A note on the use of chlorine dioxide vs. chlorine for potable water treatment

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Abstract

This paper deals with the results achieved by using ClO_2 in the treatment of raw water rich in Mn (more than 0,90 mg/ℓ) during August and September 1991. Removal of Mn (II) by using the conventional process with Cl_2 yielded treated water in which the Mn residual levels were higher than those prescribed in the Spanish Drinking Water Law (50 µg/ℓ). The use of ClO_2 solved this problem and, at the same time, brought about a reduction in both the UV-absorbance values (at 254 nm) of the water, and the production of THM (trihalomethanes) during the potable water treatment processes. However, the real production cost of potable water increased from \$13,0 /1 000 m³ (chlorine) to \$27,5 / 1 000 m³ (chlorine dioxide).

Introduction

Chlorine dioxide was first used as a water treatment process in the world at Niagara Falls, New York, in 1944 (Lykins et al., 1990). This substance can be effective in potable water treatment for controlling taste and odour, and for removing Fe and Mn, as well as for providing a lasting residual in water distribution systems (Masschelein, 1989). Likewise, it does not form chlorinated by-products (Beltrán et al., 1991; Craig Vogt, 1980).

Adverse tastes and odours may be caused (in drinking water) by a variety of industrial waters, and by metabolites of algae and bacteria. Furthermore, these may be agravated through chlorine oxidation, which leads to the formation of chlorinated compounds.

Reactions between humic substances and chlorine lead to the formation of trihalomethanes (THM) in potable water (Beltrán, 1991) ; these can also be produced by reactions between algae (or their metabolites) and chlorine (Wardlaw et al., 1991). Due to their toxicity, THM concentrations in drinking water must be decreased (WHO, 1986).

Chlorine dioxide is very effective in reducing the THM levels in water, especially when the ClO_2 dosed has been produced without excess chlorine (Craig Vogt, 1980).

When the raw water which is to be treated shows high levels of Fe and especially Mn (associated with humic substances), the ClO_2 can be used as a substitute for Cl_2 with several advantages (Masschelein, 1989; Tirado et al., 1987).

Finally, for control of bacteria and viruses, ClO_2 is as effective as or superior to free Cl_2 (Lykins et al.,1990); this action could be due to a reaction between ClO_2 and the proteinic amino-acids of the cellular wall of the micro-organisms (Masschelein, 1989).

Summarising, ClO_2 is a suitable drinking-water disinfectant and estimates indicate that 300 to 400 utilities in the United States have ClO_2 treatment equipment. The situation in Europe shows an increasing trend in the use of this disinfectant (Masschelein, 1989).

Industrial-scale production of ClO_2 can be obtained in two forms: reaction between Cl_2 (strongly chlorinated water) and sodium chlorite, and through hydrocloric acid and sodium chlorite; the first method is probably the most used (Masschelein, 1989; Monscvitz and Rexing, 1980).

The aim of this paper was to compare the results (technical and economical) achieved in the treatment of water containing high concentrations of Mn, by using both Cl_2 and ClO_2. At the same time, reduction in THM formation (total, chlorinated and brominated), and in the 254 nm UV-absorbance were observed with ClO_2 in comparison with Cl_2.

Experimental

Drinking-water plant

Villa Azul Drinking-water Plant (Córdoba,Spain) currently produces 150 000 m³ (maximum) of potable water per day. The applied treatment scheme is as follows: pre-aeration of raw water (air, low pressure), pH correction with lime ($Ca(OH)_2$) ozonisation (out of service during our study), pre-oxidation (Cl_2 gas, or ClO_2), decantation (one "floc recirculation settler" and two "lamella settlers"), filtration through 30 rapid sand filters, post-disinfection (Cl_2 or ClO_2), pH correction with lime, and fluoridation of treated water. (A complete description on the Drinking-water Plant of Villa Azul has been given in previous papers (Marín Galvín, 1991b and 1992a)).

Samples of water investigated corresponded to raw water before pre-aeration, decanted water in FRS (floc recirculation settler) and LS (lamella settlers), and filtered water before fluoridation (this was also considered as "treated water").

