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Photochemical treatment for water potabilization. Influence of wavelength and hydrogen peroxide concentration on the reduction of trihalomethanes

Sergio Navalon[a], Mercedes Alvaro[a], Hermenegildo Garcia[a]*, Lorenzo Monforte[b]

[a]*Department of Chemistry, Universidad Politecnica de Valencia , Camino de Vera S/N, Valencia, Spain*
Tel.:+34 96 387 7807; Fax: +34 96 387 78 09; email: hgarcia@qim.upv.es; malvaro@qim.upv.es
[b]*Aguas de Valencia S.A., C/ Dels Pedrapiquers (Polígono Vara de Quart), Valencia, Spain*
email: lmonforte@aguasdevalencia; sernaol@doctor.upv.es

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ABSTRACT

Pre-chlorination, a common practice consisting of addition of a large chlorine dosage at the entrance of the water treatment plant, is responsible for the formation of a large percentage of the final trihalomethane (THM) content. In order to reduce the THM formation potential of potable waters, it is of interest to develop alternative potabilization treatments that could replace pre-chlorination. In this work we report the results obtained for the natural waters of Turias's River (Valencia, eastern Spain) with a photochemical treatment using a 500 L continuous flow photoreactor adapted in a pilot plant. Under optimized conditions (100 L/h, twelve 36 W lamps 185 nm, 44 ppm of hydrogen peroxide), reduction efficiencies of 41% THM formation potential and 49% of total organic carbon were accomplished. These remarkable results contrast with those obtained under analogous conditions using the same plant but with 254 nm lamps. In the latter case, although the reductions in total organic carbon were also substantial (40%), the relative decrease in THM formation potential of the treated and untreated water was significantly lower (11%). A reasonable explanation based on the depth of light penetration is given to rationalize the lower THM potential reduction of the 254 nm lamps compared to 185 nm lamps.

Keywords: Advanced oxidation process; Photochemical treatment; Potabilization treatment; Trihalomethane reduction

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1. Introduction

The European Commission issued a new regulation for drinking water quality for Europe in 1998 [1]. In this European directive a transitory period was established to allow a gradual change of national laws to the new regulatory framework. As a consequence of this new regulation, many drinking water supply companies must adapt their current technologies to meet the new quality water parameters that were to be fully implemented in 2008.

In particular, one of the parameters that will be controlled and forced to be limited is trihalomethane (THM) content [1–4]. THMs are suspected to be carcinogenic [5–7] compounds by the EPA, and when present in the daily diet, they can at long term be negative for many human organs, particularly for the liver.

One widely used potabilization process consists of effecting an initial massive pre-chlorination treatment to raw water to reach a certain level of chlorine at the entrance of the factory, followed by final chlorination before submitting to the distribution network to fulfil the legal requirement in residual free chlorine content in drinking water. Pre-chlorination ensures that no micro-

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*Corresponding author.

organisms and algae proliferate in the plant during the potabilization process. This extensive use of chlorine, combined with high organic material content in the raw water and long pipeline residence time, increases the THM content. The common pre-chlorination practice is responsible for a large percentage of the total THM content that can, in some cases, overcome the maximum legal 100 ppb limit. As a result of the establishment of a limit for THM, water treatment plants employing pre-chlorination need to find alternative treatments able efficiently to replace the initial use of chlorine.

One of the most general potabilization treatments alternative to the chlorination consists of photochemical UV irradiation of raw waters in the presence or absence of hydrogen peroxide [8–17]. Obviously, photochemical irradiation in the absence of oxidizing chemicals has considerably lower efficiency compared to the combination of light and oxidant that has been established to be among the most powerful advanced oxidation processes. In the present work we report the results obtained with a photochemical treatment for THM reduction working in a continuous flow photoreactor with the natural water of the Turia River. This river is used as the resource that supplies the drinking water of the Valencia metropolitan area (eastern Spain; 1,500,000 inhabitants).

2. Experimental methods

2.1. Chemicals

All chemicals reagents used were of analytical grade and are commercially available.

