

Studies of Interactions of Aquatics Disinfectants (Chlorine Dioxide and Chlorine) with Tropical Aquatic Fulvic Acids Monitored by Differential Absorbance Spectroscopy

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Abstract. The interactions of tropical aquatic fulvic acids (AFA) with chlorine, chlorine dioxide and formation of disinfection by-products, were characterized using differential absorbance spectroscopy, to explore the formation by-products, such as chloroform (CHCl₃) during halogenation of natural organic matter with chlorine and chlorine dioxide. The interactions of AFA with chlorine and chlorine dioxide were characterized by using different disinfectants concentrations (2.5, 5.0, 10.0 and 20.0 mg.L⁻¹) after 24 h of reaction, in solutions phosphate buffer at pH 7.0. Both disinfectants promote a decrease in absorbance at 254 nm and 272 nm, with the increase of the concentration. The concentration of CHCl₃ formed was extremely well correlated, with the decrease of the absorbances, with values for R² of 0.99, which was also observed correlating with the magnitude of the differential absorbance at $-\Delta A_{272}$ and $-\Delta A_{254}$. The differential spectrum of chlorinated natural organic matter (NOM) has a peak near 270 nm, being more defined, in the samples with chlorine, in contrast with samples with chlorine dioxide that does not have defined peaks. Differential absorbance spectroscopy proved to be as a powerful tool in monitoring transformations in the chemical state of humic species (HS) as the aquatic fulvic acids.

Palavras-chave: formation of by-product, aquatic disinfectants, drinking water and spectroscopy

Recebido: 17 de Outubro de 2014; aceito: 17 de Novembro de 2014, publicado: 18 de Dezembro de 2014.

DOI: 10.14685/rebrapa.v5i3.160

INTRODUCTION

The study of organic compounds in drinking water continues to be of intense interest. Extensive work in this research area began with the disclosure of the results of a 1974 study of New Orleans where source water contaminants were still found in treated drinking water (EPA, 1974).

Chlorine is used universally as a disinfectant in drinking water. However, it has been shown that reaction between organic compounds and halogen-based oxidants can lead to the formation of halogenated disinfection by-products (DBPs) with proven or suspected adverse health effects (KRAMER *et al.*, 1992). The most important and dangerous by-products are halogenated organic substances, such as trihalomethanes (THMs), haloacetic acids (HAAs) and disinfection by-products derived from the addition of Cl₂ and NaOCl in the disinfection process (ROOK, 1974; KOCH;

KRASNER, 1989; PETERS; LEER; GALAN, 1990; PRAKASH, *et al.*, 2012; YANG, *et al.*, 2013, ÖZDEMİR, *et al.*, 2013).

When gaseous Cl₂ is used in bleaching, for example, considerable amounts of organochlorine compound of high molecular mass are formed. These are lipophilic, and persist in the environment. About 30 % of the organically bound chlorine in spent chlorination water and about 5 % in spent alkali water are of low relative molecular mass. Cl₂ largely been replaced by ClO₂ (chlorine dioxide) in recent years and this has reduced the formation of lipophilic organochlorine compounds considerably. Also the formation of volatile low molecular chlorinated compounds has been shown to be decreased (CARVALHO, 2003, PRAKASH; 2012).

Studies have shown that when natural organic matter (NOM) is halogenated, changes in certain portions of the absorbance spectrum of

the NOM can serve as a surrogate for the progress of the reactions and the concentration of DBPs (KORSHIN; LI; BENJAMIN, 1997, 1998, 1999; KARANFIL *et al.*, 2000; WU *et al.*, 2000; PRAKASH, *et al.*, 2012).

In particular, it has been found that the absorbance of solutions declines monotonically with both increasing dose of free chlorine and reaction time, and that the magnitude of this decrease near 270 nm is a sensitive and reliable indicator of the formation of total organic halogen, trihalomethanes and haloacetic acids (KORSHIN; WU; XIAO, 2000).

