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EFFICACY OF CHLORINE DIOXIDE AND SODIUM HYPOCHLORITE IN REUSE WATER DISINFECTION

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Abstract

Potable water is becoming day by day more difficult and more expensive to obtain. Therefore to reduce the pressure in natural water resources, wastewater reclamation is expanding through many municipalities and industries for applications where potable water is not required. However, specific treatments must be performed before the water reuse. These treatments are necessary to reduce physical-chemical and microbiological contaminants. This work has evaluated the action of chlorine dioxide (ClO_2) and sodium hypochlorite (NaOCl) in reducing the mesophilic aerobic micro-organisms population as well as diminishing the chlorine demand in the water used. The results have shown that chlorine dioxide is less affected by water contaminants when compared to sodium hypochlorite; a 3 log cycle reduction in mesophilic aerobic micro-organism population was obtained by using a ClO_2 residual concentration of 0.2 $mg \cdot L^{-1}$ and a chlorine residual, from NaOCl, of 0.8 $mg \cdot L^{-1}$. To obtain these concentrations, it is necessary to dose 5.0 $mg \cdot L^{-1}$ of ClO_2 and 15.5 $mg \cdot L^{-1}$ of NaOCl in water.

Key words: chlorine demand, ClO_2 residual, Cl_2 residual, decimal reduction, mesophilic aerobic microorganisms

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1. Introduction

Potable water is becoming day by day more difficult and more expensive to obtain. Therefore to reduce the pressure in natural water resources, wastewater reclamation is expanding among many countries, municipalities and industries for applications in activities where potable water is not required (Amin et al., 2013; Bixio et al., 2006; Dolnicar and Schäfer, 2009; Dolnicar et al., 2010; Hochstrat et al., 2008; Lonigro et al., 2015; Menses et al., 2010; Yi et al., 2011). The U.S. Environmental Protection Agency defines wastewater reuse as, "using wastewater or reclaimed water from one application for another application" (USEPA, 2012). Before wastewater can be used, specific physical-chemical treatments could be necessary to remove many types of contaminants such as oils and fats, surfactants, heavy metals, solids in suspension and micro-organisms (Meneses et al., 2010). These treatments include coagulation, sedimentation, filtration as well as microbial population reduction by using disinfectants (Bixio et al., 2006; Carvalho and Machado, 2010; Dolnicar et al., 2010; EPA Victoria, 2002; Giuliano et al., 2017; Hani et al., 2012; Kunigk et al., 2014; McKenzie, 2005; Narkis et al., 1995a, b). In Brazil, wastewater reuse is regulated by Law through Federal Resolution Nº 54 from National Water Resources Council (CNRH, 2005; NRMMC). In this Federal Resolution, procedures, guidelines and general criteria for the practice of direct reuse of non-potable water were established for applications such as in refrigeration towers (CNRH, 2005). In Europe, although there is the European Council Directive 91/271 EEC concerning urban wastewater treatment (EC Directive 271, 1991), each country has their own

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standards, guidelines and technical norms about wastewater reuse (Bixio et al., 2006; Environment Agency, 2012; Hochstrat et al., 2008; Takacs et al., 2016).

The U.S. Environmental Agency (2012) has shown several possibilities in wastewater reuse such as car washing or toilet flushing. McKenzie (2005) reported that wastewater reuse can be grouped into the following categories: urban reuse (irrigation of public parks, fire protection systems and toilets flushing); agriculture reuse (irrigation of nonfood crops and pasture lands) or food crops irrigation with high-quality reclaimed water; recreational impoundments (ponds and lakes); environmental reuse (enhancing natural wetlands and sustaining stream flows); industrial reuse (process or make-up water and cooling tower water). Hochstrat et al. (2008) have shown the wastewater reuse pattern at different regions. While Europe and Israel focused the reuse of wastewater mainly for agriculture irrigation (70% of total wastewater obtained), Australia reuse only 30% of the wastewater for agricultural irrigation and 40% of it for industrial uses. In China, since 1958, government has played a significant role to promote the production and utilization of reclaimed water. During the last decade the Chinese government has established reclaimed water quality standards to ensure its safety (Yi et al., 2011). Dolnicar and Schäfer (2009) observed that the Australian population accepts the use of desalinated water for close-to-body uses but due to their perception of a possible public health hazard recycled water should be used for garden watering and general cleaning uses only. Scholze (2011) has shown several examples of water reuse and wastewater recycling at U.S. Army installations. However, in all these usages, the microbial population must be reduced to the lowest possible level to prevent biofilm formation and unpleasant odors. For this purpose a disinfection process must be used (Amin et al., 2013). The Environmental Protection Authority from Victoria, Australia (EPA Victoria, 2002) shows disinfection levels for reclaimed water depending on its usage. Table 1 shows these recommendations.

However, Koning et al. (2008) observed that the quality requirements for the reclaimed water depend strongly on its application. For instance, the quality requirements for industrial reuse of reclaimed water vary widely from ultra-pure water (semi-conductor industry) to cooling water (power plant). These authors also observed that some functional aspects must be prevented (clogging, corrosion and sedimentation) and also health aspects cannot be neglected (e.g. spreading of micro-organisms from cooling towers) when reclaimed water is used. As observed by Hassen et al. (2000) disinfection is often a stage for the reusability of treated wastewater and the main objective of disinfection is to reduce sanitary risks related to the presence of pathogens. Therefore for industrial reuse, a tertiary treatment – a disinfection process – must be applied to the water. The water disinfection process is based on the oxidation potential of the chemical compound which will be used to damage the cellular wall by oxidation and eventually to promote the death of the microorganisms (Acher et al., 1997; EPA Victoria, 2002; Katz et al., 1994; Meyer, 1994).

