5000 analyzer connected to a Shimadzu ASI-5000 liquid autosampler was used to quantify the total organic carbon in the samples. The determination of AOX was performed by a Mitsubishi 10Σ analyzer after trapping suspended and dissolved organic compounds in an activated-carbon cartridge. The concentration of ammonium ion was measured by means of an ammonia-selective electrode using known additions. Both nitrite and nitrate were determined in situ through the Griess colorimetric method applied before and after reducing nitrate to nitrite in the presence of cadmium and copper.

Water temperature, pH, electrical conductivity, dissolved oxygen and redox potential (E_h) with respect to the Standard Hydrogen Electrode potential were valued in the field with a multi-parametric probe during sampling operations.

All off-line spectrophotometric measures were carried out by using a Perkin-Elmer 550S spectrophotometer equipped with a 1 cm pathlength flowcell.

2.4. Microbiological analyses

Three replicated samples were collected at the inlet and at the exits of the pilot plant in 750-ml polypropylene sterile bottles containing 1 ml of sodium thiosulfate 100 g/l and 0.1 ml of catalase to reduce any disinfectant residue. They were transported in the laboratory and analyzed within 2 h. The determination of the microbiological parameters examined in this research was carried out on three dilutions of each replicated sample.

Bacterial indicators of fecal contamination, such as total coliforms (TC), fecal coliforms (FC), *E. coli* (*E. coli*) and fecal streptococci (FS), as well as the environmental microorganism *Pseudomonas* sp. (*Pse*) were determined by the membrane filtration technique using a cellulose-nitrate filter with 0.45-μm pore size (Millipore, Bedford, MA, USA). The enumeration of TC was performed using the chromogenic substrate C-EC Agar (Biolife Italiana, Milan, Italy) at an incubation temperature of 36 ± 1°C for 18–24 h. At the end of the incubation period, all the blue–green colonies were counted. FC and *E. coli* were recovered on the same substrate at the discriminating temperature of 44.0 ± 0.5°C for 18–24 h. On this substrate FC grew as blue–green colonies, while *E. coli* grew as blue–green colonies fluorescent under ultraviolet light (366 nm). FS were recovered on Slanetz-Bartley Agar (Difco, Detroit, MI, USA) at an incubation temperature of 36 ± 1°C for 48 h. A confirmation test was carried out on Esculin Iron Agar (Difco) by evaluating the esculin hydrolysis (1 h at 42 ± 1°C). Pink to red colonies with black halos in the backside of the membrane were counted. The concentration of *Pse* species was determined on *Pseudomonas* sp. Agar Base supplemented with *Pseudomonas* sp. C-N Selective supplement (Oxoid, Basingstoke—Hampshire, UK) at an incubation temperature of 37 ± 1°C for 72 h. All and fluorescent colonies were counted. The results obtained for all of these parameters are expressed as colony forming unit (CFU)/100 ml.

The pathogen *Salmonella* sp. was detected by the multiple-tube fermentation procedure after applying a pre-enrichment step in Peptone Water (Oxoid) at 37 ± 1°C for 24 h and an enrichment step in Rappaport–Vassiliadis Enrichment Broth (Oxoid) at 42 ± 1°C for 24 + 24 h. The isolation of the microorganism was carried out on Enteric Agar (Oxoid) where blue–green colonies with and without a black center were counted after a 24-h incubation period at 37°C. The results are expressed as the most probable number (MPN)/100 ml.

Bacteriophages anti-*E. coli*, chosen as viral indicators, were determined using the plate count method described by Havelaar and Hogeboom [15]. *E. coli* 8113 ATCC 9723 C was the phage-sensitive marker strain. The results are expressed as plaque forming unit (PFU)/100 ml.

In this research classical cultural methods were used. Notwithstanding it is well known that they underestimate the actual population (injured and stressed bacteria are detected with difficulty), they still remain the commonest used methods.

3. Results and discussion

3.1. Characterization of the pilot plant

Temporal trends of electrical conductivity and instantaneous flow rate of sewage were obtained during the characterization of the pilot plant as described previously. Every value of the residence time was determined by evaluating the centroid of the area under the corresponding conductivity profile [16–18]. The associated average flow rate was calculated as

follows:

$$\bar{Q} = \frac{\int_0^{t_R} Q(t)\,dt}{t_R}, \quad (1)$$

where $Q(t)$ was the polynomial interpolating the data of the instantaneous flow rates recorded during the acquisition of each conductivity profile. Its order and coefficients were estimated using the least-squares method.

All t_R values were plotted against the corresponding average flow rates (Fig. 2) in order to define an empirical relationship between the two parameters that was used to calculate contact times from experimental values of $Q(t)$ measured in all the subsequent disinfection tests. The experimental points shown in Fig. 2 were fitted by means of the following equation chosen with an iterative process by examining the residue plots resulting from the application of the least-squares method:

$$t_R = \alpha \ln \bar{Q}^2 + \beta \ln \bar{Q} + \gamma. \quad (2)$$

The best estimate of the coefficients and their corresponding standard errors (SD) were 6 min (SD = 2 min) for α, −39 min (SD = 5 min) for β and 63 min (SD = 3 min) for γ.

3.2. General remarks on indicator organisms in water hygiene

The number and variety of microorganisms present in wastewater and associated solids are legion. Their sources are the excreta of humans and animals, other waste materials that find their way into domestic sewage, and the microbial flora in the source water. This great diversity and associated variety of required growth conditions hamper attempts to isolate, identify, and enumerate most organisms members of this microcosm. The number of pathogens that might be present in wastewater and biosolids is a function of the disease morbidity in the community from which the waste materials are derived and the degree of sewage treatment received. Relative to the total number of organisms present, the pathogens normally represent but a minor part. In most instances, these pathogens play a passive role in the dynamics of the microbial ecosystem; the waste environment is hostile, and consequently the number of pathogens present tends to decrease over time [19].

Since the pathogenic microorganisms appear intermittently in natural waters at low concentrations, and the techniques available for the selective recovery and enumeration are, generally, very complex, routine microbiological water analyses are based on detecting