Data of water quality (untreated, decanted and filtered) oxidised with only Cl_2 corresponded to average values obtained between 13 and 19 August 1991. Data of water quality oxidised with ClO_2 dioxide corresponded to average values obtained between 20 August and 27 September 1991.

Chlorine dioxide production

Industrial ClO_2 generation was by means of the reaction between Cl_2 (2,0 g/ℓ in water) and $NaClO_2$ (25 %), within a reactor of 1 100 ℓ capacity, which contained 750 ℓ of Rashing's rings (in

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PCV, PFV), the reaction time being around 8 min.

The pH value of the reactant medium was always less than 3,9, and at that value, the production yield of ClO_2 was higher than 95%. Concentration of non-desirable residual chlorite has been less than 0,5 mg/ℓ in treated water. The ClO_2 dosage ranged between 1,2 and 2 g/m³, depending on the raw water quality.

Analytical methods

All the analytical methods used for the determinations in raw, decanted, or treated waters are in accordance with *Standard Methods* (1989).

Total Fe and Mn were analysed by using molecular absorption methods. Organic matter was determined by means of the $KMnO_4$ method in hot and acidic media. Chlorine dioxide and different related Cl_2 compounds were determined by means of the DPD technique: these will be expressed in the paper as mg/ℓ, while the reactant doses (Cl_2 or ClO_2, and lime and coagulants) should be more correctly expressed as g/m³.

Values of 254 nm UV-absorbance were obtained by recording the UV spectrum of waters, after centrifuging the sample for 5 min at 5 000 g.

Trihalomethane analyses (chloroform, dichlorobromoform, dibromochloroform and bromoform) were made by the liquid-liquid extraction gas chromatographic method (*Standard Methods*, 1989). We have considered as "total" THM the sum of the above 4 species.

Results and discussion

Guadalmellato Reservoir water was used in the full-scale industrial experiment. This is the usual water supply for the Villa Azul Drinking-water Plant, (Córdoba, Spain) (Marín Galvín, 1991a). The dynamics experienced by this reservoir implies that during the summer or autumm months, the available raw water has high concentrations of Mn, Fe, ammonia, nitrite and organic matter. The treatment of this water is very difficult when using only Cl_2 as oxidant, and treated water with relatively large amounts of THM, residual Mn and tastes and odours is commonly produced.

In the past, the reduction in the residual Mn levels was obtained by using high dosages of Cl_2 as well as by dosing some alkaline reagent lime ($Ca(OH)_2$) to obtain a value of the raw water pH higher than 9,50 prior to the flocculation step (Giannissis et al., 1985). Nevertheless, the result thus obtained was not totally optimal.

Since the introduction of ClO_2 in the plant, it has certainly been effective in the treatment of waters rich in Mn and organic matter, and so, in reducing undesirable THM levels.

In our case, the quality of influent raw water to the drinking water plant deteriorated during the months of July and August, and so, during 13 to 19 August especially, the Mn concentrations in untreated water increased to 0,40 to 0,45 mg/ℓ: oxidation via Cl_2 yielded residual Mn levels in treated water higher than 50 μg/ℓ. For this reason, on 20 August it was necessary to begin dosing of ClO_2. This situation was maintained up to 27 September with good results (subject of this paper).

Table 1 shows the results achieved by the treatment of raw water in the 2 situations studied (oxidation via Cl_2 and ClO_2). The raw water quality was roughly similar : NH_3 and Fe concentrations were approximately 0,40 mg/ℓ in both instances, and organic matter to $KMnO_4$ around 4 mg/ℓ. Furthermore, it can be pointed that the maximum concentration of Mn in the raw