Table 1. *Escherichia coli* population that could be present in reclaimed water

Reclaimed water use	***E. coli/100 mL***
Class A (required where there is high risk of direct human contact with reclaimed water)	< 10 organisms
Class B (required where there is medium risk of direct human contact with reclaimed water)	< 100 organisms
Class C (required where there is a low to insignificant risk of human contact with reclaimed water or livestock access)	< 1000 organisms
Class D (required where there is insignificant risk of human or livestock contact with reclaimed water)	< 10000 organisms

Adapted from EPA Victoria (2002)

Among the chemical compounds used for this task, the most used are: chlorine (Cl_2), sodium hypochlorite (NaOCl), chloramine (RNHCl), chlorine dioxide (ClO_2), Bromine (Br_2) and Ozone (O_3). Evaluating only the standard oxidation potential of these compounds the chosen order would be (Acher et al., 1997; EPA Victoria, 2002; Lopez-Velasco et al., 2012; Silva and Souza, 2011) (Eq. 1):

$$O_3 \gg Cl_2 > Br_2 > ClO_2 > ClO^- > RNHCl \quad (1)$$

However the choice is much more complex. Their antimicrobial property is only one of the aspects that must be considered. Other points to be analyzed are: suspended solids concentration; oxidizable organic and inorganic matter concentration; dissolved oxygen; pH; and temperature. (Acher et al., 1997; Adin et al., 1991; Ayyildiz et al., 2009; Clark and Sivaganesan, 1998; Meyer, 1994; Narkis et al. 1995[a,b]; Ölmez and Kretzschmar, 2009). Barbeau et al. (2005) arranged all these variables into three groups: (i) variables influencing the activity of the disinfectant (temperature, pH), (ii) variables interfering with the availability of the disinfectant in water (all inorganic and organic reduced compounds), and (iii) variables interfering with the accessibility of the disinfectant to the target organism (entrapment microorganism and biofilms presence). Another important point to be considered is that some chemicals which are used in the disinfection process can produce undesirable by-products that could be carcinogenic, mutagenic or possibly teratogenic (Acher et al., 1997; Adin et al., 1991; Chang et al., 2000; Hni et al., 2012; Junli et al., 1997; Liu et al., 2013; Wei et al., 2011; Ye et al., 2013). It is well known that Cl_2 and hypochlorite can

react with some kinds of organic compounds to produce organohalogens like trihalomethanes (THMs) which are hazardous to public health or harmful to the environment (Gagnon et al., 2005; Liu et al., 2012; Meyer, 1994; Narkis et al., 1995a; 1995b; Navalon et al., 2009; Wei et al., 2011). Amin et al. (2013) and Clark and Sivaganesan (1998) have shown in their work that the formation of THMs is a direct result of the consumption of chlorine.

The THMs formation triggered the search for alternative disinfectants to prevent or reduce the formation of these hazardous substances. One of the possibilities to promote the disinfection of the water is chlorine dioxide, ClO_2, (Liu et al., 2013; Volk et al., 2005). Some authors showed that ClO_2 is an excellent alternative to promote water disinfection mainly because it produces smaller quantities of THMs than liquid Cl_2 (Chang et al., 2000; Gagnon et al., 2005; Hoigné and Bader, 1994; Junli et al., 1997; Liu et al., 2013; Navalon et al., 2009; Narkis et al., 1995; Vaezi et al., 2004; Vandekinderen et al., 2009; Volk et al., 2005; Yang et al., 2013; Ye et al., 2013). Junli et al. (1997) have shown that ClO_2 solutions destroyed bacterial populations from industrial sewage within a pH range from 3.0 to 9.0. This pH range was narrowed (6.5 to 7.5) when Cl_2 or hypochlorite solutions were used. Several authors reported that ClO_2 solutions are only slightly superior to chlorine as bactericide but they are much superior as a virucide (Amin et al., 2013; Liu et al., 2013; Vaezi et al., 2004; Veschetti et al., 2005; Yang et al., 2013; Ye et al., 2013). Further, chlorine dioxide has additional advantageous characteristics: it is less corrosive than both chlorine and ozone; it can eliminate bad odor and oxidize ferrous (Fe^{2+}) and manganous (Mg^{2+}) ions; smaller ClO_2 dosages and shorter reaction time are required to ClO_2 to produce the same disinfection effect; the solubility at 20°C of ClO_2 in water is greater than that of Cl_2 which means that more concentrated solutions can be prepared (Adin et al., 1991; Chang et al., 2000; Korn et al., 2002; Ölmez and Kretzschmar, 2009). Although ClO_2 has many favorable characteristics for the disinfection process, some authors pointed the following disadvantage: it requires on-site generation; it could be explosive; and the formation of chlorite (ClO^-_2) and chlorate (ClO^-_3) can be hazardous to public health (Hoigné and Bader, 1994; Katz et al., 1994; Narkis et al., 1995b; Katz and Narkis, 2001; Korn et al., 2002; Veschetti et al., 2005; Liu et al., 2013; Rav-Acha et al., 1985; Sorlini and Collivignarelli, 2005; Yang et al., 2013). Volk et al. (2002) observed that using chlorine dioxide instead of chlorine in a water disinfection plant an 85% reduction in trihalomethanes and a 60% reduction in haloacetic acid were obtained. The concern about the presence of chlorite ion can be mitigated by using iron salts, activated carbon or applied together with Cl_2 (Gagnon et al., 2005; Katz et al., 1994; Narkis et al., 1995b; Sorlini and Collivignarelli, 2005).

