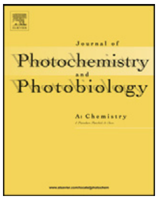
Journal of Photochemistry and Photobiology A: Chemistry 229 (2012) 46–52

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Significant decrease of THMs generated during chlorination of river water by previous photo-Fenton treatment at near neutral pH

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ARTICLE INFO

Article history:
Received 13 May 2011
Received in revised form
28 November 2011
Accepted 2 December 2011
Available online 10 December 2011

Keywords:
Advanced oxidation processes
Solar treatment
Neutral photo-Fenton
Trihalomethanes
NOM oxidation
Drinking water disinfection
Disinfection by-products

ABSTRACT

An important issue in chlorine drinking water disinfection is the generation from natural organic matter (NOM) of disinfection by-products (DBPs), especially trihalomethanes (THMs). The THMs generation can be limited by reducing the levels of NOM prior to the chlorination step. Herein, photo-Fenton system under solar simulator degraded humic acid solutions (as NOM model compounds), as well as NOM contained in river water (Pance River, Cali-Colombia), and dramatically reduced THMs formation during the subsequent chlorination step. In both cases the initial pH of treated water was near to 7. In no pre-treated river water 100–160 μg/L of THMs are formed during chlorination while values of 20–60 μg/L were reached in water previously treated for 4 h by neutral photo-Fenton under solar simulator. The decrease in the generated THMs/total organic carbon ratio suggests that mainly the NOM fraction sensitive to THMs formation was photo-degraded. Therefore, the neutral photo-Fenton reagent could be implemented as a technological option for NOM removal for limiting THMs formation during a subsequent chlorination step.

1. Introduction

The elimination of pathogens and related microorganisms is frequently carried out by using chlorine. This leads to the formation of chloro-organic compounds when chlorine comes into contact with natural organic matter (NOM). According to Bull and Kopfler, these chloro-organic compounds, belonging to the family of disinfection by-products (DBPs), are carcinogenic and mutagenic [1]. The guideline-permitted concentration levels of total trihalomethanes (THMs) and haloacetic acids (HAAs) are 80 and 60 μg/L, respectively [2]. These values are difficult to reach since NOM has been reported to form concentrations of THMs as high as 90 μg per mg of total organic carbon (TOC). Coagulation and flocculation (classical processes) are widely used to treat large concentrations of NOM. These processes typically remove 50–80% of dissolved organic carbon (DOC) but they are limited when trying to reach DOC levels below 1.0 mg/L [3].

To minimize DBP production, different advanced oxidation processes (AOPs) could be alternatives for NOM degradation [3–10] or to replace chlorination by TiO_2 photo-catalytic process as a disinfecting step [11–14]. AOPs are characterized by the presence of highly reactive oxygen species (ROS) as ($^{\bullet}OH$), which are suitable for rapid and indiscriminate reaction with a great number of organic compounds and bacteria [15–20]. Among the processes that can be used to generate hydroxyl radicals, Fenton (Eqs. (1) and (3)) and photo-Fenton processes (Eqs. (1)–(3)) have been used in the treatment of organic pollutants alone [21–23], coupled to biological [24–26] or chemical systems [27,28].

In recent years, the using of direct solar light as source of photons for the degradation of pollutants in aqueous solutions by photo-Fenton reagent has been explored [29–31]. Homogeneous Fenton (Eqs. (1) and (3)) and photo-Fenton processes (Eqs. (1) and (2)) are of interest given their large potential for application [32]. The Fenton reagent (H_2O_2 with Fe(II)/Fe(III) ions) in water produces $^{\bullet}OH$ (Eq. (1)) and peroxy ($HO_2^{\bullet}/O_2^{\bullet-}$) radicals (Eq. (3)). Those species, especially $^{\bullet}OH$, attack almost every organic compound and bacteria.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\bullet}OH \quad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (3)$$

The effect of light irradiation in Eq. (2) leads to Fe^{2+} formation by photo-reduction of the aqua-Fe(III) complexes inducing additional production of $\bullet OH$. The main advantage of the photo-Fenton

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doi:10.1016/j.jphotochem.2011.12.001

process is light absorption up to 580 nm comprising 35% of the solar spectrum. Additionally, in the homogeneous photo-Fenton process, the interaction between pollutants and oxidizing agents is favored [33]. The overall process is described in Refs. [21,23,34–37].