2.2. Analytical methods

Analysis of the parameters of the water was carried out as follows. pH was measured with a pH-Metro Crison GLP 21 (APHA 4500-A method). The conductivity was measured with a GLP 32 conductimeter (ISO 7888:1985 method). Turbidity was measured using the nephelometric method with a Hach 2100N turbidimeter (ISO 7027:1990 method). The water samples were shaken vigorously and then left stand for 3 min before measurement. Nitrates were analysed directly at 220 nm in UV in water samples previously filtered (APHA 4500-NO_3^-). This method requires that the ratio of absorbance measured at 275 nm (specific for the dissolved organic matter) and 220 nm should be lower than 0.05. In our case, A_{275}/A_{220} was 0.0063. Nitrites were measured by a colorimetric method (ISO 6777:1984) by adding 5 drops of N-(1-naphthyl)ethylendiamine-dihydrochloride (1 $g.L^{-1}$) to water samples (10 mL), previously filtered, and monitoring after 15 min at 543 nm. Ammonium was determined (APHA Method 4500-NH_3) by adding 5 drops of Seignette salt (30%), to 10 mL of sample and then 3 drops of Nessler reactive, and 3 drops of NaOH (9 N) before monitoring at 410 nm after 15 min. The H_2O_2 content was measured using a colorimetric method, adding 1 mL of titanium oxalate stock solution (25 g of this salt in 250 ml H_2SO_4 and 10 ml of HNO_3 diluted up to 1 L using milliQ water) to 20 mL of sample from the photoreactor containing a residual amount of H_2O_2. After 10 min, absorptivity of the sample at 420 nm was measured in a cuvette of 5 cm. Total organic carbon (TOC) analyses were conducted with a High-TOC Elementar (5310 B, APHA method). Typically, the dissolved organic carbon (after filtering the water through a 0.45 μm membrane) was about 0.95 the TOC values, indicating that most of the organic matter was really dissolved and not in suspension. Trihalomethane formation potential (THMFP) was measured by an automatic Head Space injector connected to a Fisons GC 8130 chromatograph equipped with an electron capture detector (ECD) (UNE-EN ISO 10301 method). Chromatography was performed using helium as carrier gas (85 kPa) in a DB.624 capillary column, injecting 0.4 mL of the head gas. The injection temperature and detector temperature were 220 and 330°C, respectively. The temperature program started at 50°C for 1 min, then increases at a rate of 3°C/min up to 180°C and subsequently at a rate of 10°C/min up to 210°C.

For determination of the THFMP values the samples were chlorinated with a stock solution of NaClO (1000 ppm) to achieve 10 ppm residual, sealed and stored in the dark at 20°C for 72 h. The stock NaClO solution was prepared by diluting commercial NaClO (10–13%). Free chlorine were determined by the N,N′-diethyl-1,4-phenylenediamine (DPD) method (ISO 7393-2:1985). Since chlorine reacts with H_2O_2, the amount needed to obtain the required residual chlorine concentration depended on the H_2O_2 content of the water.

2.3. Procedures

2.3.1. Operation

The water from Turia River was pumped to the pilot plant at a controlled flow ranging between 50 and 400 L/h. Once the water was circulating through the photoreactor, hydrogen peroxide was injected into the flow by means of a dose meter. H_2O_2 concentration at the photoreactor outlet was measured and the dose adjusted to obtain the desired concentration. After a few minutes of operation, the lamps were switched on. The effect of the photochemical reaction was determined analyzing periodically samples after passing through the photoreactor.

2.3.2. Photochemical pilot plant

The photoreactor was a poly(methyl methacrylate) tank of 100 L capacity that is connected to an electric

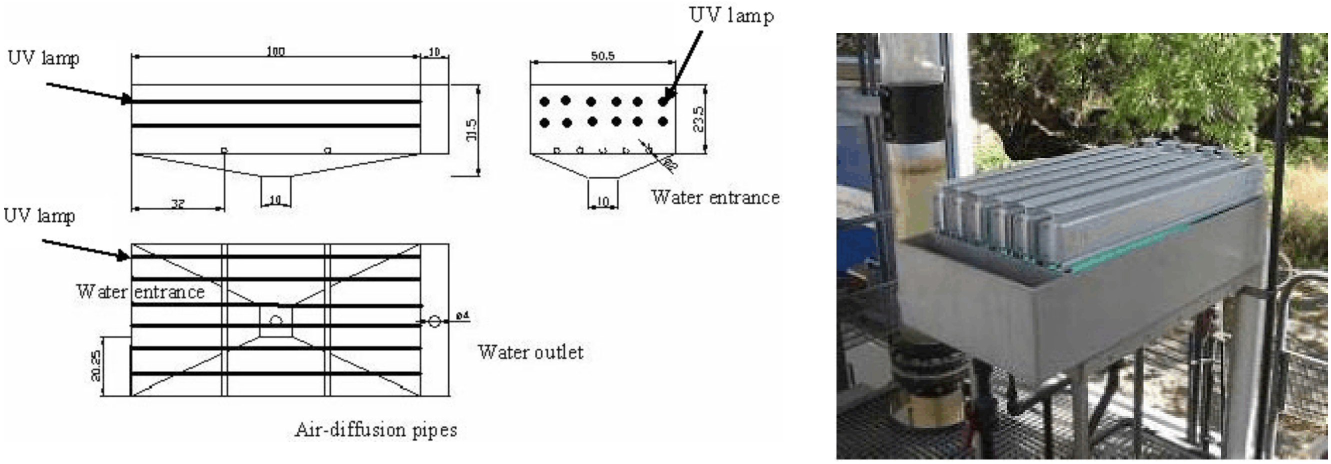

Fig. 1. Schematics (left, dimensions in cm) and photograph (right) of the photochemical plant for water potabilization.