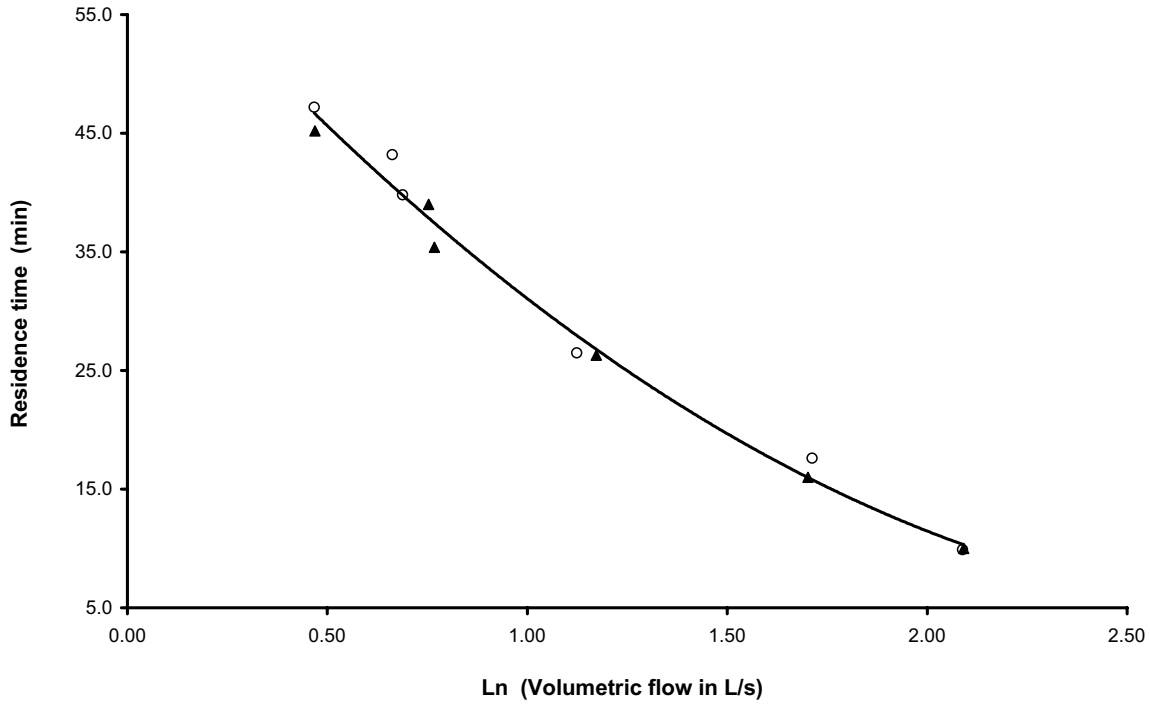

Fig. 2. Residence time as a function of the average volumetric flow at the entrance of the pilot-plant tanks. (Disinfectants: ▲ peracetic acid, ○ sodium hypochlorite).

other microorganisms (surrogates) that share the same habitats. These microorganisms are named indicators of fecal pollution. Historically the coliform group, the enterococci, and *Clostridium perfringens* have, in descending priority, been the bacterial indicators of choice. In all of these cases, the indicator bacteria are assumed to be indigenous to faeces, and thus their presence in environmental samples is considered as indicative of fecal contamination. The presence, and in some instances the absence, of these indicators is not an absolute indication of the presence of pathogens. Rather, they indicate the potential for the presence of pathogens because of the likelihood that infectious faeces are present in wastewater or sludge. The bacterial indicators' greatest weakness as a public health monitoring tool for water and wastewater is their greater sensitivity to disinfection relative to viruses and protozoan parasites [20,21]. No consistent relation has been observed between indicator bacteria levels and density of viruses and (oo)cysts of *Cryptosporidium* and *Giardia* [22–24]. In particular, investigations of commonly used water treatment technologies indicate that both the parasites are more resistant to water treatment processes [25–27]. Physical methods (microfiltration and UV irradiation) or sequential treatment using different disinfection agents have been found to be useful in certain circumstances [28]. In these instances, the absence of indicator bacteria is not a guarantee that other, more resistant microbial forms are not present. Because of these problems, there have been ongoing efforts to find better indicators for the presence of microbial pathogens in environmental samples. The ideal would be to monitor for the presence of all microbial pathogens that might be present in a liquid or solid sample, an ideal not likely to be realized any time in the foreseeable future.

Recently, indicators more closely related to enteric viruses have been taken into account in the evaluation of virological water quality [29,30]. Bacteriophages have played a valuable role in this regard because their structure, composition, morphology, and size closely resemble those of enteric viruses [31–33].

In the present work, TC, FC, *E. coli*, FS and *Pse* were chosen as bacterial indicators of biocidal efficiency, whereas bacteriophages anti-*E. coli* were determined as an indicator of removal efficiency.

3.3. Evaluation of microbial data acquired for the pilot-plant influent

The concentration values of the seven microbiological parameters in sewage samples collected before the disinfection (Table 1) are comparable to the corresponding data reported in literature [34–36]. A significant variability in the cohort can be noticed as regards *Salmonella* sp. and bacteriophages anti-*E. coli*. The reason for such a phenomenon was partly that the analytical method applied for their determination as well as other currently available methods are not very accurate. The result of the *Salmonella* sp. test is, in fact, obtained using a probabilistic method (MPN) instead of the actual enumeration, which is applicable with difficulty to this pathogen. On the contrary, the analysis of the bacteriophages requires a concentration step characterized by variable recoveries of the virus [37,38]. As regards the former microorganism, the fluctuation also depends on endemic conditions and diffusion processes in the community located near the wastewater treatment plant. In this connection, it is necessary to consider the role of casual carriers, which can contribute to its elimination in the environment [39].

3.4. Disinfectant performances in the reduction of microbial pollution

The results of microbiological analyses carried out on sewage before and after the two disinfection treatments were correlated to the products of the biocide initial concentration (C_0) and the contact time (t_R) as suggested by Collivignarelli et al. [40]. Figs. 3–9 show survival ratios, as common logarithm of the ratio of microbial populations at the exit (N) and at the inlet (N_0) of each tank, at varying of common logarithm of $C_0\,t_R$. Table 2 lists the regression coefficients and the corresponding standard errors of the straight lines that fit the experimental points in the above-mentioned graphs. The two regression models (HYP and PAA lines) obtained for every microbiological parameter were compared each other by testing the significance of the difference between their slopes and, subsequently, the hypothesis of their coincidence. Both tests were carried out on the basis of the difference between their variances produced by the scattering of the points with respect to the corresponding straight lines [41,42]. Table 3 summarizes the results of such a statistical analysis. The regression coefficients were used to calculate the minimum concentrations of HYP or PAA necessary to remove 90% (corresponding to a survival ratio of a logarithmic unit) of each microbial contaminant examined (Table 4). The disinfectant actions of the two reagents against five microbiological parameters (total and fecal coliforms, *E. coli*, *Salmonella* sp. and *Pseudomonas* sp.) are not significantly different to each other. On the contrary, the bactericide activity of the peracetic acid against fecal streptococci and bacteriophages anti-*E. coli* seems less than the corresponding hypochlorite action in all $C_0\,t_R$ range studied. The different behavior of fecal streptococci and bacteriophages towards the tested biocides is due to their major resistance to disinfectants with respect to other organisms. Both of these organisms show a higher resistance also to

