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WATER DISINFECTION WITH ClO_2 AND NaClO: A COMPARATIVE STUDY IN PILOT-PLANT SCALE.

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KEYWORDS

chlorine dioxide, disinfection, pilot plant, sodium hypochlorite, wastewater

ABSTRACT

The results of a pilot experimental study on the disinfection of treated municipal wastewater (Darsena wastewater plant, AMGA, Genoa) are presented. A comparative evaluation has been carried out on a pilot-scale disinfection plant (disinfection basin 1 m^3, wastewater flow 1-10 m^3/h) using sodium hypochlorite (diluted solutions freshly prepared just before the test) and chlorine dioxide (produced on site with a generator of a maximum capacity of 45 g/h). Three different contact times (10 - 40 min) and four different concentrations (0.5 - 4.0 mg/l) were investigated collecting physical, chemical and microbiological data on treated and untreated wastewater to identify, compare and contrast performances of each biocide. The influence of the experimental conditions on the reduction of four microorganisms (total coliforms, fecal coliforms, fecal streptococci, and Escherichia coli) as well as on the presence of residual biocide and on the formation of some by-products (chlorite, chlorate and halogenated organic compounds) were evaluated.

The results obtained in this research indicate that chlorine dioxide and sodium hypochlorite have similar bactericide power against the four microorganisms. However, if the comparison is made taking into account the different equivalent weight of the two disinfectants, it is evident that the first biocide is more effective than the later. The minimum initial concentration of sodium hypochlorite necessary to meet microbial Italian requirements has produced a residual concentration of total chlorine greater than 0.2 mg/l, which is the current maximum allowable concentration. On the contrary, such a limit has never been exceeded when the corresponding ClO_2 concentration was initially present in the sewage. On the other hand, the use of chlorine dioxide as disinfectant has resulted in the introduction of other inorganic chemicals (e.g., chlorite and chlorate) whose effects on the effluent quality and safety should be studied in depth in the near future. Moreover, AOX production operated by ClO_2 was significantly less than the amount generated by NaClO in the same experimental conditions.

INTRODUCTION

The recent European Directives 91/271 and 91/676/CEE (and, in Italy, the Legislative Decree 152 of 11 May 1999) on water protection from pollution has drawn attention to the quality of the receiving streams to define the strategy of their progressive reclamation. In the last years the interest towards the final disinfection step of purified wastewaters has grown up in relation to the possibility of their exploitation for recreational and agricultural reuse and to the necessity to provide for the up-grading of the extant plants due to the more stringent limits.

The requirement to obtain higher inactivation yields of pathogens and to minimize the alterations of the purified wastewaters (disinfectants residues, disinfection by-products) induced the development of "alternative" technologies. Nevertheless, the small number of real applications and experiments indicates the necessity to go deep into some essential aspects like dosages and contact times, qualitative alterations induced on the treated sewage, parameters that can influence the disinfection treatment.

According to this research strategy, it was decided to compare chlorine dioxide to sodium hypochlorite, the most generally accepted disinfectant, in a pilot-scale disinfection plant fed with effluents from an activated-sludge wastewater plant. This paper summarizes physical, chemical and microbiological data obtained in the first year of the research.

MATERIALS AND METHODS

Description of the Pilot Plant

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

The municipal plant (about 220,000 equivalent inhabitants corresponding to a maximum load of 26,400 Kg COD/day) uses a conventional sewage-treatment system based on screening, aeration in grit chamber and biological oxidation through activated sludge, secondary clarification, and chlorination.

The pilot plant consisted of a stainless steel structure made up of a premixing chamber (35 cm long, 25 cm wide and 58 cm high), a contact basin (200 cm long, 70 cm wide and 89 cm high) and a final weir, which set liquid level (about 1.0 m^3) in the contact basin. It was fed by the effluent from the secondary settler placed after the activated-sludge biological tank of the municipal plant. The effluent sucked by a centrifugal pump was introduced in the premixing tank containing a stirrer (350 rpm) and directly connected to the contact basin subdivided crosswise by seven septa (70 cm x 70 cm) with staggered openings (10 cm x 59 cm). The flow rate (1.0 - 10.0 m^3/h) was regulated by a throttle valve and checked with a volume meter both installed immediately after the feeding pump. Residence times (t_R) in the pilot plant were determined at chosen values (1.0 - 6.0 m^3/h) of sewage flow rate Q by injecting rapidly a tracer (about 5 l of a saturated solution of sodium chloride) into the sewage stream at the inlet of the premixing tank and by measuring the electrical conductivity at the exit of the contact basin.