Korshin *et al.* (2002), shows that the differential absorbance ΔA_λ , after and prior to chlorination, can be used to evaluate the formation of by-products after chlorination.

In particular, differential spectra have a well-defined peak near 272 nm, in contrast with the conventional absorbance spectra of NOM either prior to or after chlorination, which have no identifiable peaks. Results have suggested that the $-\Delta A_{272}$ is correlated with the formation of by-products as the total organic halogen (TOX) (KORSHIN; WU; XIAO, 2000). The significance of the differential absorbance is related to the fact that the ultraviolet absorbance of natural waters is attributable overwhelmingly to the diverse population of organic molecules in the water referred to collectively as natural organic matter. When the NOM molecules react with oxidants, DBPs are formed and, simultaneously, the absorbance of the NOM changes, giving rise to the differential absorbance spectrum (KORSHIN *et al.*, 2002).

The connection between organic compounds and THM, for example, is based in part on similarities in the rates of THM formation and THM yields for natural waters and extracted aquatic humic substances. The chemical basis for organic halide formation from the chlorination of humic materials is not well understood. Aquatic humic materials are thought to have a moderate aromatic character (~25% of the total carbon) with large numbers of carboxyl groups, some phenolic groups, alcohol OH groups, methoxyl groups, ketones, and aldehydes (RECKHOW; SINGER; MALCOLM, 1990). Degradative structural studies have suggested the presence of

significant phenolic content, especially when the OH groups are protected by prior methylation. This may be important because activated aromatic structures such as phenolics are known from model compound studies to be especially reactive with chlorine, producing large amounts of chlorinated by-products (SCHULTEN; GUDRUN; FRIMMEL, 1987; RECKHOW; SINGER, 1995; NORWOOD *et al.*, 1980).

When individual phenolic compounds that are thought to be reasonable analogs for the active functional groups in NOM are chlorinated, their absorbance almost invariably increases over most of the range from 250 nm to 400 nm. Because aromatic functional groups are thought to be both the dominant chromophores in NOM and the dominant sites of attack by chlorine on NOM molecules, the absorbance at 254 nm has frequently been proposed as indicator of the concentration of DBP precursor sites in a water sample (ROOK, 1977; BOYCE; HORNING, 1983).

However, the spectroscopic characteristics and the formation of by-products, of NOM in presence of chlorine dioxide have not been examined. In this paper, we explore the formation of by-product and relationships with absorbance at 254 nm and 272 nm, in samples of tropical aquatic fulvic acids (AFA) in presence of chlorine and chlorine dioxide, as alternate disinfectant and show the applicability of differential absorbance spectroscopy for studies of the by-product formation, as the chloroform.

MATERIALS AND METHODS

Materials

Chemicals

All reagents used were high-purity grade, unless otherwise stated. Diluted acid and base solutions required for the aquatic humic substances (AHS) isolation were prepared by convenient dilution of 30% (v/v) hydrochloric acid (suprapur, Merck AG) or sodium hydroxide monohydrate (suprapur Merck AG) dissolved in high-purity water (Milli-Q system, Millipore). The XAD 8 adsorbent (Serva Feinbio-chemica), used for isolation of AHS, was purified before

use by successive soaking with 0.5 mol L⁻¹ HCl, 0.5 mol L⁻¹ NaOH and methanol p.a. (24 h each).

HS isolation by XAD 8 resin

The AHS's were isolated from a sample collected from a tributary stream of River Itapanhaú within of the State Park called "Serra do Mar". This is an environmentally protected area located in the seaboard, 7th UGRHI of 11th group of UGRHI from São Paulo State/Brazil. For this purpose, 50 liters of surface water were filtered through 0.45 µm cellulose-based membranes and acidified with concentrated HCl solution to pH 2.0. Afterwards, the AHS from the acidified sample were isolated on the XAD-8 collector (AIKEN, 1985) following the recommendations of Malcolm (1989). After elution with 0.1 mol L⁻¹ NaOH solution, the obtained concentrate (4.5 mg mL⁻¹ DOC equivalent to 9.0 mg mL⁻¹ aquatic HS) was acidified to pH 2.0 with 6.0 mol L⁻¹ HCl solution and the aquatic fulvic acid AFA (soluble fraction) were separated from aquatic humic acid (AHA) by centrifugation at 12000 rpm (40 min). The determination of dissolved organic carbon (DOC) in the aquatic HS concentrate was carried out by catalytic combustion in oxygen stream and subsequent infrared detection by Analyser Shimadzu TOC 2000 (WANGERSKY, 1993). Metal concentrations