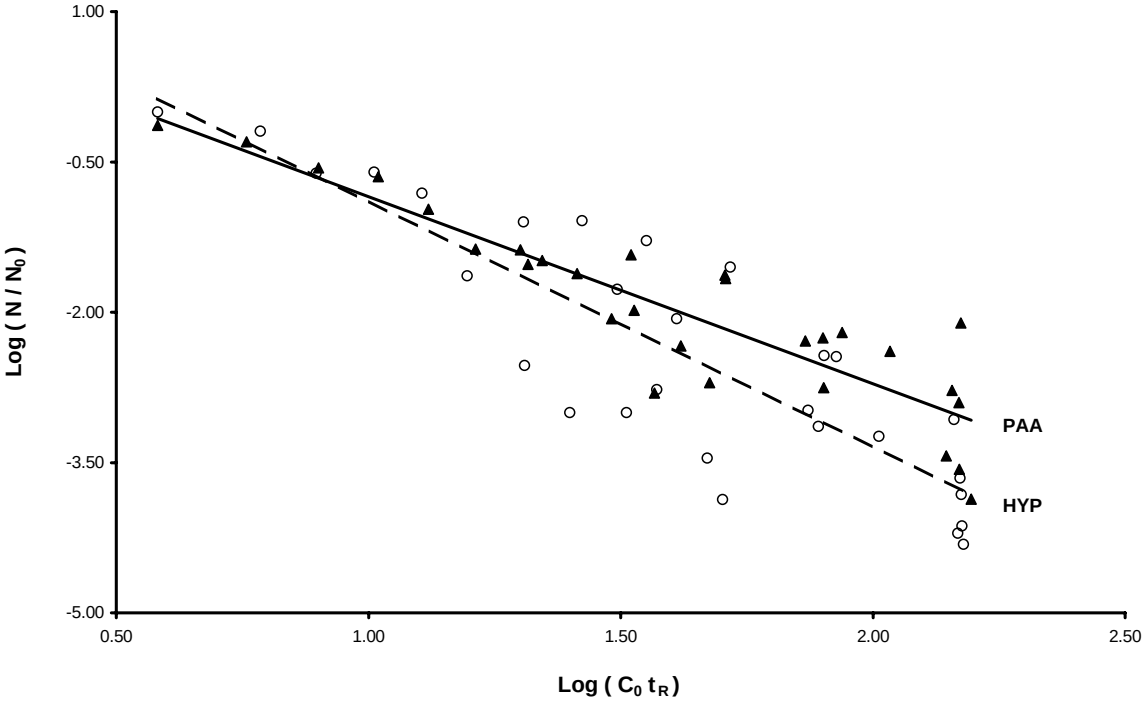

Fig. 3. Reduction of total coliform concentration as a function of the product of biocide initial concentration (in mg/l) and contact time (in min). (Disinfectants: ▲ peracetic acid, ○ sodium hypochlorite).

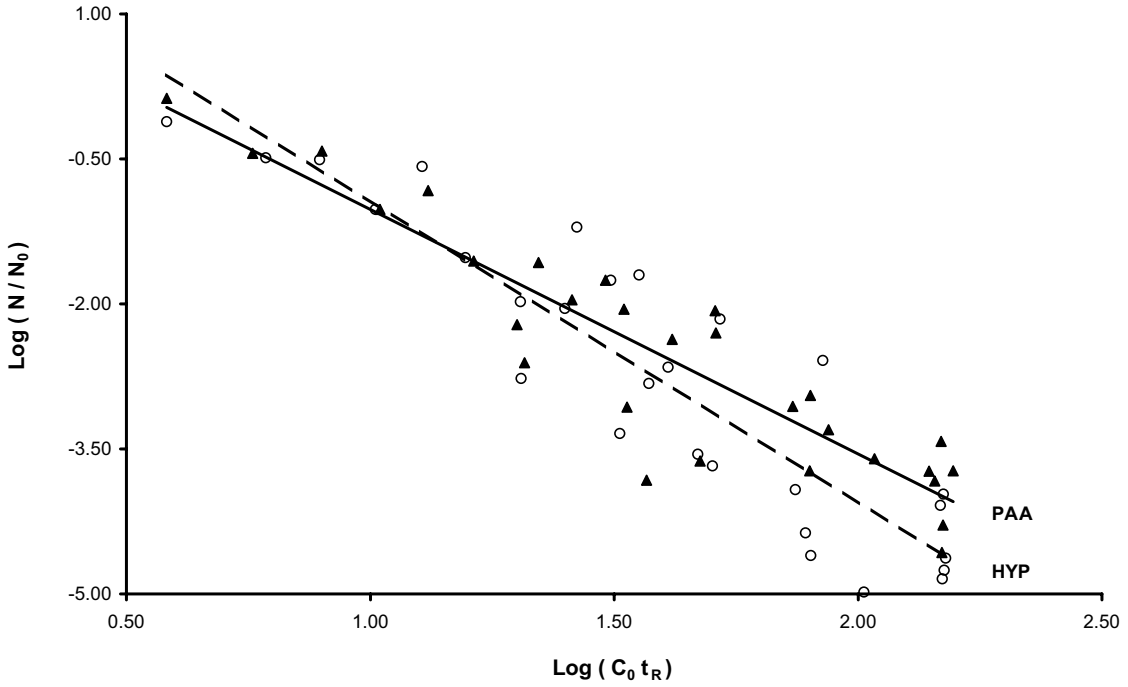

Fig. 4. Reduction of fecal coliform concentration as a function of the product of biocide initial concentration (in mg/l) and contact time (in min). (Disinfectants: ▲ peracetic acid, ○ sodium hypochlorite).

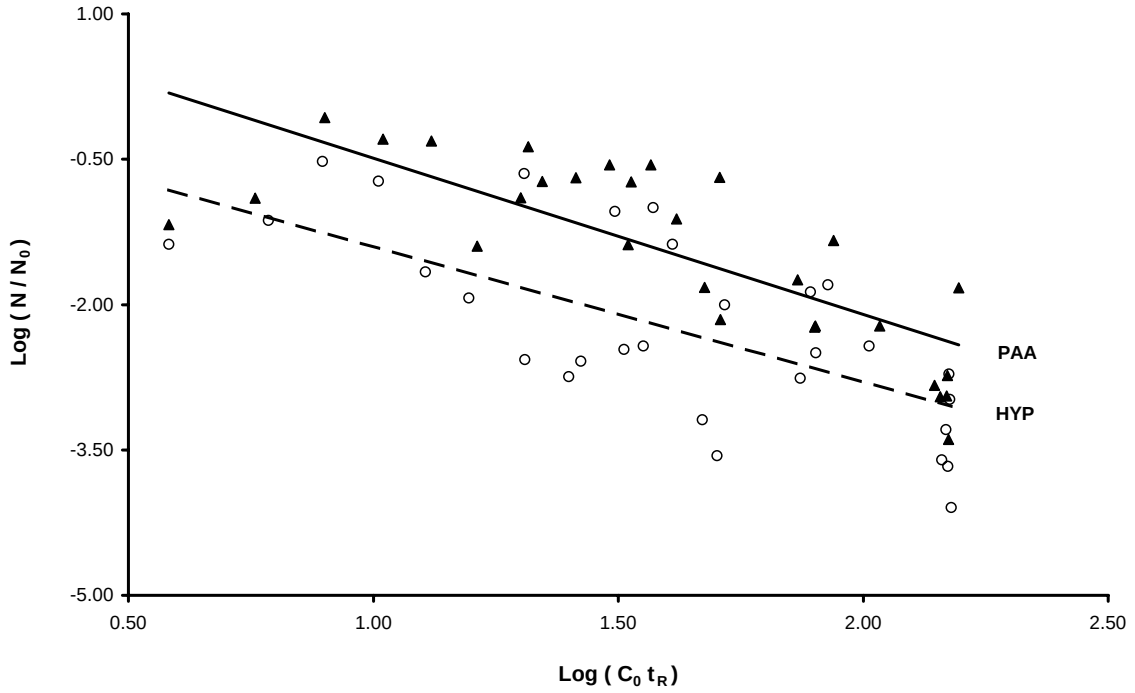

Fig. 5. Reduction of fecal streptococci concentration as a function of the product of biocide initial concentration (in mg/l) and contact time (in min). (Disinfectants: ▲ peracetic acid, ○ sodium hypochlorite).