Disinfection

Two different disinfectants, sodium hypochlorite and chlorine dioxide, were tested sequentially as experimental conditions varied. Chlorine dioxide was produced on site with a Prominent generator (maximum capacity: 45 g/h) by mixing $NaClO_2$ 6-8% and HCl 10% in a chamber containing Raschig rings. The introduction of the two reagents in the mixing chamber was carried out with two metering pumps operating at the same flow rate (0.3 - 7.7 ml/min). The produced ClO_2 was subsequently diluted with distilled water (29 - 31 ml/min) in a second mixing chamber and added to the sewage flow before the premixing tank. Diluted solutions (1.3 - 11.5 g/l) of sodium hypochlorite were prepared freshly and introduced (11 - 44 ml/min) in the sewage flow at the entrance of the premixing chamber by a metering pump. Every flow rate was checked with a flowmeter or by timing weighted aliquots of liquid just before and after the related disinfection test.

In this research we have studied the effect of disinfectant concentrations (0.5, 0.9, 1.7, and 3.6 mg/l on average) and reaction times (14, 23 and 37 min on average) on microorganism reduction and sewage chemical characteristics. The contact time between sewage and each disinfectant was varied acting on the feeding flow of the sewage in the range 2.0 - 5.0 m^3/h.

Chemical Analyses

Unless specified otherwise, grade chemicals from Aldrich (Milwaukee, WI, USA) and Carlo Erba (Milan, Italy) were used to prepare reagents and standards. Technical grade $NaClO_2$ (purity: 25 $\%_{w/w}$, balance: NaCl and $NaClO_3$), HCl 33% $_{w/w}$ and NaClO 12 % $_{w/w}$ were suitably diluted during the preparation of the reagents employed in the pilot plant. The concentration of NaClO diluted solutions was determined daily before starting chlorination tests and checked at their end by iodometric titration.

The actual concentration of chlorine dioxide produced by the generator and the presence of other chemicals (chlorite, chlorate and chlorine) were measured before and after every ClO_2 disinfection test by applying a method developed on the basis of Sullivan and Douek's work (1998). Likewise, aliquots of wastewater disinfected with ClO_2 and sampled with a peristaltic pump in a Teflon line from the exit of the contact basin were analyzed with the same procedure. In this case no dilution with Na_2CO_3 was operated on the sewage effluent.

Total residual chlorine in pilot-plant chlorinated effluents as well as in purged effluents from the generator or the pilot plant during ClO2 tests was dosed spectrophotometrically at 512 nm by applying the DPD colorimetric method in APHA, AWWA and WEF 's Standard Methods (1998).

Aliquots of the sewage were collected in glass bottles at the inlet and outlets of the pilot plant, stored at approximately 4°C and subsequently analyzed in the laboratory. Sampling operations were repeated three times at each programmed experimental condition to determine the reproducibility of the obtained results. About 0.50 g of sodium sulfite were introduced in every bottle containing the disinfected wastewater in order to reduce the residues of the oxidizing agents. Some aliquots were also acidified with 1 ml of sulfuric acid 4.5 N per 250 ml of water. Total organic carbon (TOC), chemical oxygen demand (COD), adsorbable organic halogens (AOX) and ammonia were determined in the acidified samples, while nitrite and total suspended solids (TSS) were dosed in the remaining samples. All these determinations were carried out as indicated in APHA, AWWA and WEF 's Standard Methods (1998).

Turbidity, water temperature, pH, electrical conductivity and dissolved oxygen were evaluated in the field. The first one was measured with a HACH 2100P nephelometer, while the remaining parameters were recorded with a multi-parametric probe during the disinfection tests.