The present work had the following objectives: evaluate the ClO_2 and NaOCl demand and the disinfection efficacy of their solutions, using water obtained from an oral care industry waste water treatment facility.

2. Material and methods

The water used in this work was obtained from a wastewater treatment facility at an oral care industry which was used in its cooling towers. 135 water samples were analyzed over a 6 month period. Their physical-chemical characteristics were registered and the averages of these values are given in Table 2.

Table 3 shows the wastewater physical-chemical characteristics recommended by Brazilian National Water Agency (ANA, 2005), by the US *Environmental Protection Agency* (Carvalho and Machado, 2010; Sousa, 2008; USEPA, 2012) and by the Eureau which is the Union of the most National Associations of Water Suppliers and Wastewater Services in Europe (Angelakis and Bontoux, 2001). The Italian national standards (D.M. 185/03, 2003) for reclaimed waste water have the same values showed by Eureau (Cirelli et al., 2008).

Table 2. Physical-chemical characteristics of the wastewater

Parameter	*Unit of measure*	*Jan*	*Feb*	*Mar*	*Apr*	*May*	*Jun*	*Jul*	*Average*
pH		6.9	6.9	6.9	6.6	6.5	6.3	6.4	6.6
EC*	$\mu S \cdot cm^{-1}$	4398	5030	5217	5930	5878	6610	7043	5729
Total dissolved solids	$mg \cdot L^{-1}$	3958	4527	4696	5337	5290	5949	6338	5156
Turbidity	NTU	8.6	2.5	1.7	3.1	3.1	11.0	4.0	4.9
Temporary hardness ($CaCO_3$)	$mg \cdot L^{-1}$	405	495	513	520	586	690	659	553
Total hardness ($CaCO_3$)	$mg \cdot L^{-1}$	425	533	528	545	608	735	719	585
Chlorites	$mg \cdot L^{-1}$	941	1056	1109	1216	1264	1535	1677	1257
Iron (Fe)	$mg \cdot L^{-1}$	0.1	0.2	0.1	0.2	0.1	0.2	0.2	0.2
Phosphorus (PO_4)	$mg \cdot L^{-1}$	2.6	1.7	< 1.0	1.2	1.8	2.6	1.1	1.8
Sulfates (SO_4)	$mg \cdot L^{-1}$	46.9	57.6	58.8	35.6	45.1	33.2	19.2	42.3
Chemical oxygen demand	$mg \cdot L^{-1}$	168	163	168	169	113	159	164	158

**EC = electrical conductivity*

Table 3. Physical-chemical characteristics of the wastewater – Class 4 (Angelakis et al., 2007; Carvalho and Machado, 2010; Sousa, 2008)

Parameter	*Unit of measure*	*Brazilian National Water Agency (ANA)*		*EPA*	*EUREAU EU1/2-07-WR-40(1)*
		without recirculation	*with recirculation*		
pH		5.0 – 8.3	6.8 – 7.2	6.9 – 9.0	6.0 – 9.5
Total dissolved solids	$mg \cdot L^{-1}$	1000	500	500	
Turbidity	NTU			50	
Total hardness ($CaCO_3$)	$mg \cdot L^{-1}$	850	650	650	
Chlorites	$mg \cdot L^{-1}$	600	500	500	250
Iron (Fe)	$mg \cdot L^{-1}$	--	0.5	0.5	2.0
Phosphorus (PO_4)	$mg \cdot L^{-1}$			4	2.0
Sulfates (SO_4)	$mg \cdot L^{-1}$	680	200	200	500
Chemical oxygen demand (COD)	$mg \cdot L^{-1}$	75	75	75	100

The solutions of chlorine dioxide were prepared in a small batch reactor by using technical grade sodium chlorite ($NaClO_2$) from Sigma-Aldrich (Cat. 244155) and reagent grade hydrochloric acid (HCl) from VETEC (Cat. V000154) in distilled water at 20°C. Therefore, ClO_2 was produced in gaseous form according to the stoichiometry given by Eq. (2) (Ayyildiz et al., 2009; Chang et al., 2000; Ölmez and Kretzschmar, 2009; Petrucci and Rosellini, 2005).

$$4HCl + 5NaClO_2 \leftrightarrows 4ClO_2 + 5NaCl + 2\,H_2O \quad (2)$$

The concentration of the chlorine dioxide solution was determined by using the colorimetric disc from HACH, Co., USA after mixing N, N-diethyl-p-phenylenediamine (Cat. 14077-99) and glycine (Cat. 27621-33) (Hatch, 2003). A volume of the ClO_2 solution was then transferred to a flask containing 90 mL of wastewater at 20°C to obtain the desired concentration which was evaluated as described above. This methodology can evaluate solutions of ClO_2 with a concentration up to 5.0 $mg \cdot L^{-1}$. Therefore, in some cases, the ClO_2 solution must be diluted in distilled water to evaluate the concentration that will be used.