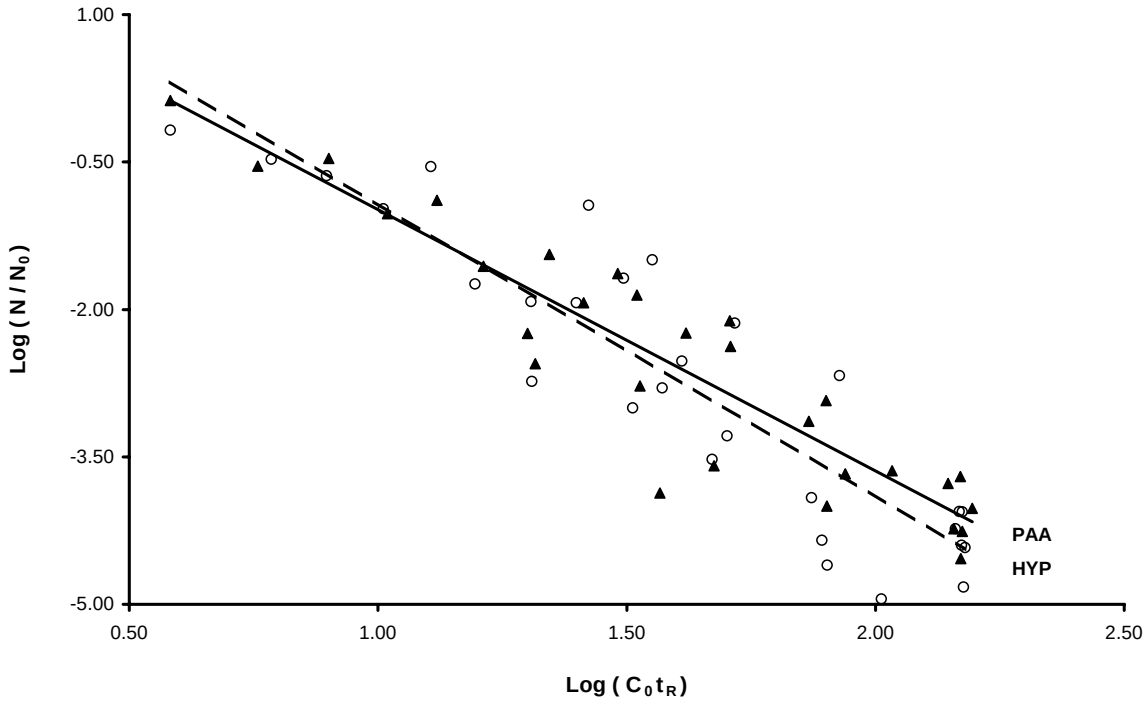

Fig. 6. Reduction of *E. coli* concentration as a function of the product of biocide initial concentration (in mg/l) and contact time (in min). (Disinfectants: ▲ peracetic acid, ○ sodium hypochlorite).

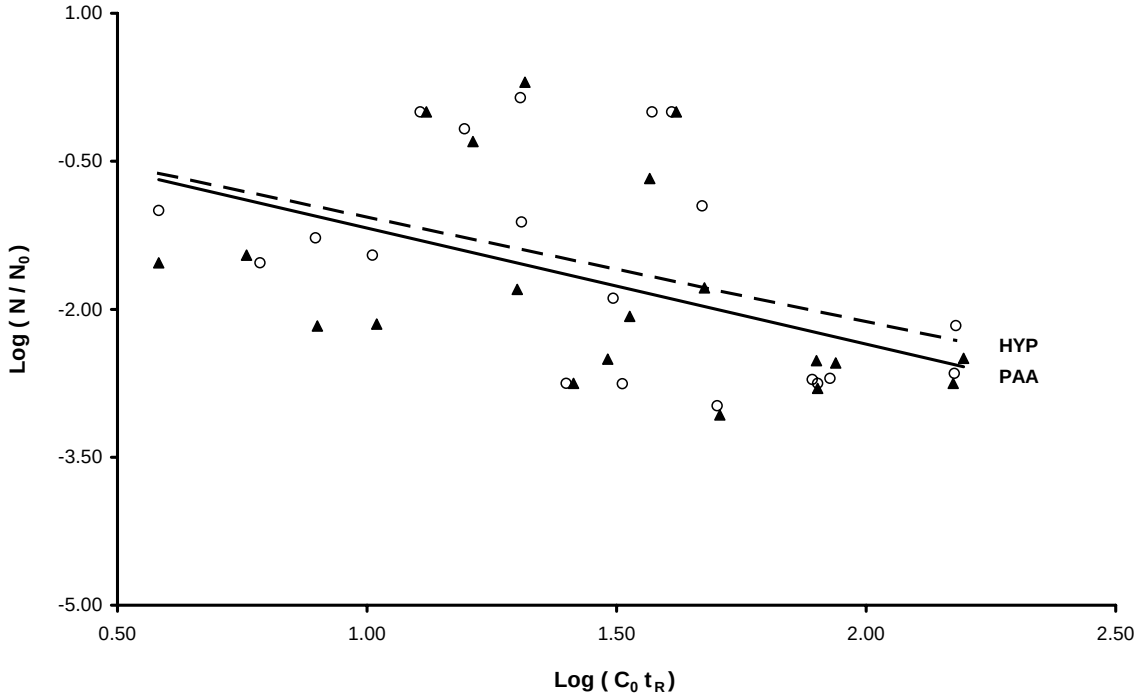

Fig. 7. Reduction of *Salmonella* species concentration as a function of the product of biocide initial concentration (in mg/l) and contact time (in min). (Disinfectants: ▲ peracetic acid, ○ sodium hypochlorite).