in the AHS were determined by ICP-OES spectrometer (ROSA; ROCHA; BURBA, 2002). The studied aquatic HS are summarized in Tables 1 and 2.

Chlorination and UV Absorbance spectroscopy

AFA samples (8.0 mg L⁻¹), with 4.0 mg L⁻¹ of dissolved organic carbon (DOC), were treated with chlorine and chlorine dioxide, in different disinfectants concentrations (2.5, 5.0, 10.0 and 20.0 mg L⁻¹), in vials of 10 ml with stirring for 10 min. Solutions were prepared in phosphate buffer (KH₂PO₄/NaOH) at pH 7.0, at room temperature between 20 and 25°C. The reaction time was typically 24 h. These different disinfectants concentrations were chosen in exploratory character. All samples were placed in a dark glass bottle and sealed to protect against solar radiation (which could degrade the oxidant).

The experimental conditions to chlorination were conducted following the recommendations of the literature (APHA; AWWA; WPCF, 2005). Chlorination was carried in the presence of 0.1 M phosphate buffer at temperature between 20 °C and 25 °C. Chlorine stock solution was prepared by dilution of a reagent-grade sodium hypochlorite solution (5% available chlorine) with Mili-Q water.

Table 1- The humic substances from Itapanhaú Stream, São Paulo State, Brazil.

Origin	Itapanhaú Stream
pH	5.0
Conductivity	58 µ S.cm ⁻¹
Temperature	25 °C
DOC	4.5 mg.mL ⁻¹
UVA ₂₅₄	0.2 cm ⁻¹
SUVA ₂₅₄	0.044 cm ⁻¹ .mg ⁻¹ L
Complexation capacity	3.4 mmol Cu(II) per g DOC

Table 2- Metal concentrations as determined by ICP-OES in water and in the aquatic humic substances isolated from Itapanhaú Stream-São Paulo State-Brazil (n=5).

Metals	Concentration	
	Water ^a [µ g.L ⁻¹]	Isolated HS ^b [mg.L ⁻¹]
Cu	79.9 ± 0.6	20.20 ± 1.60
Co	≤ 0.5 (LD)	0.69 ± 0.04
Ni	11.6 ± 0.1	3.12 ± 0.24
Cd	≤ 0.25 (LD)	5.53 ± 0.42
Mn	18.7 ± 0.1	4.71 ± 0.16
Hg	≤ 0.5 (LD)	0.04 ± 0.00

^aTotal metals in the 0.45 µm membrane filtered original sample;

^bAfter isolation by the XAD 8 resin procedure (concentration 250x); (LD) Limit of Detection

The chlorine dioxide was produced from sodium chlorite activated by HCl 10% solution (APHA; AWWA; WPCF, 2005). The concentrations of these disinfectants was measured using the N,N-diethyl-p-phenylenediamine (DPD) methods just before application. Residual chlorine was quenched with sodium sulfite (MASSIMILIANO; KORSHIN, 2005).

The absorbance spectra were recorded using a Shimadzu model UV-1601 PC spectrophotometer, with 10 cm quartz cells. The instrument baseline was established using Milli-Q water. The differential absorbance ΔA_λ , what is defined by the equation (1):

$$\Delta A_\lambda = \Delta A_\lambda^{\text{chl}} - \Delta A_\lambda^{\text{init}} \quad \text{Eq. (1)}$$

where $\Delta A_\lambda^{\text{chl}}$ and $\Delta A_\lambda^{\text{init}}$ are the absorbance of light at wavelength λ after and prior to chlorination, respectively, were used to evaluate the formation of by-products after chlorination, second Korshin *et al.* (2002).