TABLE 1
AVERAGE QUALITY OF STUDIED WATERS

| | Raw water | | Settled water | | | | Filtered water | |
| | | | LS | | FRS | | | |
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Colour (mg/ℓ Pt-Co)	35	30	25	7	20	10	5	<2
Turbidity (NTU)	8,5	7,5	3,5	1,7	4,0	2,5	1,0	0,4
Conductivity (μS/cm)	170	165	-	-	-	-	-	-
Bicarbonate (mg/ℓ $CaCO_3$)	95	90	-	-	-	-	68	65
pH	7,2	7,1	6,8	6,8	6,7	6,8	6,9	6,9
Fe (mg/ℓ)	0,35	0,55	0,05	0,10	0,07	0,15	<0,02	0,03
Mn (mg/ℓ)	0,95	0,45	0,08	0,40	0,07	0,35	0,01	0,07
O.M. (mg/ℓ O_2)	3,8	3,9	1,9	2,1	1,7	2,0	1,6	1,6
Ammonia (mg/ℓ)	0,30	0,50	-	-	-	-	<0,02	<0,02
Nitrite (mg/ℓ)	0,02	0,015	-	-	-	-	<0,005	<0,005
Nitrate (mg/ℓ)	<1	<1	-	-	-	-	1,1	1,0
O_2 (mg/ℓ)	2,6	3,0	-	-	-	-	-	-

LS   :   Lamella settlers
FRS :   Floc recirculation settler
(a) :   Use of chlorine dioxide
(b) :   Use of chlorine
OM   :   as organic matter to permanganate
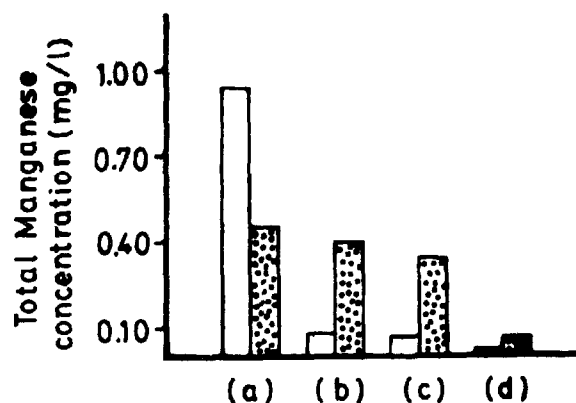Ammonia, nitrite and nitrate as NH_3, NO_2 and NO_3, respectively

Figure 1

Removal of Mn oxidised with ClO_2 (white bars) or Cl_2 (dotted bars). (a) raw water; (b) settled water (lamella clarifiers); (c) settled water (floc recirculation decanter); (d) filtered water

water, treated with Cl_2, was sufficiently lower than that of raw water treated with ClO_2 (0,45 mg/ℓ vs. 0,95 mg/ℓ, respectively).

The use of Cl_2 and coagulant (polyaluminium chloride, 10 % in Al_2O_3 and lower than 5 % in sulphate) provided an optimal elimination of turbidity, colour and organic matter in both the decantation and filtration steps. Reductions in Fe levels were also

acceptable.

It can be noted in Table 1 that the use of ClO_2 led to higher colour and turbidity of settled water than with Cl_2. This was probably due to the optimal oxidation experienced by the concentrations of Fe and Mn (II) present in raw water. Amounts of oxidised Mn and Fe were produced and then removed along the treatment processes (especially in filters).

The use of ClO_2 (as a substitute for Cl_2) together with higher polyaluminium chloride and lime dosages used, produced higher amounts of sludge in the settling tanks; consequently, greater volumes in the decantation purges (4,12 % vs. 0,70% in relation to the total water treated) must be discarded. Moreover, a bigger filter backwash frequency (1,97 % vs. 1,50 %, expressed as above) must be used in the plant.

The estimated cost of the processes when chlorine was dosed (5,8 g/m³ of total chlorine, 14 g/m³ of polyaluminium chloride) amounted to $13,0/1 000 m³. On the other hand, if the oxidation only was possible with Cl_2 but not with ClO_2, when the raw water Mn concentration increased up to 0,95 mg/ℓ, approximately 6,2 g/m³ of Cl_2, 30 g/m³ of lime (pH around 9,5), and 25 g/m³ of polyaluminium chloride would be required, according to previous results obtained in similar situations experienced in the drinking-water plant (Marín Galvín, 1992b). In this hypothesis, the estimated cost of the processes should amount to $22,7/1 000 m³.

The main problem encountered with the use of Cl_2 has been the high residual levels of Mn in treated water. According to the Spanish Drinking-water Law, this water should be classified as "unpotable". Likewise, accumulation of residual Mn in the settling tanks was high and thus troublesome (Fig.1).