Chlorine solutions were prepared with reagent grade sodium hypochlorite 4-6% from VETEC (Cat. V001019) in distillated water at 20°C. The concentration of residual chlorine solutions was determined by using the colorimetric disc from HACH, Co., USA after mixed N,N-diethyl-p-phenylenediamine (Cat. 14077-99) (Hatch, 2003). A volume of this solution was then transferred to a flask containing 90 mL of wastewater at 20°C to obtain the desired concentration which was then evaluated as described above. This methodology can evaluate solutions of Cl_2 with a concentration up to 5.0 $mg \cdot L^{-1}$. Therefore, in some cases, the Cl_2 solution was diluted in distilled water to evaluate the concentration that will be used.

The bactericidal efficiency of both chlorine dioxide and sodium hypochlorite were evaluated using materials autoclaved at 121°C for 15 min. Disinfection tests were conducted at 20°C. The efficiency was assessed by comparing the number of microorganisms measured before and after the application of ClO_2 or NaOCl to the wastewater. Detection and enumeration of the mesophilic aerobic microorganisms were done by pour plate count method using Merck's Plate Count Agar (Casein-peptone Dextrose Yeast Agar). The plates were counted after 48 hours of incubation at 35.5°C in plates that had between 30 - 300 colonies. Results were multiplied by dilution factors and the number of bacteria was always expressed as $CFU \cdot mL^{-1}$ (Allen et al., 2004; Environmental Agency, 2012; Reasoner, 2004). The assays were done at least in triplicate. The figures and equations were obtained by using Origin 6.0 software.

3. Results and discussion

The water used in this work had some parameters higher than those shown in Table 3 which are: total dissolved solids 5156 $mg \cdot L^{-1}$; chlorites, 1257 $mg \cdot L^{-1}$; and chemical oxygen demand 158 $mg \cdot L^{-1}$. All other water parameters used in this work have values lower than the upper recommended limits. Water with high levels of total dissolved solids could promote mineral deposition on the surface of equipment; high chemical oxygen demand gives an indirect measure of organic compound concentration which can suffer chemical oxidation by chemical oxidants like chlorine (Hur et al., 2010). Therefore, the higher the Chemical Oxygen Demand (COD), the smaller is the residual chlorine available to provide water disinfection (Haute et al., 2013).

The amount of chlorine added to the water is known as chlorine dose. After the addition to water, some chlorine reacts first with organic materials and metals in the water and is no more available for disinfection. This is called the chlorine demand of water. The amount of chlorine remaining in the water after the reactions of chlorine with substances in the water is known as chlorine residual. Fig. 1 illustrates

the relation between the chlorine dosed (ClO_2 or NaOCl) in wastewater described in Table 3 and chlorine residual obtained after 20 minutes. Neither the equation that represents the ClO_2 (Eq. 3) nor from NaOCl (Eq. 4) residual could be represented by a first-order equation within the dosing range (0 to 25 $mg \cdot L^{-1}$) used:

$$[ClO_2]_R = 4.696 \cdot 10^{-1} \cdot e^{1.730 \cdot 10^{-1}} \cdot [ClO_2]_D \quad (3)$$

$r^2 = 0.984$

$$[Cl_2]_R = 7.34 \cdot 10^{-2} \cdot e^{1.551 \cdot 10^{-1}} \cdot [NaOCl]_D \quad (4)$$

$r^2 = 0.993$

where: $[ClO_2]_R$ and $[ClO_2]_D$ are chlorine dioxide residual and the amount of chlorine dioxide dosed to water ($mg \cdot L^{-1}$), respectively and $[ClO_2]_R$ is chlorine residual ($mg \cdot L^{-1}$) and $[ClO_2]_D$ is the amount of sodium hypochlorite dosed to water ($mg \cdot L^{-1}$).

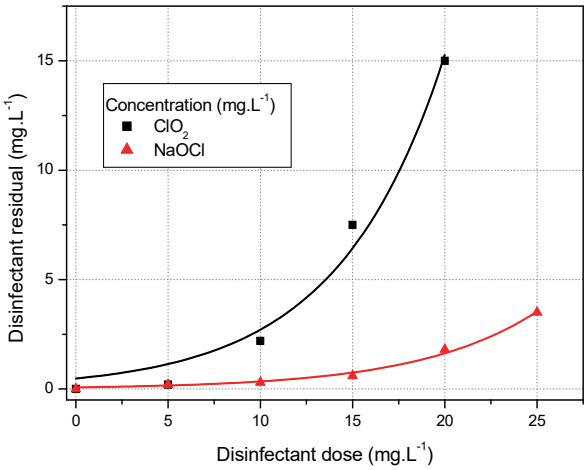

Fig. 1. Chlorine dioxide residual and Chlorine residual in wastewater after 20 minutes

Fig. 1 shows that water contamination affects more the content of residual chlorine from NaOCl than the residual concentration of ClO_2. Adding 20 $mg \cdot L^{-1}$ NaOCl, after 20 min the chlorine residual was 1.8 $mg \cdot L^{-1}$ (an 11 times reduction).