Microbiological Analyses

Three replicated samples were collected at the inlet and at the exits of the pilot plant in 500-ml polypropylene sterile bottles containing 1 ml of sodium thiosulfate 100 g/l to reduce any disinfectant residue. They were transported in the laboratory and analyzed within 24 hours. 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), *Escherichia coli (E. coli)* and fecal streptococci (FS), 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 m-ENDO Agar-LES (Merck, Darmstadt, Germany) at an incubation temperature of 36 ± 1°C for 20- 24 hours. At the end of the incubation period, all the red colonies on the filter having the characteristic metallic sheen were counted. FC and *E. coli* were recovered on the C-EC Agar (Biolife Italiana, Milan, Italy) substrate at the discriminating temperature of 44.0 ± 0.5°C for 18 - 24 hours. On this substrate FC grew as blue-green colonies, while *E. coli* grew as blue-green colonies fluorescent under ultraviolet light (366 nm) and positive for indole reaction. FS were recovered on Slanetz-Bartley Agar (Merck) at an incubation temperature of 36 ± 1°C for 48 hours. On this substrate they grew as pink to red colonies. A confirmation test was carried out on Esculin Bile Agar (Merck) by evaluating the esculin hydrolysis (1 hour at 42 ± 1°C). Dark red colonies with black halos in the backside of the membrane were counted. The results obtained for all of these parameters are expressed as Colony Forming Unit (CFU)/100 ml.

RESULTS AND DISCUSSION

ClO_2 generator efficiency

The chromatographic analysis of the generator effluents provided data consistent with the corresponding on-line spectrophotometric measurements. The average value of the two data sets was examined at varying of the nominal concentration of ClO_2 calculated on the basis of reagent flow rates. The slope of the regression line so obtained was significantly less than 1.00 indicating a generator efficiency of about 73% (standard error: 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.* (1998). Survival ratios expressed as common logarithm of the ratio of microbial populations at the exit (N) and at the inlet (N_0) of each tank were plotted at varying of common logarithm of $C_0 \cdot t_R$. Table 1 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 (NaClO and ClO_2 lines) obtained for every microbiological parameter studied 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 [Nalimov (1963); Lentner *et al.* (1991)]. The disinfectant actions of the two reagents against three microbiological parameters (fecal coliforms, fecal streptococci, *Escherichia coli*) are not significantly different each other. On the contrary, the bactericide activity of the chlorine dioxide against total coliforms seems slightly greater than the corresponding hypochlorite action in all $C_0 \cdot t_R$ range studied.

The regression coefficients were used to calculate the minimum concentrations of NaClO or ClO_2 necessary to reduce the level of each microbial indicator below the limits specified in the Italian normative in force (Legislative Decree 152/99) and in the previous one (Law 319/76). The limit values for N/N_0 were calculated by dividing Italian legal limits for fecal indicators (N_{law}) by the corresponding average concentrations (geometric means of N_0 values) in the examined sewage. The limiting factor in the disinfection of the examined sewage seems the reduction of fecal streptococci as reported in literature for other urban effluents [Funderburg *et al.* (1985)]. The treatment of the tested sewage with NaClO has also revealed an unexpected resistance of total coliforms to the biocide action and a behavior comparable to that showed by fecal streptococci.

Table 1 - Regression coefficients of the straight lines concerning microbiological reductions.

Parameter	Disinfectant	Data No.	SE (y)	α	SE (α)	β	SE (β)
Total coliforms	NaClO	18	0.6	-2.8	0.4	3.0	0.6
	ClO_2	18	0.9	-2.9	0.6	2.4	0.9
Fecal coliforms	NaClO	18	0.8	-3.9	0.5	3.4	0.8
	ClO_2	18	0.9	-3.2	0.6	2.5	0.8
Fecal streptococci	NaClO	18	0.4	-2.7	0.2	2.7	0.4
	ClO_2	18	0.8	-3.0	0.6	2.9	0.8
Escherichia coli	NaClO	18	0.9	-4.6	0.6	4.3	0.9
	ClO_2	18	0.9	-3.3	0.7	2.6	0.9

α: slope coefficient; β: intercept coefficient; SE (α), SE (β), SE (y): standard errors of α, β and dependent variable, respectively.

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.

No chlorine dioxide residue was found in the disinfected sewage after the contact times investigated. This finding is consistent with the sewage ClO_2 demand (mean: 6.9 mg/l; standard error: 0.7 mg/l) that was always greater than the initial concentration of the biocide introduced.

On the contrary, the concentration of total chlorine in sewage disinfected with NaClO was always detectable even though it resulted less than the corresponding values associated to chlorine no-demand (line slope: 0.85; standard error: 0.02). Moreover, it was not affected significantly by the contact time in the range investigated, suggesting a rapid reaction between the oxidizing agent and the sewage matrix.