Figure 2 compares THM formation in the treated water obtained with Cl_2 and ClO_2. When chlorine was dosed the total THM level was 94,8 µg/ℓ. The main THM formed was chloroform, at a concentration of 73,4 µg/ℓ, i.e., far higher than the 30 µg/ℓ recommended limit of the WHO (WHO, 1986); bromoform occurred in very low concentrations (0,9 µg/ℓ).

When ClO_2 was dosed it was demonstrated that the formation of total THM decreased to 50,8 µg/ℓ; in this case chloroform was also the main product (38,3 µg/ℓ) i.e., approaching the WHO limit, and that of bromoform again the minor product (0,6 µg/ℓ).

Summarising, the use of ClO_2 caused a reduction of 46% in the average percentage generation of total undesirable THM in drinking water. This result agrees with that reported in the literature when ClO_2 without ammonia addition was used: reductions of around 60% (Craig Vogt, 1980) and residual THM levels of 40 to 70 µg/ℓ (Lykins et al., 1990) are commonly obtained (ClO_2 used in preoxidation).

Figure 3 shows the 254 nm UV-absorbance values of water for conventional treatment processes, for the 2 situations studied. This parameter is usually connected with the presence of naturally occurring organic matter in waters, such as humic substances (Edzwald et al., 1985). The decreases in absorbance imply an optimal flocculation process (Viraraghavan and Wimmer, 1988; Yao and O'Melia, 1989) and a fine total potable water treatment process.

As can be seen in Fig. 3, the reduction in absorbance with chlorine was 60% of that of the absorbance in untreated water. When ClO_2 is dosed, a reduction of almost 81% could be achieved.

No variation of organic matter to $KMnO_4$ levels in treated waters were observed by using ClO_2 or Cl_2. This can be explained by assuming that the organics absorbing at 254 nm contribute only a small proportion to the global measure
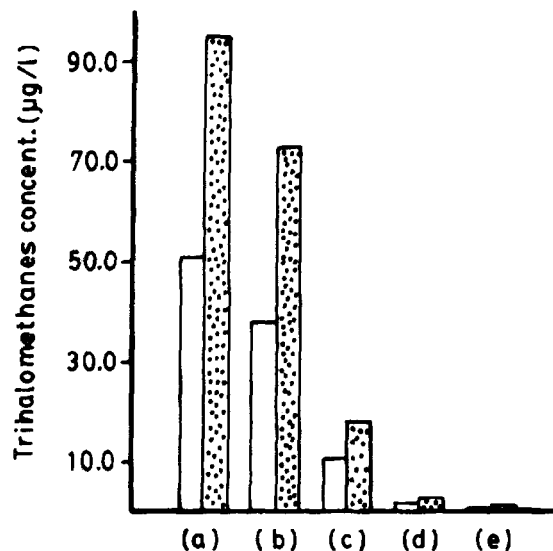

Figure 2

THM formation in drinking water under oxidation with ClO_2 (white bars) or Cl_2 (dotted bars). (a) total THM; (b) chloroform; (c) dichlorobromoform; (d) chlorodibromoform; (e) bromoform
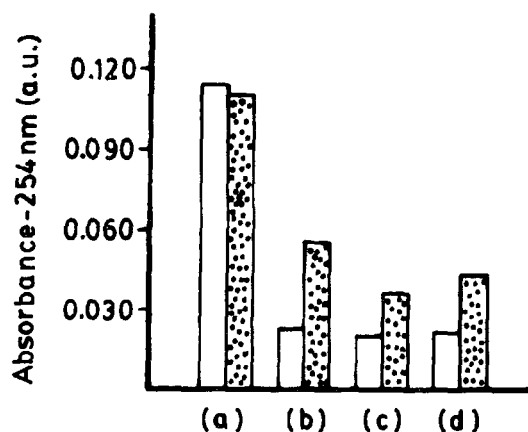

Figure 3

Reduction in the 254 nm UV-absorbance of waters treated with ClO_2 (white bars) or Cl_2 (dotted bars). (a) raw water; (b) settled water (lamella clarifiers); (c) settled water (floc recirculation decanter); (d) filtered water

corresponding to "organic matter to $KMnO_4$".