However, if it was dosed at 10.0 $mg \cdot L^{-1}$ ClO_2, after 20 min, the residual concentration was 2.2 $mg \cdot L^{-1}$ (4.5 times reduction). Several authors have observed that suspended solids, organic matter as chemical oxygen demand, as biological oxygen demand or as total organic carbon (TOC) can hinder the water disinfection process (Narkis et al.., 1995a; 1995b; Petrucci and Rosellini, 2005; Ayyildiz et al., 2009; Liu et al.., 2012).

These same authors pointed out that the efficacy of the disinfection process can be reduced due to parallel chemical reactions which decrease the chlorine content in water or by physical protection of the microorganisms by suspended solids.

Narkis et al. (1995a) observed that the residual ClO_2 increases by increasing the ClO_2 dose and decreases with time. They showed in their work that dosing 44.2 $mg \cdot L^{-1}$, a residual of 3.12 and 0.11 $mg \cdot L^{-1}$ ClO_2 were found after 2 h and 24 h contact time, respectively if using a water containing 422 $mg \cdot L^{-1}$ suspended solids and 615.2 $mg \cdot L^{-1}$ COD. In another work, Narkis, et al. (1995b) observed that dosing 2.50 $mg \cdot L^{-1}$ ClO_2, a residual of 0.77 $mg \cdot L^{-1}$ was obtained after 60 s using a water containing 1418.6 $mg \cdot L^{-1}$ suspended solids and 104.3 $mg \cdot L^{-1}$ COD. When the initial dose of ClO_2 was 5.00 $mg \cdot L^{-1}$ the ClO_2 residual concentration was 2.91 $mg \cdot L^{-1}$ after 60 s contact time and 0.11 $mg \cdot L^{-1}$ after 24 h. Clark and Sivaganesan (1998) reported that dosing Cl_2 at 2.0 $mg \cdot L^{-1}$ after 12 h the chlorine residual was 0.35 $mg \cdot L^{-1}$ if the water has a TOC of 3.55 $mg \cdot L^{-1}$, pH 9.0 at 25°C. Haute et al. (2013) observed that within 2 min, 50 $mg \cdot L^{-1}$ free chlorine was reduced to below 0,1 $mg \cdot L^{-1}$, and an initial addition of 100 $mg \cdot L^{-1}$ free chlorine resulted in a residual concentration below 1 $mg \cdot L^{-1}$ free chlorine after 5 min. using a water with a COD value of 456 $mg \cdot L^{-1}$. Therefore, it can be observed that organic matter even in very low concentrations in water, promote significant reductions in Cl_2 or ClO_2 concentrations justifying the results obtained in our work which showed, for instance, a reduction from 10 $mg \cdot L^{-1}$ to 1.17 $mg \cdot L^{-1}$ using ClO_2 and from 10 $mg \cdot L^{-1}$ to 0.3 $mg \cdot L^{-1}$ using Cl_2 with a water containing 5156.4 $mg \cdot L^{-1}$ dissolved solids and 157.6 $mg \cdot L^{-1}$ COD. Nurizzo et al. (2005) reported that using a water containing a COD concentration usually below 25 $mg \cdot L^{-1}$, TOC and Total Suspended Solids (TSS) were, respectively, in the range of 2.4 – 12 $mg \cdot L^{-1}$ and 3 – 24 $mg \cdot L^{-1}$ observed that dosing 5 $mg \cdot L^{-1}$ NaOCl a residual of 1.1 $mg \cdot L^{-1}$ were found after 36 minutes. All these data confirm the results showed by Haute et al. (2013) who observed that higher COD values necessitate the addition of more chlorine to maintain the desired chlorine residual concentration.

An interesting conclusion that could be taken using data shown above is that the initial concentration affects the decomposition rate. Using data from Narkis et al. (1995[b]) and data from Haute et al. (2013) it can be demonstrated that lower the initial disinfectant concentration, lower were the decomposition rate. Using a ClO_2 concentration of 2.5 $mg \cdot L^{-1}$ at 60 s, the decomposition rate was 1.7 $mg \cdot L^{-1} \cdot min^{-1}$.

On the other hand, having a ClO_2 concentration of 5.0 $mg \cdot L^{-1}$ at 60 s, the decomposition rate was 2.1 $mg \cdot L^{-1} \cdot min^{-1}$. This same behavior can be observed for Cl_2 (from NaOCl). Using an initial concentration of 50 $mg \cdot L^{-1}$the decomposition rate was 2.45 $mg \cdot L^{-1} \cdot min^{-1}$ and about 19.8 $mg \cdot L^{-1} \cdot min^{-1}$ using an initial Cl_2 concentration of 100 $mg \cdot L^{-1}$. Using the data from Fig. 1 in which are represented the disinfectant residual concentrations, the decomposition rate for each point was calculated. Fig. 2 represents the relation between the decomposition rate and disinfectant concentration dose.