However, Fenton and photo-Fenton processes for the treatment of chemical and biological contamination of drinking water sources have been rarely explored because the optimal efficiency of those oxidative systems is reached at pH 2.5–3.0 because the solubility of Fe salts decrease with the pH rise. Therefore, the required acidification and neutralization procedures have been considered as the limiting factor for the application of this process in the treatment of drinking water sources. However, we have recently shown for the first time that natural water from Switzerland, Colombia and Africa can be completely disinfected [15–20], and the NOM partially degraded in presence of a solar photo-Fenton reactant. In both latter tropical contexts, Fe salts naturally present in natural sources are often enough for assuring the photo-catalytic turnover in the photo-Fenton process. In natural water, NOM complexes and Fe salts naturally present in natural sources maintains Fe ions available for homogeneous Fe-photo-assisted generation of reactive oxygen species (ROS) as $^\bullet OH$.

Concerning NOM removal from water, several studies have been published. The treatment of commercial humic acid and NOM-rich waters with Fenton and photo-Fenton reagent showed that the optimal pH was 4.0 [3]. However, another study revealed that, in spite of pH 3.0 is often claimed as necessary for optimal photo-Fenton processes, the TOC reduction in water was insensitive to pH in the 3.0–7.0 range [4]. Moncayo-Lasso et al. evaluated the NOM degradation via photo-Fenton reaction in river waters at pH 5.0 and using a compound parabolic concentrator (CPC) solar reactor. The presence of natural metallic species in water bodies may be favorable for NOM degradation under solar light [27].

Moreover, the photosensitization of humic substances, which is the major fraction of NOM, generate oxidative conditions via a chain of reactions presented below that positively influence the photo-Fenton process specially by the generation of $HO_2^\bullet/O_2^{\bullet-}$ that subsequently lead, by dismutation, to additional production of H_2O_2 and $^\bullet OH$: production of $HO_2^\bullet/O_2^{\bullet-}$ (Eq. (4)) via O_2 reduction by photo-excited humic substances:

$$\mathrm{NOM} + O_2 + h\nu \rightarrow \mathrm{NOM_{ox}} + HO_2^\bullet/O_2^{\bullet-} \tag{4}$$

The NOM may also be considered as the main precursor of excited triplet states, which leads to the formation of singlet oxygen [38–40].

An additional source of $HO_2^\bullet/O_2^{\bullet-}$ is the possible reduction of O_2 by the primary photo-oxidation product of ligand-to-metal charge-transfer reactions of Fe(III)–humate complexes formed with naturally occurring Fe(III) ions. The photoactive character of Fe–humate complexes can undergo photo-assisted self-degradation [9,41,42].

The end product of $HO_2^\bullet/O_2^{\bullet-}$ dismutation [9] is hydrogen peroxide (Eq. (5)), which is catalyzed in the presence of dissolved Fe (Eqs. (6) and (7)).

$$HO_2^\bullet/O_2^{\bullet-} \rightarrow H_2O_2 + O_2 \tag{5}$$

$$HO_2^\bullet/O_2^{\bullet-} + \mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)} + H_2O_2 \tag{6}$$

$$HO_2^\bullet/O_2^{\bullet-} + \mathrm{Fe(III)} \rightarrow \mathrm{Fe(II)} + O_2 \tag{7}$$

The hydrogen peroxide formed from $HO_2^\bullet/O_2^{\bullet-}$ is another potentially significant oxidant of Fe(II) leading to the additional generation of $^\bullet OH$, which subsequently oxidize the NOM regenerating $HO_2/O_2^{\bullet-}$ (Eq. (8)) [38–40]:

$$\mathrm{NOM} + {}^\bullet OH \rightarrow \mathrm{NOM_{ox}} + HO_2/O_2^{\bullet-} \tag{8}$$

Murray and Parsons showed that the treatment of commercial humic acid and NOM rich waters with Fenton and photo-Fenton processes at pH 4.0 led to rather than underwent to both DOC and 254 nm absorption values lower than with coagulation [3]. Ribordy et al. have demonstrated that photo-Fenton treatment of organic matter in presence of Cl^- salts does not generate chlorinated organic compounds [29]. Mosteo et al. evaluated the impact on THMs production in water previously treated with different types of AOPs excepted photo-Fenton [43].