Inorganic by-products

The residual concentrations of chlorite, chlorate and total chlorine in sewage disinfected with ClO_2 or NaClO and the corresponding contribution from the ClO_2 generator were plotted as a function of the initial concentration of each biocide. About 74% of the initial ClO_2 concentration in the sewage was reduced to chlorite (line slope: 0.74; standard error: 0.05) while the fraction introduced by the generator was negligible (1.2%; standard error: 0.1%). On the other hand, the presence of ClO_3^- in the disinfected effluent can be attributed exclusively to the contribution made by the generator (line slopes: 0.10 and 0.09 for total ClO_3^- and generator fraction, respectively; standard error: 0.01 for both regression lines). Total residual chlorine detected in wastewater treated with chlorine dioxide was considerably less than the corresponding level found at the exit of the pilot plant during NaClO tests (line slopes: 0.201 and 0.85, respectively; standard errors: 0.007 and 0.02, respectively). The fraction introduced by the generator was about 23% (standard error: 3%) of the residual concentration in the sewage disinfected with ClO_2.

The minimum initial concentrations of disinfectant necessary to reduce the microbial indicators at the level settled by Italian normative were used to calculate the corresponding residual concentrations of the inorganic by-products studied in this research. Table 2 summarizes the results obtained for two contact times (20 and 30 min).

Table 2 - Residual concentration of ClO_2^-, ClO_3^- and Cl_2,tot at the minimum initial concentration of disinfectant necessary to reduce the microbial parameters at the levels established by Italian normative.

Parameter	**Disinfectant**	**C at t_R = 20**				**C at t_R = 30**			
		Law 319/76		LAW 152/99		**Law 319/76**		**Law 152/99**	
ClO_2^-	ClO_2	0.66	*(0.08)*	0.44	*(0.09)*	0.44	*(0.09)*	0.3	*(0.1)*
ClO_3^-	ClO_2	0.09	*(0.04)*	0.06	*(0.05)*	0.06	*(0.05)*	0.04	*(0.06)*
$Cl_{2,\,tot}$	ClO_2	0.18	*(0.01)*	0.12	*(0.01)*	0.12	*(0.01)*	0.08	*(0.02)*
$Cl_{2,\,tot}$	NaClO	1.10	*(0.05)*	0.59	*(0.05)*	0.76	*(0.05)*	0.42	*(0.06)*

C in mg/l and t_R in min. Data in parentheses represent standard error of the corresponding values.

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 contact basin. The experimental data so obtained were diagrammed as a function of the initial concentrations of the two disinfectants. A progressive increment of the AOX content was found when increasing quantities of each disinfectant were added to the sewage. According to other studies [Chow *et al.* (1981)], the halogenating action produced by sodium hypochlorite was remarkably greater than the corresponding action shown by chlorine dioxide.

In both cases, the increment of AOX resulted correlated to the organic content in the sewage.

CONCLUSIONS

The results obtained in this research indicate that chlorine dioxide and sodium hypochlorite have similar bactericide power against the four organisms (total coliforms, fecal coliforms, fecal streptococci, *Escherichia coli*) studied. However, if the comparison is made taking into account the different equivalent weight of the two disinfectants, it is evident that the first biocide is more effective than the later. It follows that the initial equivalent concentration of NaClO in the sewage should be about twice as big as the ClO_2 equivalent concentration to obtain the same microbial removal.

As regards inorganic by-products and residues, the minimum initial concentration of sodium hypochlorite necessary to meet microbial legal requirements has produced a residual concentration of total chlorine greater than 0.2 mg/l, which is the current maximum allowable concentration. On the contrary, such a limit has never been exceeded when the corresponding ClO_2 concentration was initially present in the sewage. On the other hand, the use of chlorine dioxide as disinfectant has resulted in the introduction of other inorganic chemicals (e.g., chlorite and chlorate) whose effects on the effluent quality and safety will be studied in depth in the near future.

An increment of the background concentration of halogenated by-products was detected in the effluent disinfected with ClO_2. However, the AOX production operated by ClO_2 was significantly less than the amount generated by NaClO in the same experimental conditions.

Thus, data acquired so far seems to indicate the possibility of using chlorine dioxide as an alternative agent in the disinfection of urban wastewater. However, it will be necessary to seek other potential by-products and to study the potential mutagenicity and ecotoxicity of treated sewage before carrying out any global evaluation on ClO_2 performances.

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