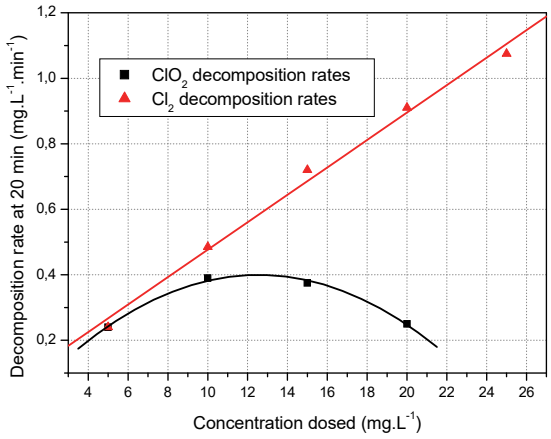

Fig. 2. Disinfectant decomposition rate after 20 minutes of the contact with wastewater

Fig. 2 and Eqs. (3-4) show the relationship between the decomposition rate and the disinfectant dose. Fig. 2 shows that increasing NaOCl concentration dose, the decomposition rate increases. However, increasing ClO_2 concentration dose, the decomposition rate has increased until a given value. After this value the decomposition rate has decreased. Therefore the maximum decomposition rate can be determined by deriving Eq. (5) and equating it to zero. So the maximum decomposition rate was obtained at 12.55 mg·L^{-1} and by Eq. (6) the decomposition rate was calculated in 0.4 mg·L^{-1}·min^{-1}. Hence, using the wastewater described in Table 2 a concentration dose around 12.55 mg·L^{-1} must never be used to avoid the ClO_2 maximum decomposition rate.

NaOCl

$$v = 5.75 \cdot 10^{-2} + 4.19 \cdot 10^{-2} \cdot [NaOCl]_D$$

$r^2 = 0.997$ (5)

ClO_2

$$v = -3.38 \cdot 10^{-2} + 6.91 \cdot 10^{-2} \cdot [ClO_2]_D - 2.75 \cdot 10^{-2} \cdot ([ClO_2]_D)^2$$

$r^2 = 0.997$ (6)

where: ν is the decomposition rate (mg·L^{-1}·min^{-1}).

Over the six-month period, we observed that the average population of mesophilic aerobic microorganisms found in the water used in this work was 5.89·10^5 CFU·mL^{-1} called N_o hereafter. Table 4 shows the final population of mesophilic aerobic bacteria that survived from treatment with NaOCl or ClO_2.

Table 4. Numbers of mesophilic aerobic bacteria that survived after 20 minutes of the disinfection treatment

NaOCl			*ClO_2*		
$[NaOCl]_R$	*Log (CFU·mL^{-1})*	*ΔN **	*$[ClO_2]_R$*	*Log (CFU·mL^{-1})*	*ΔN **
0.80	2.32	3.45	0.20	2.38	3.39
1.17	2.26	3.51	2.20	2.18	3.59
2.00	2.26	3.51	7.50	1.62	4.15
			15.0	0.81	4.96
			18.0	0.30	5.47

**ΔN=(log N_o - log N) where N_o is the initial number of mesophilic aerobic bacteria and N is the number of mesophilic aerobic bacteria after 20 minutes*

Fig. 3 shows the influence of ClO_2 residual after 20 minutes on the number of surviving microorganisms presented in wastewater described in Table 2. Fig. 4 shows the decimal reductions obtained by using ClO_2.

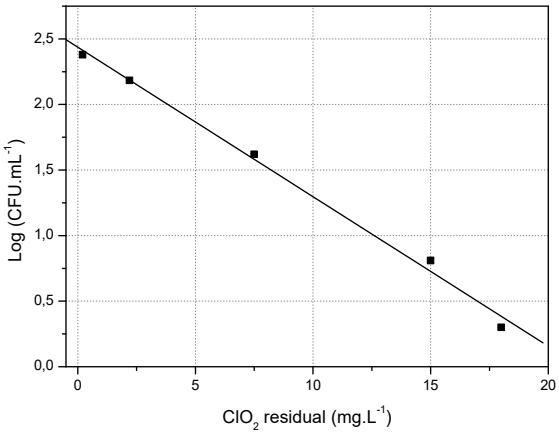

Fig. 3. Effect of ClO_2 residual on surviving microorganisms after a 20 minutes contact

Both relations can be represented by first-order equations obtained from linear regression from data shown in Table 4 (Eqs. 7-8):

$$N = 2.437 - 1.140 \cdot 10^{-1} \cdot [ClO_2]_D \quad (7)$$

r = 0.997

$$N = 3.334 + 1.140 \cdot 10^{-1} \cdot [ClO_2]_R \quad (8)$$

r = 0.997

where: ***N*** is Log (CFU·mL^{-1}) and $[ClO_2]_R$ is ClO_2 residual concentration in mg·L^{-1} and ***ΔN*** are the decimal reductions obtained in the disinfection process.

Fig. 3 (or Eq. 7) shows that a microorganism population of 1.0 CFU·mL^{-1} (point where the regression line crosses the x-axis) could be obtained by using a 21.4 mg·L^{-1} chlorine dioxide residual. Meanwhile Fig. 4 and Eq. 4 show that using a 0.2 mg·L^{-1} has promoted, after 20 min., a microbial population reduction of 3.4 Log cycles. Increasing ClO_2 residual to 15.0 mg·L^{-1} the disinfection process could promote a population reduction greater than 5.0 Log cycles after 20 minutes. Vandekinderen et al. (2009) observed in their work that different microorganisms had different susceptibilities to the antimicrobial effects of ClO_2. They showed that using a 0.1 mg·L^{-1} ClO_2, in 60 seconds, the mean reductions for Gram-negative bacteria and Gram-positive bacteria were 3.5 and 2.6 log cfu·cm^{-2}, respectively. They also observed that the mean reduction for yeast was 1.1 log cfu·cm^{-2}, but *B. cereus* and mould spores were little or not affected by this product. The National Health and Medical Research Council – NHMRC – recommends for water disinfection a contact time of 30 minutes when a dose of chlorine dioxide between

1.0 to 2.5 mg·L^{-1} or slightly higher is used to ensure a ClO_2 residual of 0.3 mg·L^{-1} (NHMRC, 2011).