The chloroform was analyzed using a SHIMADZU 17A, gas chromatograph equipped with an electron capture detector (ECD) and a system of Solid-Phase Microextraction (SPME). The extractions were made with standard solution (5.0 mL) of the analytes, in a bottle of 10.0 mL with bar of agitation. The thermal desorption was effected the 250 °C for 5 min in the injector of the chromatograph the gas in the mode splitless, with column CROMA-5 (30 m x 0.25 mm x 0.33 μm). The temperature program was as follows: the initial temperature of 35°C was held for 3 min and then increased at a rate of 4 °C min⁻¹ to 44 °C (6 min) at 8 °C min⁻¹ to 150 °C. The extractions were made with the optimized parameters, for the extraction of standard sample chloroform, where the fiber was kept in headspace of the solution during 5 minutes at an extraction temperature of 32 °C with equilibrium time in the “headspace” of the solution of 10 min.

RESULTS AND DISCUSSION

Figs 1a and 1b, shows a set of UV absorbance spectra for tropical acids fulvic of the River Itapanhaú from São Paulo State/Brazil subjected to chlorination with chlorine and chlorine dioxide. In both cases, of decrease UV with

increasing oxidant dose is apparent, what also it was observed with the increase of the reaction time (data not shown). It has been shown that the chlorination also produces a decrease of absorbance in chlorinated coastal and deep ocean seawater at all wavelengths >250 nm (MONSALLIER *et al.*, 2000).

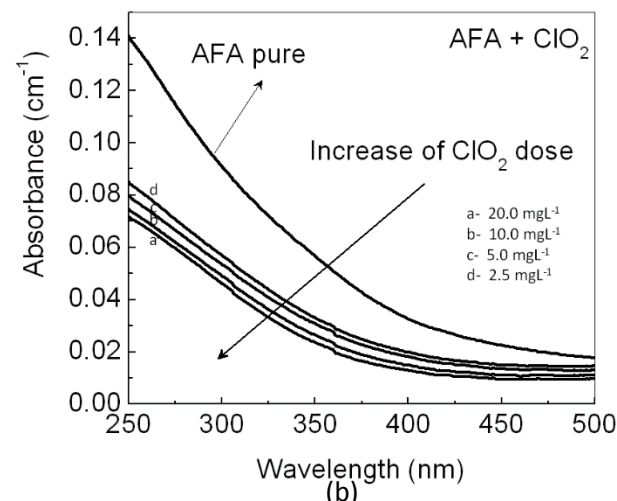
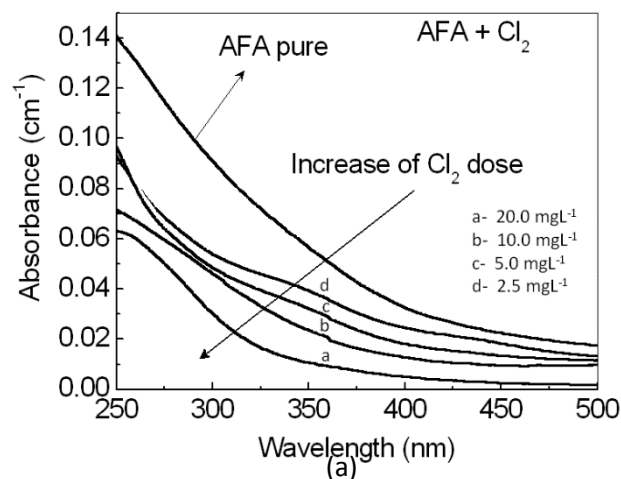


Figure 1- UV spectra for tropical acids fulvic of the River Itapanhaú from São Paulo State/Brazil chlorinated, at pH 7.0, after reaction time 24 h. In (a) with chlorine and (b) with chlorine dioxide.