In the present paper is reported for the first time the significant decrease of formed THMs during river water chlorination via a previous NOM degradation by means of solar photo-Fenton reagent ($Fe^{2+/3+}$, H_2O_2 and light) at natural neutral pH.

Table 1
Physical–chemical characteristics of the Pance River water after SSF treatment. The values correspond to the average of five samples taken between May and August of 2008 at the water harnessing station of "El Retiro" near from Cali-Colombia.

Parameter	Value
Turbidity (NTU)	0.37
Fe (mg/L)	0.21
pH	6.5
Color (PCU)	13.88
Absorbance 254 nm (cm^{-1})	0.045
TOC (mg/L)	7.1
$SUVA_{254}$ (L/(m mg))	0.64

2. Experimental details

2.1. Reagents

Hydrogen peroxide at 35% (Riedel-de Haën) and $FeCl_3 \cdot 7H_2O$ at 98% (Merck) were used as furnished. Commercial sodium hypochlorite solution (6.0% of Cl_2) was used as chlorination reagent. Surface water was obtained from a natural source (Pance River in Cali-Colombia). This river is a water supply for some communities (i.e., "El Retiro"), which use a slow sand filtration (SSF) as pre-treatment system. Sampling was carried out after SSF. The water samples collected were stored at 4 °C to preserve physical–chemical characteristics given in Table 1. Humic acid (Aldrich) solutions were prepared with Milli-Q water (18.2 MΩ cm).

2.2. Analytical methods

The TOC was measured by using a Shimadzu 5050 TOC analyzer calibrated with standard solutions of hydrogen potassium phtalate. Ultra-violet (UV) absorbance of water samples at 254 nm (UV_{254}) was measured by using a Shimadzu UV 160A spectrophotometer. Concentration of H_2O_2 was monitored via Merkoquant (Merk) peroxide analytical test strips (Test Peroxides, Merck Merckoquant). After 4 h of treatment, less than the method detection limit (0.5 mg/L of H_2O_2) was attained. All experiments were carried out within a pH range of 5.0–7.0, which was measured with a pH-meter Metrohm 827 pH-lab using a glass electrode.

Color and turbidity measurements were carried out by following the standard methods methodology [44].

The THMs formation potential (THMFP) was measured by following a modified version of *Standard Methods* Number 5710B [45]. This modification allows using low amounts of sample and assures residual chlorine between 0.3 and 1.0 mg/L. Photo-catalytic treated sample (5.0 mL) was combined in a 250 mL brown glass bottle with 5.0 mL of phosphate buffer (pH 7.0) and 1.0 mL of commercial sodium hypochlorite solution (6.0% of Cl_2), and diluted to the top with Milli-Q water without headspace. The samples were sealed with a Teflon-lined screw cap, shaken well and stored in the dark for 7 days at 25 °C. Headspace or air bubbles at the top of the vials or glass containers were avoided to reduce loss of volatile

THMs. Subsequently, THMs formed were measured by using gas chromatography with head-space method. 15.0 mL of chlorinated sample and 10 μL of internal standard (1-bromo-3-chloropropane, 100 μg/L) were added to amber glass vial of 20 mL, which contained 4.0 g of NaCl at 98% (Riedel-de-Haën) [46]. The vials were sealed with a cap (with septa) and placed into thermostat at 45 °C for 40 min to reach the equilibrium between vapor and liquid phase. Then, vapor phase (500 μL) was directly injected on the gas chromatograph with a syringe for gases (Hamilton).