pump through a flow controller that allows regulating the water flow from 50 to 500 L/h. The corresponding residence time inside the photoreactor ranges between 120 to 12 min. A scheme of the complete photochemical unit is provided in Fig. 1. The bottom of the photoreactor contains air-diffusion pipes through which an intense air stream causing turbulence is passed. This air comes from an air pump at a 5 L/min flow. This turbulence ensures a good mixing of reagents in the tank, providing at the same time sufficient oxygen to produce a high oxidation degree. The bottom of the tank has a slope with a valve to evacuate sludge if necessary.

Immersed in the tank, there is a series of six tubular lamp ballasts (Trojan UVM 2-36 PTP) of two lamps each with 36 W nominal power. Two types of lamps from Trojan Technologies (models G36T6L/2 for 254 nm, and UV 3614VH for 185 nm) were used independently. Thus, some experiments were carried out with 12 lamps of 185 nm and others with 12 lamps of 254 nm. These low-pressure mercury lamps are fairly monochromatic. It has to be noted that although the nominal power of the 254 and 185 nm lamps was identical (36 W), the light intensity was different due to the inherent different electrical power to light conversion efficiency of the lamps. Thus, the standard flux was 19 mW/cm^2 and 4 mW/cm^2 for the 254 nm and the 185 nm lamps, respectively. Additional data can be obtained from the manufacturer (http://www.trojanuv.com). The lamps are hermetically sealed from the water by quartz sleeves that ensure safety and provide protection from electrical hazards.

3. Results and discussion

In the present study, we have been using the water from the Turia River whose main analytical data and physicochemical parameters are given in Table 1. This water is characterized by a relatively high hardness with low organic content that is mainly of natural origin constituted by humic and fulvic acids coming from soil infiltration into the river bed.

Table 1
Analytical and physicochemical data of Turia River water[a]

Physicochemical parameters	Value	Undesirable compounds	Value
Color, mg Pt-Co/l	<5	NO_3^-, mg/L	22
Turbidity, UNF	5	NO_2^-, mg/L	<0.02
pH	8.2	NH_4, mg/L	0.1
Conductivity 20°C, μS/cm	1093	N. Kjeldahl, mg/L	<1
Cl^-, mg/L	117	Oxidab. $KMnO_4O_2$ mg/L	3.5
Br^-, μg/L	280	Surfactants (LS), μg/L	<100
SO_4^{-2}, mg/L	286	Total Fe, μg/L	12
SiO_2, mg/L	6.4	Total Mn, μg/L	<30
Ca^{+2}, mg/L	145	Total Cu, μg/L	10
Mg^{+2}, mg/L	37	Total Zn, μg/L	20
Na^+, mg/L	72	Phosphorus, P_2O_5, μg/L	65
K^+, mg/L	3	F^-, μg/L	280
Tot. hardness, $CaCO_3$ mg/L	51.6	Ag^+, μg/L	<1
HCO_3, mg/L	251	Toxic components	
Total Al, mg/L	< 0.01	Pesticides, μg/L	<0.5
Dry residue at 180°C, mg/L	812	THM, μg/L	<5
		PAH, μg/L	<0.2

[a] Source: Aguas de Valencia, S.A.

This water has typically a very low turbidity at the entrance of the factory except in raining periods or sporadic ammonia episodes, caused by unauthorized human sewage into the river. Maximum transparency is a prerequisite for photochemical treatments. It has to be noted that due to the natural origin of the water under study, changes in the quality parameters from one experiment to the other were unavoidable, but the fluctuations in the TOC value were within 1.5–2.2 ppm and those of THMFP were in the range of 80–180 ppb. These natural fluctuations take place gradually over extended periods of time (days and weeks). Moreover, in our study, these two parameters of raw water were constant during the time of the experiment (5 h). Given that the river bed and the corresponding aquatic resources are constantly under surveillance and protection, no significant changes in the nature of the organic matter present in the water is expected during the study.