The fast decrease of the absorbance to the highest values of wavelength can be the result of the break of links in the electronic structure, or the destruction of insaturated conjugated compounds, present in the structure of the dissolved organic substance (CHANG *et al.*, 2001). The halogenation, therefore, it promotes destruction and/or alteration of cromophores present in the organic substance (KORSHIN; LI; BENJAMIN, 1997).

The increase of the chlorine concentration also produced changes in the form of the curves, in contrast with the samples in presence of chlorine dioxide. The decrease of the absorbance in samples with chlorine it was of 0.14 (sample in absence of chlorine) to ~0.09 (sample with lesser chlorine concentration). Sample with higher chlorine concentration, the decrease it was ~0.06. In samples with chlorine dioxide, this decrease it was of 0.14 (sample in absence of the oxidant) to ~0.08 and ~0.07 (sample with lesser and higher chlorine dioxide concentration, respectively).

In case of the chlorine dioxide, this reacts primarily by oxidation reactions resulting in few organic compounds, both volatile and nonvolatile, and in which chlorine atoms have been incorporated. Increasing dose of chlorine dioxide, increase the possibility of reaction with groups (-OH, -OCH₃), presents in fulvic acids. Probably the chlorine dioxide only breaks large molecules structures in lesser (CHANG *et al.*, 2001).

In contrast, the chlorine reacts in solutions of organic compounds by one or more of three basic mechanisms, namely, addition, during which chlorine atoms are added to a compound; oxidation and substitution, during which chlorine atoms are replaced with some other atoms that are present in the organic reactant (MORRIS; BAUM, 1978).

In the initial reactions between Cl and NOM, virtually 100% of the Cl that reacts is incorporated into the organic molecule. However, as the reaction proceeds (i.e., as reaction time or Cl dosage increases), less and less Cl that reacts is incorporated into the NOM molecules. Instead, most if not all of the Cl that reacts later in the process is reduced to Cl⁻ and, is released into the solution. Possibly, these differences, explain the changes observed in the spectra of absorbance for the different oxidants. The specific information about variable Cl incorporation efficiency provides important new insights into the process of DBP formation (LI; KORSHIN; BENJAMIN, 1998).

The UV absorbance spectra of pure compounds dissolved in water consist of absorbance bands with well-defined maximum values at wavelengths that correspond to the energy

needed to produce an electron in the molecule to a higher energy orbital. Most aromatic compounds have three such bands (JAFFE; ORCHIN, 1962; SCOTT, 1964). The functional aromatic groups are chromophores that constitute in large part, in dominant sites, during the attack of chlorine on molecules of the organic substance. However, aliphatic groups can also contribute (KORSHIN; CHI-WANG; BENJAMIN, 1996). When the NOM is halogenated, changes in certain portions of the absorbance spectrum of the NOM can serve as a surrogate for the progress of the reactions and the concentration of by-products that form (WU *et al.*, 2000).

It is accepted that the position at 254 nm, is mainly determined by the susceptibility of aromatical groups, and the decrease of this, suggests an attack of the oxidant in these aromatical sites, in samples of aquatic origin. This decrease, was also proposed as an indicator of the concentration of by-product precursor sites in a water (KORSHIN; LI; BENJAMIN, 1999; WU *et al.*, 2001).

Gauthier *et al.* (1987), showed that wavelength at 254 nm can occur transitions $\pi - \pi^*$ in benzenes substitutes. However, at 272 nm also it such transitions can occur. Kulovara *et al.* (1996). Also related to the degradation of aromatics parts, present in humic substances, with the decrease of the absorbance at 272 nm.

The results obtained for absorbances at 254 nm and 272 nm, in present work, between the oxidants, did not present differences. It was observed a decrease of absorbance at 254 nm with the increase of the concentration of the oxidants, varying of 0.14 (sample in the absence of the oxidants), for approximately 0.06 and 0.07 (sample with bigger concentration of both oxidants and in presence of chlorine and chlorine dioxide, respectively). At 272 nm, the decrease it was of 0.12 for 0.05 (sample with chlorine) and 0.06 (sample with chlorine dioxide).