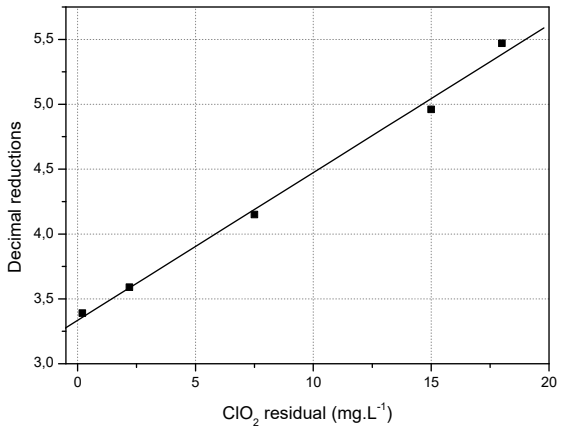

Fig. 4. Effect of ClO_2 residual on decimal reductions after a 20 minutes contact

Volk et al. (2005) observed in their work that ClO_2, due to its strong oxidant power, promoted an excellent reduction in bacterial count. Liu et al. (2013) have pointed out that the dosage of ClO_2 in water treatment should be less than 2,0 mg·L^{-1} to achieve a good reduction in microbial population. Benarde et al. (1965) showed that 2.0 mg·L^{-1} ClO_2 residual has caused in 30 seconds a 4.2 Log reduction in *E. coli* population. Chang et al. (2000) observed that ClO_2 concentration between 1 and 5 mg·L^{-1} in water induced a significant reduction in the coliform population within 1-2 minutes. Hsu et al. (2011) found that a 0.7 mg·L^{-1} ClO_2 residual or a 1.8 mg·L^{-1} Cl_2 residual from NaOCl on a spa water have given disinfection efficiencies of 99.4 and 89.5%, respectively. López-Velasco et al. (2012) showed that ClO_2 was much more effective than NaOCl solutions to inactivate *S. enterica* sv. Newport in the water used to wash tomatoes. These authors show that 5.0 mg·L^{-1} ClO_2, in a water having a turbidity of 43 NTU, has promoted an inactivation of 6 log cycles of *S. enterica* sv. Newport in five seconds. However, in these same conditions, it was necessary 120 seconds to achieve the same inactivation using 5.0 mg·L^{-1} NaOCl.

Several works have shown that chlorine dioxide is more efficient than chlorine to destroy microorganisms. Some of them are listed forward only to compare the efficiency of these to disinfectants. Ayyildiz et al. (2009) claimed that the greatest question to answer when someone plans a disinfection process is the concentration that will be needed to reach the desired reduction in microbial population. If a reduction of 3.4 Log cycles after 20 minutes is desired, this work shows that the ClO_2 residual of 0.2 mg·L^{-1}, as recommended by Ordinance Nº 2914 from Brazilian Ministry of Health (BMH, 2011), is enough as can be seen in Fig. 3 or by Eq. 6. If a complete removal of microorganism after 20 minutes from the water used in this work, a reduction of 5.9 Log cycles is necessary a ClO_2 residual of 22.5 mg·L^{-1} (this value is obtained from Eq. 6) is needed. Therefore it would be necessary to increase the ClO_2 dosage from 5.0 to 22.5 mg·L^{-1} (values obtained from Eq. 1).

Fig. 5 represents the efficiency of sodium hypochlorite on the disinfection process of the re-use water used in this work. Fig. 3 and Fig. 5 show that chlorine dioxide is more efficient than sodium hypochlorite to reduce the microbial population.

Helbling and VanBriesen (2007) also observed that after 20 minutes and using 0.8 mg·L^{-1} residual chlorine from NaOCl, a reduction on *Mycobacterium aurum* population was less than one log cycle. Macauley et al. (2006) have observed a similar behavior.

Using chlorine in a disinfection of swine wastewater they achieved a 2.2-3.4 log bacteria reduction in lagoon samples when was used a residual concentration of chlorine ranging from 4.2 to 5.4 mg·L^{-1} but increasing the concentration of chlorine did not significantly enhance the disinfection activity.

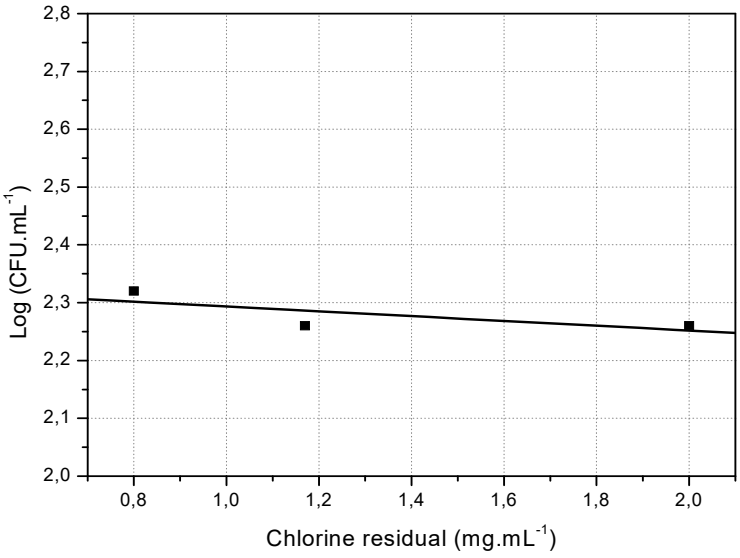

Fig. 5. Effect of Cl_2 residual on survived microorganisms after a 20 minutes' contact

The mathematical equation that illustrates the influence of chlorine residual (from NaOCl) after 20 minutes on the number of surviving microorganism is Eq. (9).

$$N = 2.336 - 4.11 \cdot 10^{-2} \cdot [Cl]_R \quad (9)$$

$r^2 = 0{,}509$

where: N is Log (CFU·mL^{-1}) and $[Cl_2]_R$ is the Cl_2 residual concentration in mg·L^{-1}.