On the other hand, the recorded UV-spectra of drinking waters (Cl_2 or ClO_2) can be observed in Fig. 4: the fitting of the 2 spectra, particularly in the 210 nm zone is quite deficient. This could be attributed to different amounts of substances (organics especially) which absorbed at these wavelengths. From the viewpoint of the global quality of drinking water, it would be reasonable to hypothesise that the lower absorption values at any wavelength should undoubtedly indicate a lower occurrence of organics in water. Identification of organics and other substances active in UV (190 to 350 nm) could be interesting in this type of studies, but it was not the subject of this paper. However, for example, it must be remembered that chloroform and other
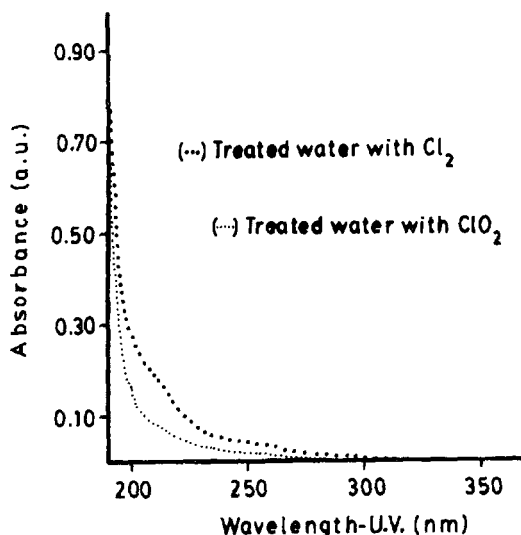
Figure 4
UV spectra of treated waters. Scan: 350 to 190 nm absorbances in "absolute units"

aromatic organic substances give UV-absorption bands approaching 208 to 210 nm.

The production cost of water with ClO_2 has been estimated around \$27,5/1 000 m^3, e.g., 112 % more than the respective cost with chlorine. The dosages in the first case were 5,4 g/m^3 of chlorine, 7,03 cc/m^3 of $NaClO_2$ (which supposes a dosage of 1,5 g/m^3 of chlorine dioxide), 10 g/m^3 of lime and 21 g/m^3 of polyaluminium chloride.

However, taking into account the estimated cost (not real) of drinking-water production with Cl_2 for the treatment of raw water rich in Mn (0,95 mg/ℓ) which amounted to \$22,7/1 000 m^3, ClO_2 was only 21 % more expensive than Cl_2.

Finally, the use of ClO_2 provided a lasting residual in the water distribution systems, even at the points furthest removed from the drinking-water treatment plant (around 25 km). The minimal residual ClO_2 level checked was 0,09 mg/ℓ (residual dioxide in output water plant : 0,28 mg/ℓ). These concentrations ensured the optimal microbiological quality of potable water, because of the superior disinfectant capacity of the reagent. Moreover, the rechlorination practices in the network (necessary when Cl_2 is dosed) were not necessary with ClO_2.

Conclusions

The use of ClO_2 as a substitute for Cl_2 in our drinking-water treatment plant has presented the folllowing advantages:

- Decreases in the residual Mn level in drinking water produced: less than 50 $\mu g/\ell$. This cannot be obtained in any case by using chlorine (and lime).
- Reduction of 46% in the average percentage generation of total THMs: around 50 $\mu g/\ell$ were obtained.
- Good reduction in the residual 254 nm UV-absorbance: 0,020

(a.u.) in drinking water. This undoubtedly indicates a lower occurrence of organics absorbed at these wavelengths.
- Elimination of the rechlorination practices in the network due to lasting residuals in water treated with ClO_2. Observed disadvantages: the cost of water treated with ClO_2 can be between 112 % and 21% more than with Cl_2. Likewise, due to the increase in the coagulant dosages for the correct water treatment when ClO_2 was used, the sludge production was therefore much higher, and consequently, it was necessary to increase the decantation purges and the filter backwash frequency.

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