THMs standard mixture (Supelco kit, 200 μg/L) was used during analysis to develop a calibration plot. The standards were prepared at concentration range of 1–200 μg/L in methanol. The formed THMs were measured by using a Perkin Elmer (PE) gas chromatograph equipped with an electron capture detector. A wide-bore capillary column (DBP-5MS: [(5%-phenyl)-methylpolysiloxane], mildly polar) was used for analysis (30 m length, i.d. 0.53 mm, and 2.65 μm thickness). An argon-methane mixture was used as carrier gas (1.8 mL/min). The injector and detector temperature were maintained at 200 and 300 °C, respectively. The oven temperature was maintained at 39 °C for 15 min. Data were analyzed based on duplicate or triplicate injections of standards and samples. The specific THMs formation, normalized to TOC, was determined by calculating the formed THM/TOC ratio.

2.3. Photo-Fenton procedures

The photo-catalytic experiments were carried out by adding Fe^{3+} (~1.0 mg/L) and H_2O_2 (60 mg/L) within a range pH 5.0–7.0 and under simulated sunlight from Hanau Suntest (AM1) lamp. An 80-mL Pyrex glass bottle (3.5-cm diameter and 10-cm high) was used as batch reactor. Solar irradiation was simulated by a Hanau Suntest (AM1) lamp with a wavelength spectral distribution with about 0.5% of emitted photons with wavelengths < 300 nm (UV-C range) and about 7% between 300 and 400 nm (UV-B, A range). The emission spectrum between 400 and 800 nm follows the solar spectrum [47]. Total intensity of Hanau Suntest solar simulator is 600 W/m^2, and UV intensity 20–30 W/m^2. The irradiation experiments were performed at room temperature (25 °C) and the temperature of the solution increased up to 30 °C during irradiation. All experiments are carried out in equilibrium with air at 700 rpm of agitation. Suitable control experiments (dark controls and systems light/H_2O_2, solely light) were performed under similar conditions (data not shown) in order to guaranty that the process photo-Fenton is really the principal process that acting in the NOM degradation. The samples were taken from the reactor at various intervals and used for pH, H_2O_2, TOC, and THMFP measurements. When the samples were not measured immediately after taking the sample out of the reactor, the reaction was stopped with sodium bisulphite.

3. Results and discussion

3.1. Degradation of humic acid (HA) in water via photo-Fenton reaction at pH 5.0 and 7.0

Absorption at 254 nm has been proposed in literature as parameter to follow the HA degradation, since indicates the presence of aromatic forms, contained in arenes, phenols, benzoic acids, aniline derivates, polyenes and polycyclic aromatic hydrocarbons with one, two or more rings; which are predominant in the complex structure of organic matter [48]. Therefore, the structural changes occurring during photo-catalytic treatments can be estimated for complementing the information of mineralization obtained by TOC results.

Fig. 1 shows that HA (50 mg HA/L) degradation carried out at pH 5.0 was more efficient than those carried out without pH modification. UV_{254} and TOC decrease were of 90% and 15%, respectively, after 3 h of treatment. Higher percentage decrease in the absorption at 254 nm than mineralization evidences structural transformation of HA molecules during the photo-catalytic treatment, although total mineralization is not reached [49]. This tendency was maintained when the pH 7 was used in the photo-treatment, reaching 7.0% and 42% of TOC and UV_{254} absorption decay, respectively. Lower HA concentrations (10 and 20 mg/L) were also evaluated (Fig. 2) using pH 7.0. Similar tendencies: higher decrease of UV_{254} than TOC decrease was observed.