In Figs. 1a and 1b, all of the absorbance spectra are broad curves that have no identifiable peaks. In contrast, Fig. 2 shows differential spectra, which have a well-defined peak between 250 nm and 300 nm, near 270 nm. In samples with chlorine this peak is well defined, main in

samples with greater oxidant dose, what also it was observed with the increase of the reaction time. The band observed main in samples with bigger concentration of the chlorine, in the 340 - 380 nm range, can be attributed to aromatic chlorinated intermediates formed prior to the release of products such as HAAs and THMs (KORSHIN; BENJAMIN; XIAO, 2000). Consistent with the trends described in further details in more publications (LI; KORSHIN; BENJAMIN, 1998); KORSHIN; WU; BENJAMIN, 2002).

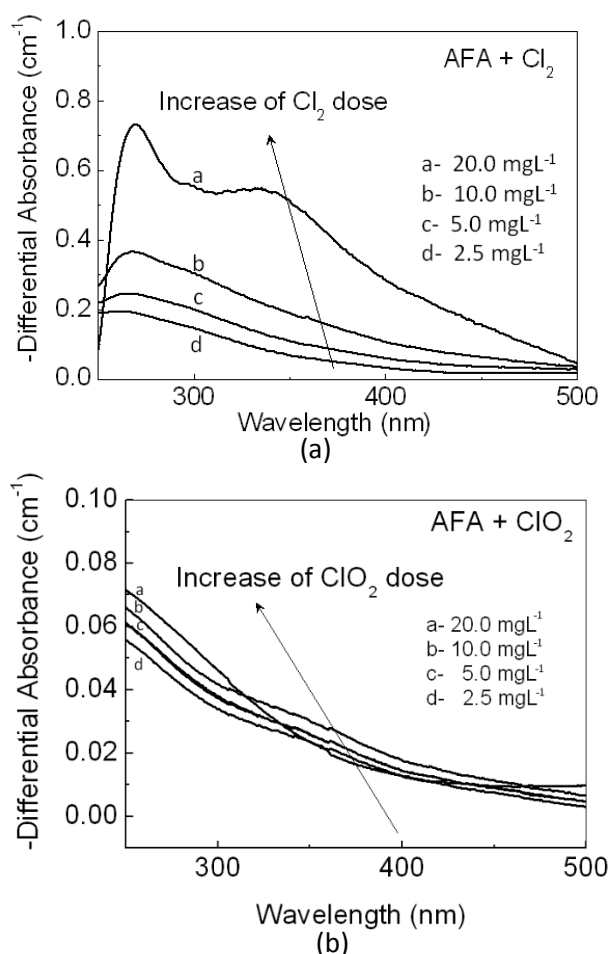


Figure 2- Differential UV spectra for tropical aquatic fulvic acids of the River Itapanhaú from São Paulo State/Brazil chlorinated, at pH 7.0, after reaction time 24 h. In (a), sample with chlorine, (b) with chlorine dioxide.

In contrast, less enhanced in the samples with dioxide chlorine, it was observed (Fig. 2). This does not present defined peaks, although the intensity of the differential spectra increased with increasing dioxide chlorine dose in region between 250 nm and 300 nm).

The sign of the differential absorbance is virtually always negative, i.e., chlorination decreases the absorbance of the NOM and therefore of the solution. In particular, differential spectra have a well-defined peak near 272 nm, in contrast with the conventional absorbance spectra of NOM either prior to or after chlorination, which have no identifiable peaks and the intensity of the differential spectra grows with increasing time of chlorination or, at a given reaction time, increasing chlorine dose (KORSHIN; WU; BENJAMIN, 2002). The tropical aquatic fulvic acids, in present work and in presence of the chlorine, also presented these characteristics.

Table 3 shows the values for the differential absorbance at $-\Delta A_{254}$ e $-\Delta A_{272}$, in different concentrations of the oxidants, obtained according Korshin *et al.* (2002) methodology.