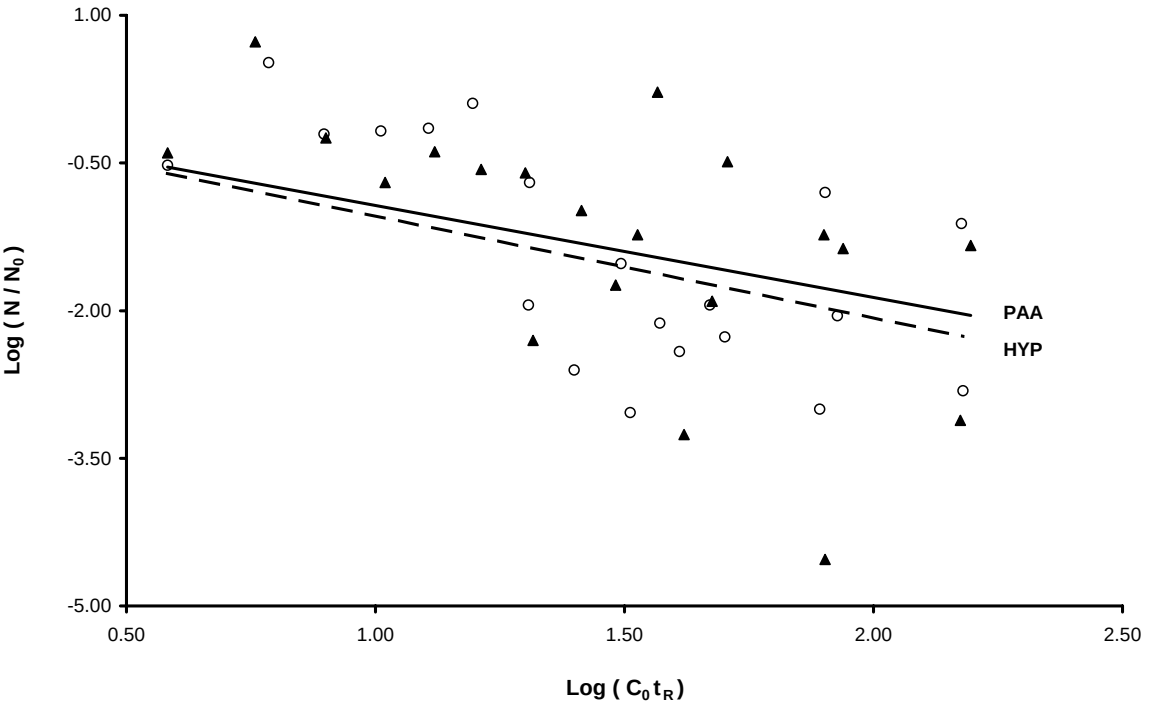

Fig. 8. Reduction of *Pseudomonas* species concentration as a function of the product of biocide initial concentration (in mg/l) and contact time (in min). (Disinfectants: ▲ peracetic acid, ○ sodium hypochlorite).

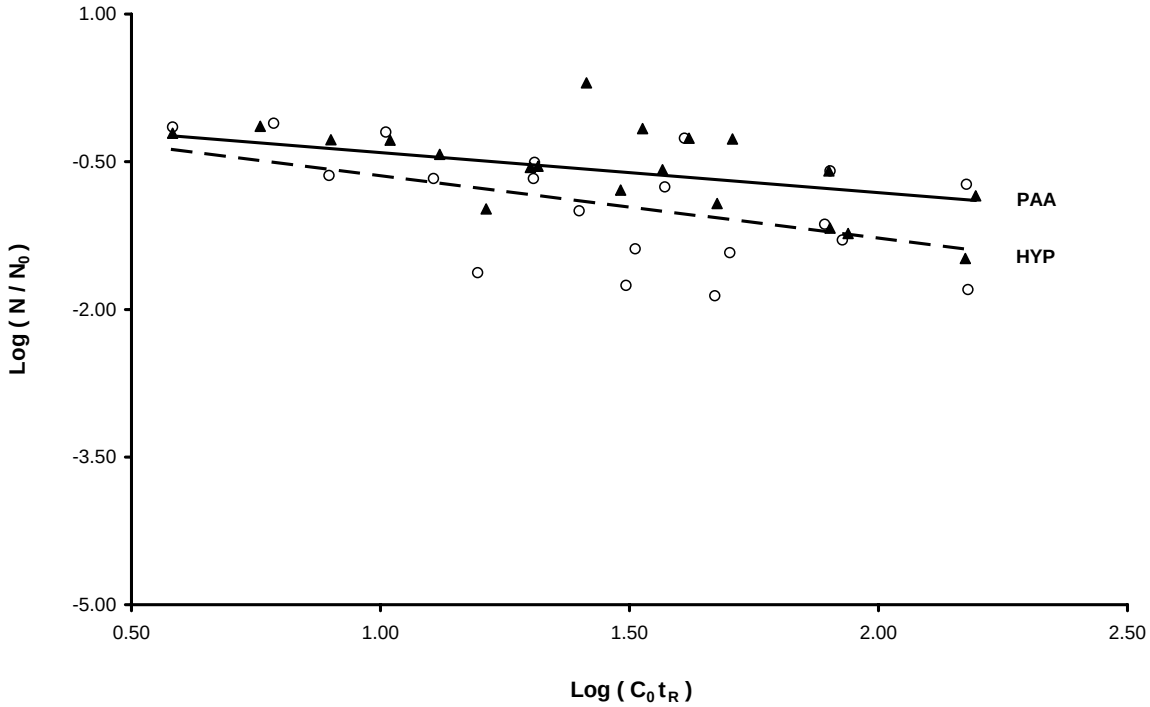

Fig. 9. Reduction of bacteriophages anti-*E. coli* concentration as a function of the product of biocide initial concentration (in mg/l) and contact time (in min). (Disinfectants: ▲ peracetic acid, ○ sodium hypochlorite).

Table 2
Regression coefficients of the straight lines plotted in Figs. 3–9[a]

Parameter	Disinfectant	Data No.	SE (y)	α	SE (α)	β	SE (β)
Total coliforms	HYP	29	0.6	−2.5	0.3	1.6	0.4
	PAA	29	0.4	−1.9	0.2	1.0	0.3
Fecal coliforms	HYP	29	0.6	−3.1	0.3	2.2	0.4
	PAA	29	0.5	−2.5	0.2	1.5	0.3
Fecal streptococci	HYP	29	0.7	−1.4	0.1	[b]	[b]
	PAA	29	0.6	−1.6	0.3	1.1	0.4
E. coli	HYP	29	0.6	−3.0	0.3	2.1	0.4
	PAA	29	0.5	−2.7	0.2	1.7	0.3
Salmonella species	HYP	20	1	−1.1	0.1	[b]	[b]
	PAA	20	1	−1.2	0.1	[b]	[b]
Pseudomonas species	HYP	20	0.9	−1.0	0.1	[b]	[b]
	PAA	20	1	−0.9	0.2	[b]	[b]
Bacteriophages anti-*E.coli*	HYP	20	0.5	−0.64	0.07	[b]	[b]
	PAA	20	0.4	−0.41	0.05	[b]	[b]

[a] α: slope coefficient; β: intercept coefficient; SE (α), SE (β), SE (y): standard errors of α, β and dependent variable, respectively.
[b] Regression through the origin according to the result of t-test for zero intercept. The slope of every regression line was significantly different from zero as indicated by the corresponding t-test.

Table 3
Statistical comparison of HYP and PAA straight-line regression models plotted for each microbiological parameter[a]

Parameter	Comparison of variances			Test for parallelism			Test for coincidence		
	$H_0 : S^2_{y\|x,\mathrm{HYP}} = S^2_{y\|x,\mathrm{PAA}}$			$H_0 : \alpha_{\mathrm{HYP}} = \alpha_{\mathrm{PAA}}$			$H_0 : \alpha_{\mathrm{HYP}} = \alpha_{\mathrm{PAA}}, \beta_{\mathrm{HYP}} = \beta_{\mathrm{PAA}}$		
	F_{found}	F_{tab}	Result	t_{found}	t_{tab}	Result	t_{found}	t_{tab}	Result
Total coliforms	2.4	1.9	False	1.8	2.0	True	1.9	2.0[b]	True
Fecal coliforms	1.6	1.9	True	1.7	2.0	True	1.7	2.0	True
Fecal streptococci	1.4	1.9	True	0.5	2.0	True	4.5	2.0	False
E. coli	1.6	1.9	True	1.0	2.0	True	0.9	2.0	True
Salmonella species	1.0	2.2	True	0.6	2.0	True	0.7	2.0	True
Pseudomonas species	0.7	2.2	True	0.5	2.0	True	0.5	2.0	True
Bacteriophages anti-*E.coli*	1.8	2.2	True	2.4	2.0	False	—	—	—

[a] H_0: null hypothesis; $S^2_{y|x}$: variance produced by the scattering of the points with respect to the straight line; α: slope coefficient; β: intercept coefficient; F_{tab}, t_{tab}: tabular values of F and t, respectively, at a significance level of 5%.
[b] Quantiles of the normalized normal distribution; true and false refer to H_0.