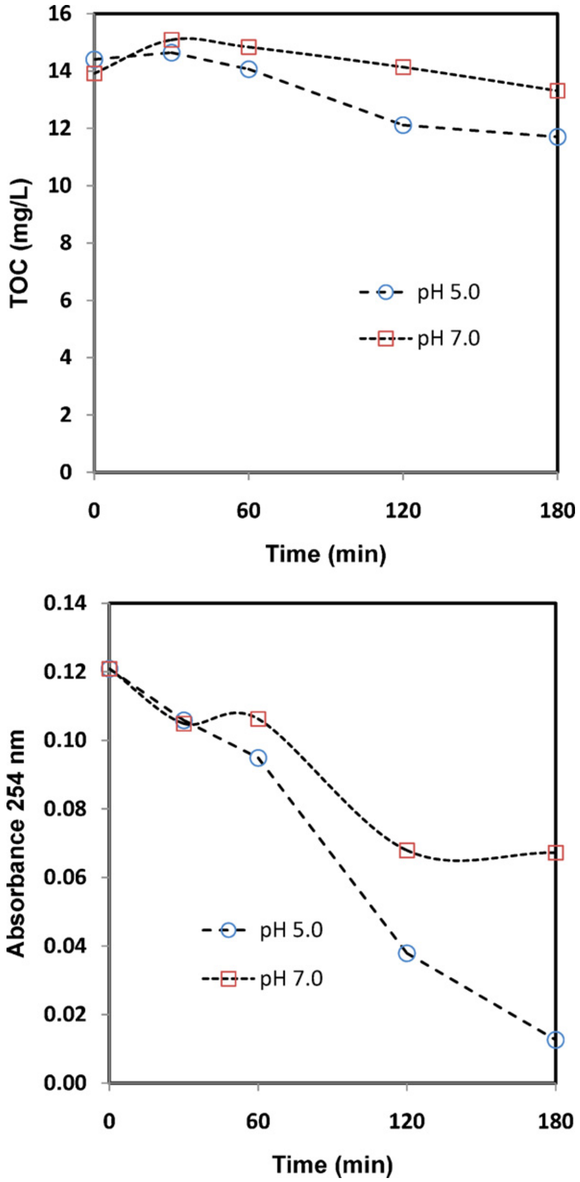

Fig. 1. Evolution of (a) TOC and (b) absorbance at 254 nm, during photo-catalytictreatment at pH 5.0 (-○-) and pH 7.0 (-□-). Time under radiation: 3 h; initial concentration of HA: 50 mg/L; [H_2O_2]: 60 mg/L; [Fe^{3+}]: 1.0 mg/L. Each point corresponds to average of three measurements of the same sample and the standard deviation was lower than 1%.

HA keep Fe ions in solution allowing the action of homogeneous photo-Fenton reactant that generates the powerful oxidant $^\bullet$OH. In addition, the whole oxidative chain initiated by photo-excited HA and presented at the end of the introduction increases ROS, and specially $^\bullet$OH generation which subsequently yield a wide variety of oxidized by-products (Eq. (9)):

$$HA + {}^\bullet OH \rightarrow \text{oxidationby-products} \quad (9)$$

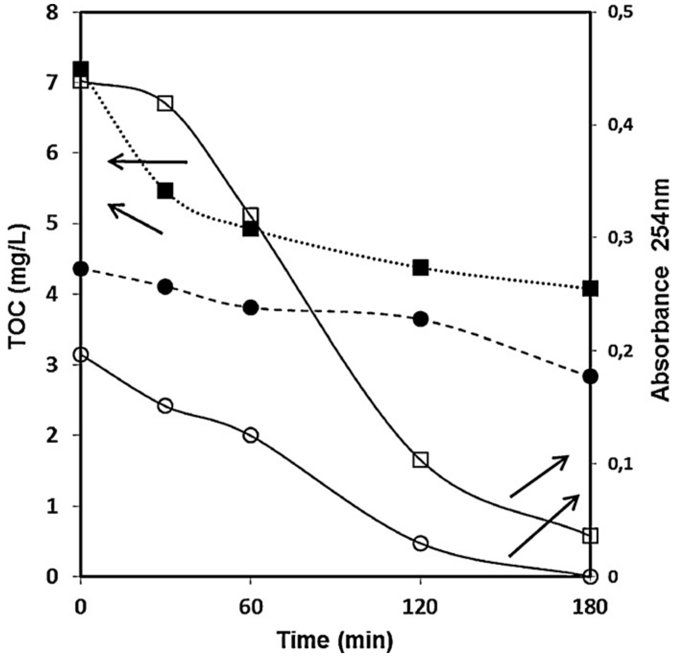

Fig. 2. Evolution of TOC and absorbance at 254 nm, during HA solution (20 mg/L, trace -□- and 10 mg/L, trace -○-) degradation via photo-Fenton reaction at pH 7.0. Time under irradiation: 3 h; [H_2O_2]: 60 mg/L; [Fe^{3+}]: 1.0 mg/L. Each point corresponds to average of three measurements of the same sample and the standard deviation was lower than 1%.