In contrast with the results obtained by absorbance spectra, differences were observed for the differential spectra (Table 3). The differential absorbance at 254 nm ($-\Delta A_{254}$), varied from 0.20 (sample with lesser chlorine concentration) to 0.32 (sample with bigger chlorine concentration). In sample with chlorine dioxide, it varied from 0.05 (sample with lesser chlorine dioxide concentration) to 0.07 (sample with larger chlorine dioxide concentration). The differential absorbance at 272 nm ($-\Delta A_{272}$) varied from 0.18 (sample with lesser chlorine concentration) to 0.73 (sample with higher chlorine concentration). In samples with chlorine dioxide, it varied from 0.04 (sample with lesser chlorine dioxide concentration) to 0.06 (sample with higher chlorine concentration) in the analyzed period.

The differential absorbance at 254 nm for sample in presence of chlorine, comparing with the samples with greater and minor concentration of the oxidant, it presented increase of 60 %. In sample with chlorine dioxide, this increase it was of 40 %. At 272 nm, the increase it was of 305% and 50 %, sample in presence of chlorine and chlorine dioxide, respectively.

These results, i.e., as increase of the differential absorbance (at 254 nm and 272 nm), evidence possible formation of byproducts and that also, possibly it is occurring degradation of aromatics

parts, presents in humic substances. The use of both wavelengths, presented results that agree with relation to the possible degradation of aromatics functional groups and formation of by-products.

The difference between the oxidants, with relation to the increase of the differential absorbance and increase concentration it suggests that, in the case of chlorine dioxide, although chlorine atoms are incorporated in the organic substance, these promote the oxidation of aromatics parts, oxidated faster the molecules presents in fulvic acids, under determined conditions and then, it stops to react, in contrast with the samples in presence of chlorine, that went on reacting with molecules present in fulvic acids. This would possibly explain the lesser formation of trihalomethanes in solutions contends chlorine dioxide, which it was verified by the gas chromatography technique.

Fig. 3 show a comparison between the results obtained by gas cromatography and differential absorbance at 272 nm ($-\Delta A_{272}$). These results show the formation of chloroform after 24 hours of reaction, in function of the variation of the concentration of the oxidants. In sample with lesser value for the differential absorbance $-\Delta A_{272}$, of 0.73 (sample with higher chlorine concentration), it was detected formation of $\sim 12.0 \mu\text{g.L}^{-1}$ of chloroform. In samples with chlorine dioxide, it was formed approximately $0.20 \mu\text{g.L}^{-1}$ of chloroform (sample with larger chlorine dioxide concentration), with a differential absorbance at 272 nm, of 0.06.

In case of the samples with chlorine dioxide, the differential absorbance at 272 nm ($-\Delta A_{272}$), it tends to stabilize itself, with the increase of the concentration of the oxidant, in contrast with samples in presence of chlorine. However, in both cases, there was an increase of the content

of formed chloroform, with the increase of the concentration of the oxidants, being that for the sample with chlorine, this increase it was of 100% and for samples with dioxide chlorine of the $\sim 33\%$, observing a reduction in the chloroform formation. Similar behavior was observed for the differential absorbance at $-\Delta A_{254}$.