Table 4
Minimum initial concentration of disinfectant necessary to remove 90% of each microbial parameter examined[a]

Parameter	Disinfectant	$\mathrm{Log}\,(C_0 t_{\mathrm{R}})_{\mathrm{min}}$	$C_{0,\mathrm{min}}$ at	
			$t_{\mathrm{R}} = 20$ min	$t_{\mathrm{R}} = 30$ min
Total coliforms	HYP	1.04 (0.08)	0.6 (0.1)	0.37 (0.07)
	PAA	1.08 (0.06)	0.6 (0.1)	0.40 (0.06)
Fecal coliforms	HYP	1.02 (0.06)	0.53 (0.08)	0.35 (0.05)
	PAA	0.99 (0.06)	0.49 (0.07)	0.33 (0.05)
Fecal streptococci	HYP	0.7 (0.2)	0.3 (0.1)	0.17 (0.08)
	PAA	1.32 (0.08)	1.0 (0.2)	0.7 (0.1)
E. coli	HYP	1.02 (0.06)	0.53 (0.08)	0.35 (0.05)
	PAA	1.01 (0.06)	0.51 (0.07)	0.34 (0.05)
Salmonella species	HYP	0.9 (0.3)	0.4 (0.3)	0.3 (0.2)
	PAA	0.8 (0.4)	0.4 (0.3)	0.2 (0.2)
Pseudomonas species	HYP	1.0 (0.2)	0.5 (0.2)	0.3 (0.2)
	PAA	1.1 (0.3)	0.6 (0.4)	0.4 (0.3)
Bacteriophages anti-*E.coli*	HYP	1.6 (0.2)	1.8 (0.7)	1.2 (0.5)
	PAA	2.5 (0.4)	14 (13)	10 (9)

[a] C_0 in mg/l and t_{R} in min. Data in parentheses represent standard error of the corresponding estimated values.

other treatment processes [43,44]. In addition, it is known fecal streptococci die-off rate is slower than the decline in coliforms in water. Their persistence patterns are similar to those of waterborne pathogenic bacteria [45–47]. Likewise, bacteriophages show a greater resistance to hostile environmental conditions and water treatments, which is comparable to that of human viruses [48,49].

3.5. Residual concentration of the disinfectants

The persistence of the two biocides at the exit of the pilot plant was studied as a function of their initial concentrations and contact times. In order to simplify the graphic analysis of the results, the experimental data were subdivided in three sets on the basis of the contact-time values: low (8–12 min), medium (20–26 min) and

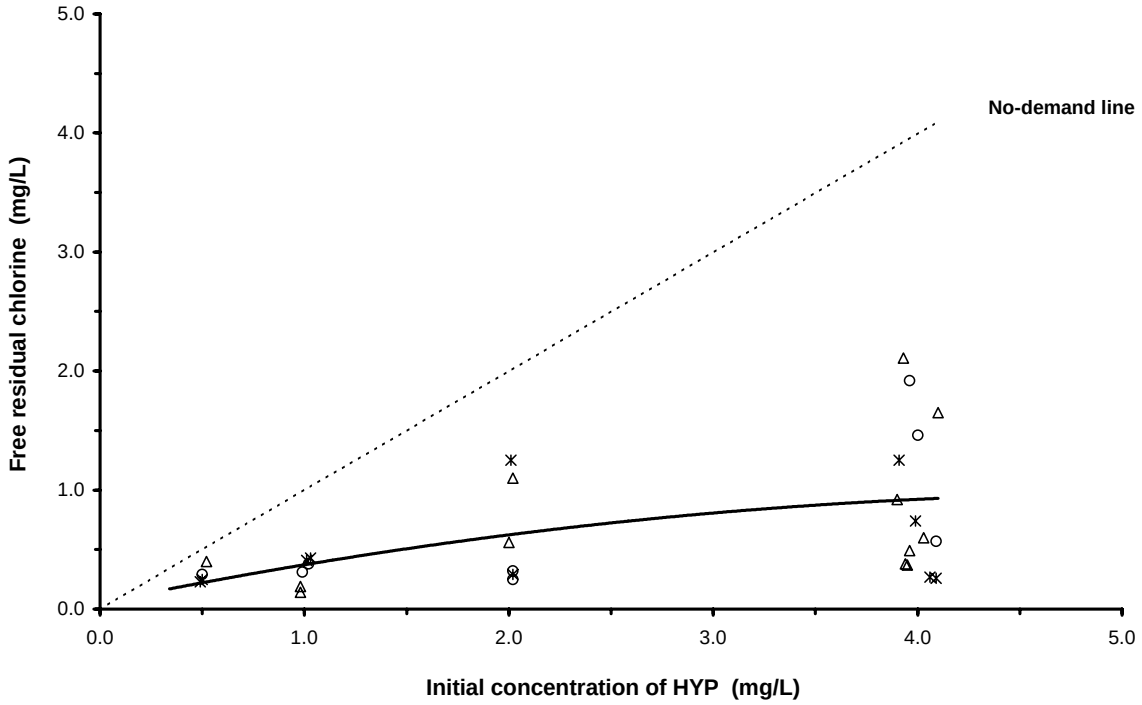

Fig. 10. Residual free chlorine in the sewage disinfected with sodium hypochlorite as a function of the initial disinfectant concentration. (✱ low t_R; ○ medium t_R; △ high t_R).

high (36–39 min) t_R. Figs. 10–13 show the residual concentrations of free chlorine, combined chlorine, peracetic acid and hydrogen peroxide for each data set as disinfectant dosages increased in the sewage. The concentrations of free chlorine, PAA and H_2O_2 were always less than the corresponding values associated to a no-demand of disinfectant. Moreover, they were not affected significantly by the contact time in the range investigated, suggesting a rapid reaction between each oxidizing agent and the sewage matrix.

On the contrary, a different behavior was recorded for the combined residual chlorine. As shown in Fig. 11, its concentration in the sewage treated with HYP increased as both disinfectant dose and contact time increased. Such a time dependence is probably due to a slow production of chloroamines from the decomposition or the transformation of organic chlorine forms rapidly produced by hypochlorite after it was added to the sewage. This hypothesis could also explain why the residual concentration of free chlorine did not vary significantly in the time interval between 8 and 39 min while a progressive increment of combined chlorine was observed. At the present a more extensive investigation is being carried out to gain greater insight into the origin of these experimental findings.