This reaction (Eq. (9)) involves mainly the $^{\bullet}OH$ addition to and the hydrogen abstraction from aromatic sites of HA structure. The addition of $^{\bullet}OH$ radicals on the aromatics rings generates radical type hydroxi-cycle-hexadienil ($HCHD^{\bullet}$) whose the subsequent oxidation result in the aromatic ring break-up and leads to open chain products [9]. It has been reported that smaller molecular size is obtained from HA by photo-Fenton reaction, as consequence of mineralization and open chain by-products formation [50]. However, the complete mechanism of humic acid degradation is not yet elucidated as HA structure is not well defined.

3.2. Decay of THMs generated during chlorination of a HA solution after photo-Fenton treatment

As photo-Fenton reaction produced a partial TOC reduction of and a clear NOM transformation of humic substances, the total THMs concentration generated by chlorination has been monitored as a function of both initial HA concentration and the photo-Fenton treatment time.

Fig. 3 shows that, after 3 h of HA solution illumination, the THMs concentrations formed by the subsequent chlorination decreased from 96 to 33 μg/L and from 51 to 26 μg/L when HA initial concentration were 20 and 10 mg/L, respectively, at initial pH 5.0. Concentrations of 10 and 20 mg of HA per liter were used since the TOC values for those solutions are approximately 3 and 7 mg C/L, respectively. These TOC concentrations are close to real total organic carbon founded in the river water used in this work (see Fig. 5, the initial TOC concentration was ~7.0 mg/L).

Fig. 4 shows that the photo Fenton-treatment at pH 5.0 decreased more than at pH 7.0 the THMs generated during chlorination step. THMs formation diminishes when humic substances concentration decreases even if complete mineralization was not reached after 3 h of light exposure. THMs concentration decreased from ~100 to ~50 μg/L at pH 7.0 and from ~95 to ~30 μg/L at pH 5.0. These values are below guideline value of THMs concentration in drinking water (80 μg/L) [2]. As conditions used in our photo-catalytic treatment (low Fe^{3+} and H_2O_2 concentrations and natural pH) are compatible with natural environment of surface waters, a real low cost application could be developed for reaching acceptable THMs values.

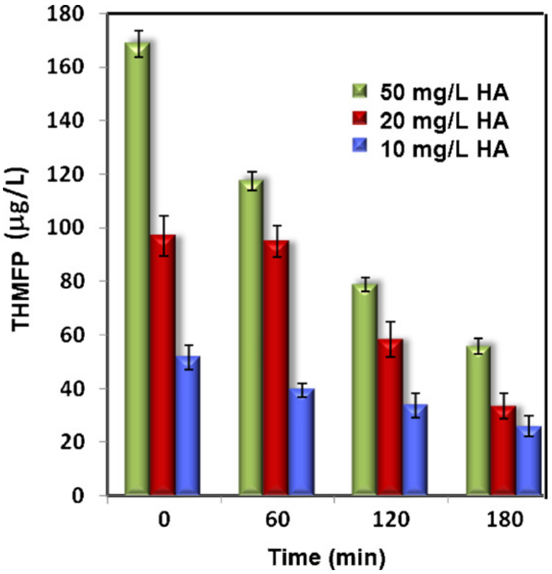

Fig. 3. Reduction in the formation of THMs with different HA initial concentration. Irradiation period: 3 h; pH 5.0; initial [H_2O_2]: 60 mg/L; initial [Fe^{3+}]: 1.0 mg/L. The error bars indicate the standard deviation (S.D.) found during the determination of these samples.

3.3. NOM removal from river water via photo-Fenton reaction at natural neutral pH. Relationship between NOM remaining in solution and THMs generated during subsequent chlorination step

The NOM photo-Fenton degradation in river water sampled after a sand filtration system is showed in Fig. 5. The samples were photo-treated without pH modification (pH = 6.5) and with initial concentrations of Fe^{3+} and H_2O_2 of 1.0 and 60 mg/L, respectively. After 3 h of treatment, the 254 nm UV-absorbance and TOC