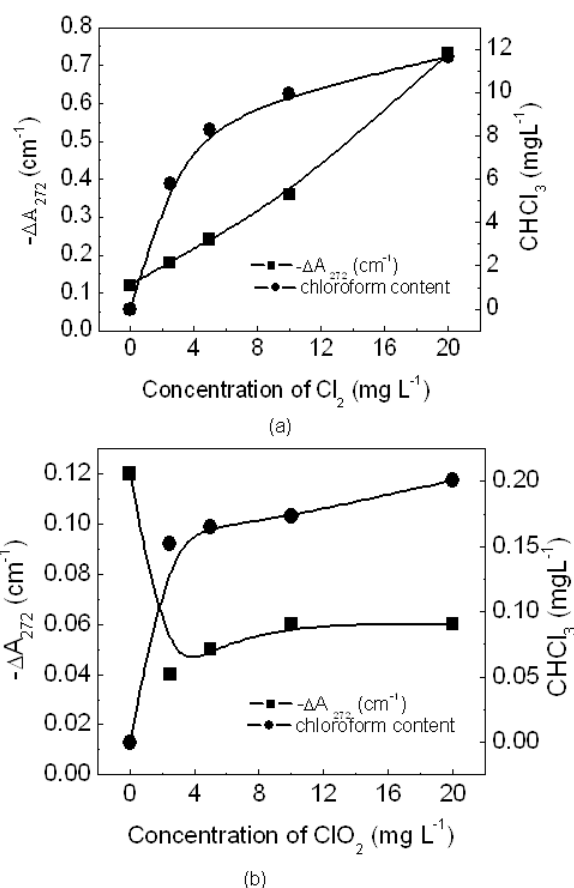


Figure 3 - Chloroform content formed and absorbance at 272 nm, in different concentrations of the oxidants. In (a) samples with chlorine and (b) samples with chlorine dioxide. Aquatic fulvic acids at 4 mg L^{-1} , solutions at pH 7.0.

Table 3 – Differential absorbance $-\Delta A_{254}$ e $-\Delta A_{272}$, obtained for samples of the fulvic acids, in presence of chlorine and chlorine dioxide, reaction time 24 hours.

Oxidant Dose (mg L^{-1})	$-\Delta A_{254}$		$-\Delta A_{272}$	
	Cl_2	ClO_2	Cl_2	ClO_2
0.0	-	-	-	-
2.5	0.20	0.05	0.18	0.04
5.0	0.23	0.06	0.24	0.05
10.0	0.30	0.06	0.36	0.06
20.0	0.32	0.07	0.73	0.06

The most important property of the differential absorbance with respect to its use as a tool for monitoring DBP formation is that the differential absorbance at 272 nm ($-\Delta A_{272}$) is extremely well correlated with the concentration of byproducts formed in that water.

This correlation is remarkable for its linearity (with R^2 of 0.99 in many cases what also it was observed at $-\Delta A_{254}$) and, its applicability to unrelated water sources over a wide variety of halogenation conditions. This linearity was observed for both oxidants.

CONCLUSIONS

This correlation is remarkable for its linearity (with R^2 of 0.99 in many cases what also it was observed at $-\Delta A_{254}$) and, its applicability to unrelated water sources over a wide variety of halogenation conditions. This linearity was observed for both oxidants.

In this paper we explore the formation of by-product and relationships with absorbance at 254 nm and 272 nm, in samples of tropical aquatic fulvic acids in presence of chlorine and chlorine dioxide, as alternate disinfectant and demonstrate the applicability of differential absorbance spectroscopy for studies of the by-product formation, as the chloroform. Both disinfectants produce a decrease in absorbance at 254 nm and 272 nm, with the increase of the concentration. The concentration of CHCl_3 formed was extremely well correlated, with the decrease of the absorbances, with values for R^2 of 0.99, showing up strongly correlated with the magnitude of the differential absorbance at 272 nm and at 254 nm.

The results are possibly associated with the fact that chlorine dioxide only breaks large molecules structures in lesser, in contrast with the chlorine, which reacts with organic compounds by one or more of three basic mechanisms, as addition, oxidation and substitution. Possibly, this explains the changes observed in the spectra of absorbance when using different oxidants and the less concentration of the chloroform formed in samples with chlorine dioxide.

Differential absorbance spectroscopy proved to be a powerful tool in monitoring

transformations in the chemical state of humic species (HS) such as the aquatic fulvic acids. The shape of the spectra provides information about the chemical nature of the reactive chromophores, when different oxidants as chlorine and chlorine dioxide are used.

ACKNOWLEDGEMENTS

The authors are grateful to FAPESP (fellowships to E.R.C., project 99/10565-6), CNPq (projects 620324/98-8 and 302756/2009-4) and Embrapa for the financial support.

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