3.6. AOX formation

AOX concentration in the sewage before and after the disinfection treatment was determined as the biocide dosage and the contact time varied in the ranges examined in this research. Increments of AOX level in the disinfected wastewater were calculated by subtracting the initial concentration of AOXs detected at the entrance of the pilot plant from the corresponding concentrations measured at the exit of the tanks. The experimental data so obtained were subdivided in three sets as described above and diagrammed as a function of the initial concentrations of the two disinfectants (Fig. 14). No significant variation of the AOX content was found in the effluent treated with PAA in the concentration range taken into account. Such findings seems not to support the hypothesis proposed by Booth and Lester [12] on the potential formation of halogenated organic by-products during PAA treatment of sewage effluent. On the contrary, a progressive increment of such by-products was found when increasing quantities of HYP were added to the sewage. In this latter case a different trend was also observed by varying the contact time: at low t_R the AOX concentration in the effluent treated with HYP was always greater than the corresponding concentration measured at medium and

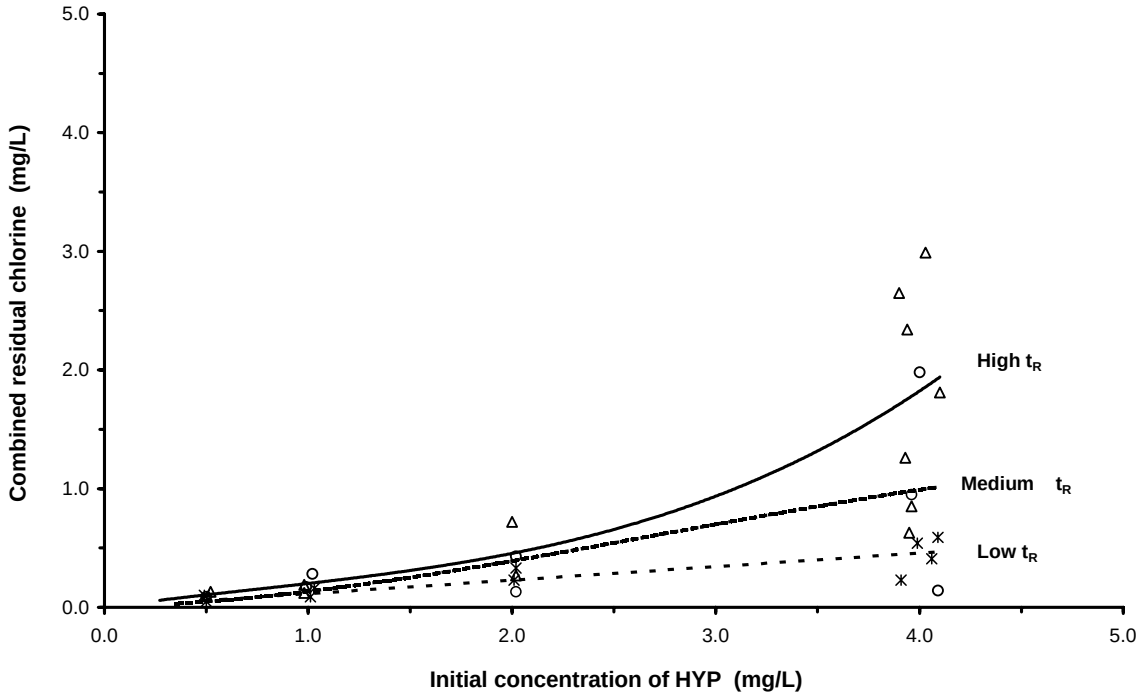

Fig. 11. Residual total chlorine in the sewage disinfected with sodium hypochlorite as a function of the initial disinfectant concentration. (✱ low; ○ medium t_R; △ high t_R).

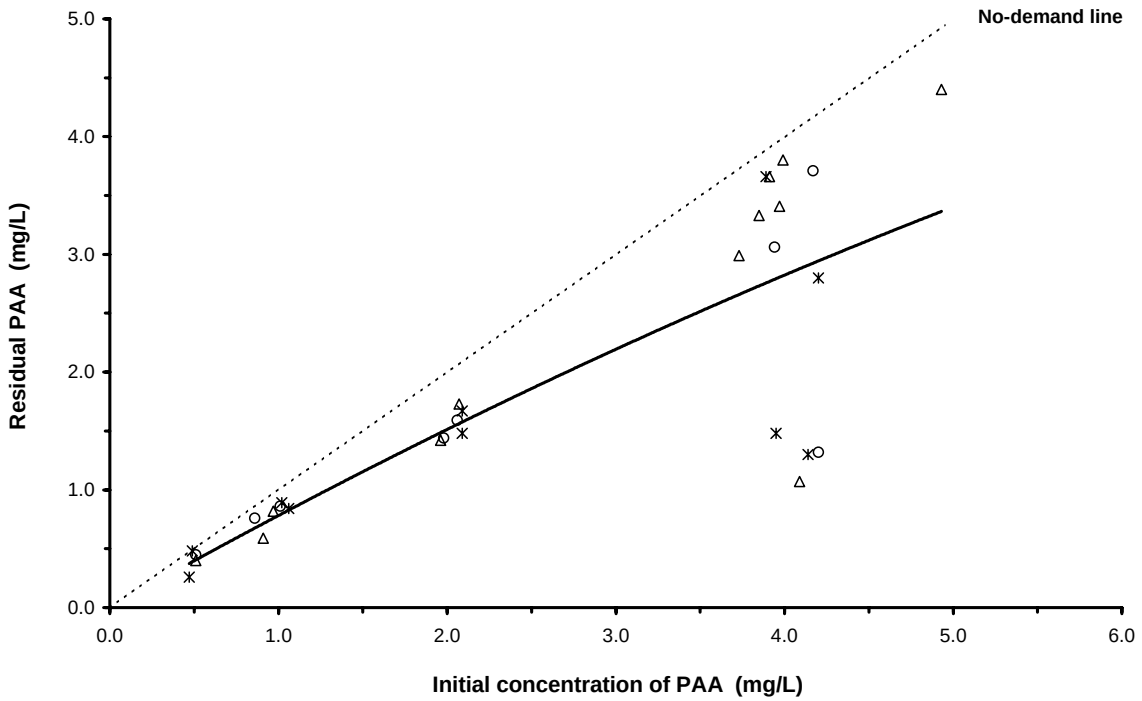

Fig. 12. Residual PAA in the sewage disinfected with peracetic acid as a function of the initial disinfectant concentration. (✱ low t_R; ○ medium t_R; △ high t_R).