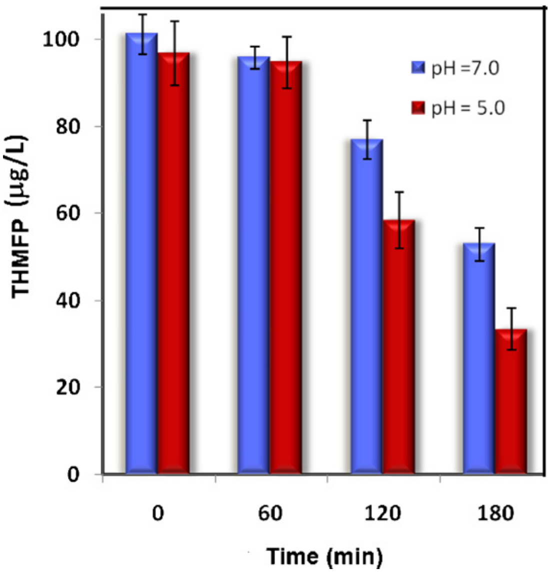

Fig. 4. Diminish of THMs formation through photo-degradation of HA aqueous solution (20 mg/L) at pH 5.0 and 7.0 via photo-Fenton reaction. Irradiation time: 3 h; initial [H_2O_2]: 60 mg/L; initial [Fe^{3+}]: 1.0 mg/L. The error bars indicate the standard deviation (S.D.) found during the determination of these samples.

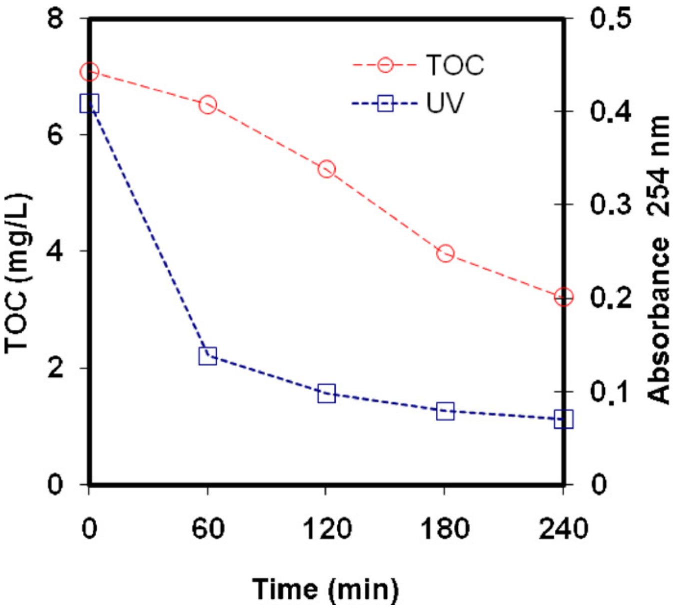

Fig. 5. TOC and absorbance at 254 nm evolution during NOM degradation via photo-Fenton reaction. Time of treatment: 4 h, pH 7.0; $[H_2O_2]$ initial: 60 mg/L; [Fe^{3+}] initial: 1.0 mg/L. Each point corresponds to average of three measurements of the same sample and the standard deviation was lower than 1%.

decreased 83 and 55%, respectively. These results have similar tendency that those obtained when HA solution were used as model compounds of NOM (Section 3.2), and the amount of THMs formed during the further chlorination are reduced as shown in Fig. 6. Indeed, water samples irradiated during 4 h reach 15.0 μg/L of THMs, when chlorine was added. In contrast water samples without previous photo-catalytic treatment reached values upper than 100 μg/L. These results demonstrated that photo-Fenton reaction, under the proposed conditions, is suitable to transform and partially remove NOM from surface waters. After only 1 h of a solar photo Fenton treatment, THMs formed during chlorination are lower than 80 μg/L, which is below guideline values (USEPA regulation [2]).