Doing a variance analysis ($p<0.05$) on Eq. (9), its angular coefficient cannot be considered as different from zero with a confidence interval between -0.282 and 0.199. Hence, using NaOCl within the range of chlorine residual studied in this work (0.8 and 2.0 mg·L^{-1}), the number of microorganisms that survived to the disinfection process, remains constant. Therefore, it could be admitted that the linear coefficient of Eq. (9), 2.34 CFU·mL^{-1} is the number of surviving microorganism after 20 minutes using residual chlorine concentrations between 0.8 and 2.0 mg·L^{-1}. So, after 20 minutes, the disinfection process promoted a reduction of 3.34 Log cycles. Thus if a 0.8 mg·L^{-1} Cl_2 residual solution is desired, it is necessary to dose 15.5 mg·L^{-1} of NaOCl in the solution (value obtained from Eq. 2). To obtain the same reduction of 3.39 Log cycle after 20 minutes using ClO_2 (from Fig. 4), it is necessary to use a solution of 0.2 mg·L^{-1} ClO_2 residual. To achieve the value of 0.2 mg·L^{-1}, a solution of 5.0 mg·L^{-1} ClO_2 (from Fig. 1) must be prepared. Kumar et al. (2011) observed a similar effect as shown in Fig. 5. In other words, increasing the chlorine concentration, the microbiological reduction was maintained constant.

Benarde et al. (1965) and Junli et al. (1997) also have noticed that a ClO_2 solution was more efficient than NaOCl as a disinfectant. Junli et al. (1997) found that to promote a 2,0 Log cycle reduction in a *E. coli* population in 20 minutes a concentration of 1.4 mg·L^{-1} ClO_2 was necessary whereas using a Cl_2 solution a concentration of 1.8 mg·L^{-1} was required. However, it is important to mention that in the work of Junli et al. (1997) there was no organic matter in suspension. On the other hand, Benarde et al. (1965) found that after 5 minutes it was obtained a reduction in *E. coli* population of less than 30% when a solution containing 0.75 mg·L^{-1} Cl_2 was used. However, these authors showed that using a solution containing the same concentration of ClO_2, a reduction up to 70% was observed. Benarde et al. (1965) also showed that after 5 minutes, a solution of Cl_2 at 5.0 mg·L^{-1} or a solution of ClO_2 at 2.0 mg·L^{-1} after 30 seconds have ensured reductions in *E. coli* population of 90% and 100%, respectively. If there was no organic matter, a solution of ClO_2 at 0.25 mg·L^{-1} caused a 2,0 Log cycles reduction in the population of *E. coli* after 110 seconds at 5°C or after 16 seconds at 30°C (Benarde et al., 1967).

If a 3 Log cycle reduction (99.9%) in *E. coli* population was desired, solutions at 3.0 mg·L^{-1} made either from chlorine dioxide or from chlorine were efficient (Junli et al., 1997). On the other hand, Silva and Souza (2011) observed that to obtain a 3 Log cycle reduction concentrations between 2.0 and 2.5 mg·L^{-1} of chlorine residual was necessary. Junli et al. (1997) also found that ClO_2 was more efficient in the destruction of *S. aureus* than Cl_2. For instance, 1.5 mg·L^{-1} of ClO_2 promoted a reduction of 98% in the population of *S. aureus* in 20 minutes. However, this same reduction was only obtained by using Cl_2 at 2.5 mg·L^{-1}. Our work shows that to reach a destruction of 3 Log cycle in mesophilic aerobic microorganisms population in 20 minutes it was necessary 0.2 mg·L^{-1} of ClO_2 residual or 0.8 mg·L^{-1} of Cl_2 residual.

4. Conclusions

Chlorine dioxide is less affected by water contaminants when compared to sodium hypochlorite. Using the same initial dose, after 20 minutes the residual concentration of ClO_2 was greater than Cl_2 residual (from NaOCl).

Chlorine dioxide is a much more powerful disinfectant as compared to sodium hypochlorite. After 20 minutes, chlorine dioxide promoted a 2.4 Log cycles reduction on microorganism population by using 0.2 mg·L^{-1}. To obtain this residual concentration, it is necessary to dose 5.0 mg·L^{-1} of ClO_2 to water. The same antimicrobial effect was achieved by using 0.8 to 2.0 mg·L^{-1} of Cl_2 residual (from NaOCl). So, as demonstrated, it is necessary to dose 15.5 to 21.6 mg·L^{-1} of NaOCl in the water to achieve the desired range (0.8 to 2.0 mg·L^{-1}) of residual chlorine from NaOCl.

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