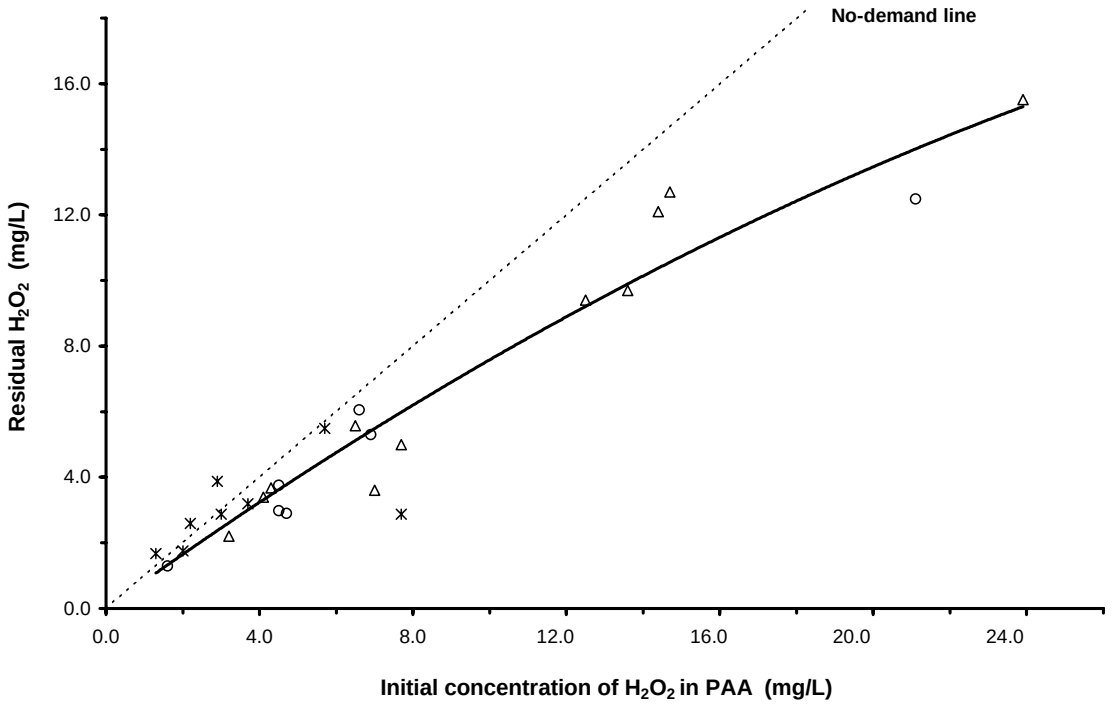

Fig. 13. Residual H_2O_2 in the sewage disinfected with peracetic acid as a function of the initial concentration of H_2O_2 in the disinfectant. (✱ low t_R; ○ medium t_R; △ high t_R).

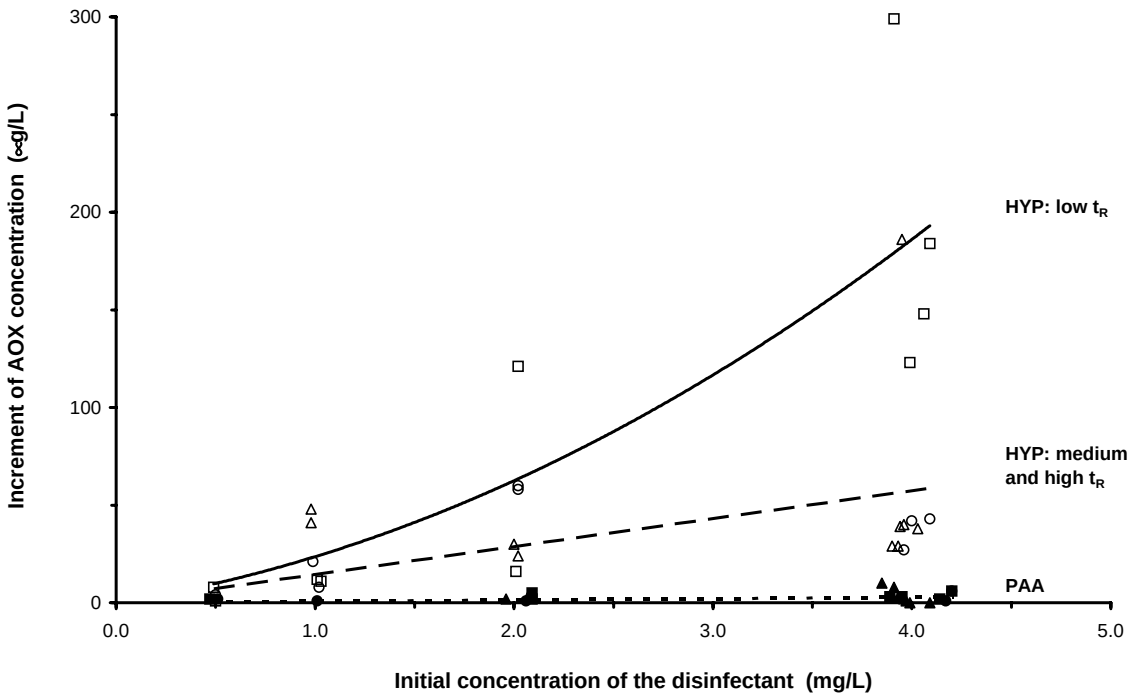

Fig. 14. Increment of AOX concentration due to sewage disinfection as a function of the initial concentration of the disinfectant. (□ low t_R for HYP; ○ medium t_R for HYP; △ high t_R for HYP; ■ low t_R for PAA; ● medium t_R for PAA; ▲ high t_R for PAA).

high t_R. Such a different behavior was probably due to a slow diffusion of the volatile fraction of AOXs into the air in contact with the flowing fluid over the top of the pilot-plant tanks. Another hypothesis involves a rapid formation of organochloroamines, as a result of the reaction between hypochlorite and amines, and their subsequent slow transformation in NCl_3 which is very volatile. In both cases, the resulting loss of chlorinated by-products was comprehensibly greater at low and medium flow rates. The phenomenon just described is going to be studied closely in a near future.

4. Conclusion

The results obtained in this research indicate that peracetic acid and sodium hypochlorite have similar bactericide power against five (total coliforms, fecal coliforms, *E. coli*, *Salmonella* sp. and *Pseudomonas* sp.) of the seven organisms taken into account. The former oxidant is less efficient than hypochlorite in the reduction of resistant organisms such as fecal streptococci and bacteriophages anti-*E. coli.* Such experimental findings are responsible for a different dosage of PAA and HYP to remove a fixed percentage of the latter two at the contact time chosen. It follows that the initial concentration of peracetic acid in the sewage should be about three and eight times as big as the HYP concentration necessary to reduce FS and bacteriophages anti-*E. coli*, respectively, to 10% of initial population.

In both cases the disinfectant quantities initially introduced in the sewage resulted in the presence of residual concentrations at the exit of the pilot plant. Only combined residual chlorine was, however, affected by contact time in the range investigated.

No significant increment of the background concentration of AOXs was detected in the effluent disinfected with PAA. This suggests that free chlorine radicals [12] were not appreciably released during the contact between the disinfectant and organic matter present in the sewage. On the contrary, the treatment carried out with HYP in the same operative conditions gave rise to the formation of halogenated by-products as described by other authors [50]. The study of AOX trend in the final effluent treated with PAA enabled us to weigh up the importance of the phenomenon described by Booth and Lester. Nevertheless, it could not provide exhaustive information on chemical transformations operated by PAA on the organic matrix of the tested sewage.

Thus, data acquired so far seems to indicate the possibility of using peracetic acid as an alternative agent in the disinfection of urban wastewater. However, it will be necessary to seek other potential by-products of PAA in order to assess its actual toxicity in comparison with hypochlorite unwanted effects.

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