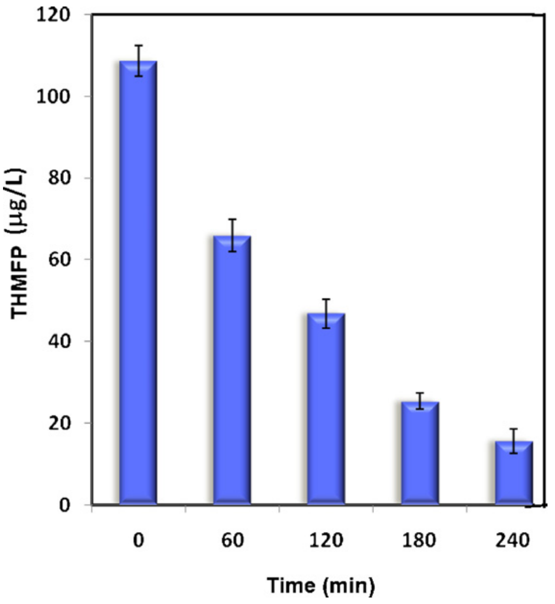

Fig. 6. Decrease of THMs formation during photocatalytic treatment of NOM present in river waters. Photo-treatment time: 4 h, pH 7.0; initial $[H_2O_2]$: 60 mg/L; initial [Fe^{3+}]: 1.0 mg/L. The error bars indicate the standard deviation (S.D.) found during the determination of these samples.

Table 2
Relationship between THMs concentration and NOM concentration (TOC) in samples taken from Pance River.

Time (min)	THMs (mg/L)	TOC (mg/L)	mg THMs/mg TOC
0	108.6	7.1	15.3
30	65.9	6.5	10.1
60	46.8	5.4	8.7
120	25.4	4.0	6.4
180	15.6	3.2	4.9

Other works have demonstrated good correlations between potential formation of THMs and 254 nm UV absorbance [51] as well as with TOC concentration [52] and the specific UV absorbance (SUVA, UV$_{254}$ absorbance divided by the TOC concentration) using raw and treated waters [53].

The SUVA$_{254}$ has been correlated with THM formation since activated aromatic structures (aromatic sites substituted with oxygen- and nitrogen-containing functional groups, i.e., phenolics and aromatic amines) constitute the primary sites attacked by chlorine or other oxidants [54]. However, the SUVA$_{254}$ value of the studied river water was only of $\sim$0.6 L/(m mg) indicating that NOM is dominantly of low molecular weight and low aromaticity. Therefore, NOM photo-Fenton degradation in water leaded during chlorination to low THM formation because, in addition to hydrophobic compounds removal (which is normally the major fraction of NOM [4,54]), photo-Fenton process is able to remove low molecular weight compounds between 0.5 and 4 kDa, which are difficult to remove during conventional treatment processes [5]. In addition, the decrease during the treatment of the THMs/TOC ratio presented in Table 2 indicates that through photo-Fenton process, mainly the NOM fraction responsible for THMs generation was degraded.

The TOC removal is not complete due to the presence from the beginning, or the generation during the process, of by-products recalcitrant to photo-Fenton treatment. Buchanan et al. demonstrated that a part of the hydrophilic NOM fraction, present in the raw water is refractory to mineralization. This fraction include short-chain aliphatic amines, alcohols, aldehydes, esters, ketones; $\langle C_5$ aliphatic amides; poly-functional alcohols, carbohydrates; cyclic amides and polysaccharides [55].

4. Conclusions

Photo-Fenton process, using low Fe^{3+} concentration and near neutral pH (6.5) under simulated sunlight, demonstrated to be an effective system for the transformation and partial mineralization of NOM from natural surface waters previously treated with a sand filter system. The NOM transformation yields a considerable decay of total THM concentrations formed during the subsequent water chlorination process reaching values below guidelines. As previous works have also demonstrated the efficiency of the same process for bacteria inactivation, solar photo-Fenton process has a high application potential to obtain at low cost drinking water safe from the microbiological and chemical point of view. An interesting treatment sequence could be (1) filtration of raw water by coarse materials and sand filters, (2) photo-Fenton treatment to transform NOM and bacterial abatement, and (3) “soft” chlorination stage for keeping a residual disinfecting action, with low or no THMs generation, since NOM has been previously reduced.

Acknowledgements

The authors wish to thank “the Administrative Department of Science, Technology and Innovation (COLCIENCIAS)-Colombia” for their financial supports in Grant No. 1106-405-20154 and for the scholarship granted to Alejandro Moncayo-Lasso. We thank to Sary Perea-Castro for their technical and scientific help.

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