Using quasi-monochromatic low-pressure mercury lamps, one of the initial parameters studied was the influence of the excitation wavelength on the improvement of the water quality parameters. In addition to the reduction in the THMFP before and after photochemical treatment, we also determined the decrease of the TOC and the residual amount of hydrogen peroxide remaining at the exit of the photoreactor. For each of the two photoexcitation wavelengths we varied the flow rate between 50–400 L/h and the initial concentration of hydrogen peroxide. We notice that since chlorine oxidizes hydrogen peroxide and the potable water pumped into the distribution pipeline network has to contain about 1 ppm of residual chlorine, whatever its concentration at the outlet of the photochemical reactor, no hydrogen peroxide is going to be present in the potable water.

Starting from an empty photoreactor and depending on the flow rate, the efficiency of the photocatalytic treatment on the water quality parameters was gradually changing until a plateau is reached indicating that the continuous flow photoreactor has arrived to the stationary regime. These variations are mainly due to the warm up of the lamps and to the establishment of a gradient of oxidizing reagent through the tank. It is obvious that to compare validly the efficiency under different conditions, data for the plateau regime have to be compared. This plateau regime is achieved after the plant operates a time sufficiently long that a constant concentration of hydrogen peroxide at the outlet of the photoreactor is achieved (typically 2–3 h). This stationary hydrogen peroxide concentration corresponds to the numbers given in Table 2. To illustrate this point, Figs. 2 and 3 show the temporal profile of the hydrogen peroxide concentration, THMFP and TOC reduction for two of the most successful experiments conducted in our photochemical pilot plant. A complete set of data showing the results of the photochemical treatment for water potabilization in the stationary regime is listed in Table 2. The values shown in Table 2 were selected into a more comprehensive set of data performed under batchwise operation and under other less efficient conditions or when occasional fluctuations at the entrance of the plant were detected. The values of Table 2 correspond to average of at least two independent experiments. When considering this table it has to be noted that an increase in the flow rate produces a proportional shortening of the residence time in the photoreactor. To compensate this residence time, an increase on the H_2O_2 dosage is necessary since otherwise no variation in the TOC or THMP were observed (data not shown in Table 2). Considering that the light flux from the lamps is constant upon increase of the flow rate, this increase in the H_2O_2 dosage may lead to an undesirable

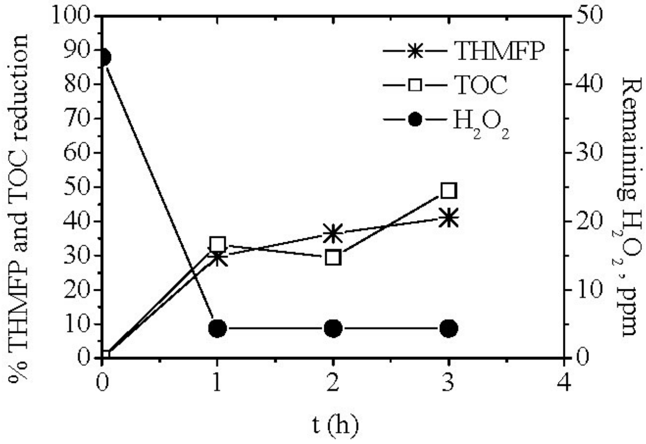

Fig. 2. THMFP and TOC reduction (left ordinate) and H_2O_2 remaining after treatment measured at the photoreactor outlet (right ordinate) as a function of time. Operating conditions: 100 L/h flow, 44 ppm of H_2O_2 and using 185 nm mercury lamps. Initial THMFP and TOC values of the raw water were 180 ppb and 1.12 ppm, respectively.

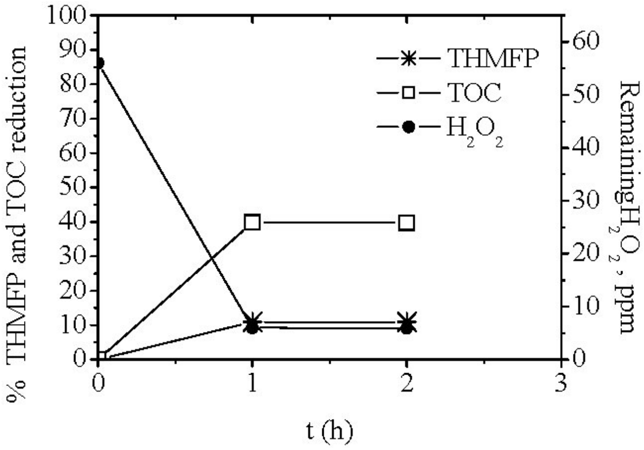

Fig. 3. THMFP and TOC reduction (left ordinate) and H_2O_2 remaining after treatment measured at the photoreactor outlet (right ordinate) as a function of time. Operating conditions of the plant: 100 L/h flow at 254 nm and 56 ppm of H_2O_2. Initial THMFP and TOC values of the raw water were 80 ppb and 1.26 ppm, respectively.

Table 2
Results of photochemical treatment in the pilot plant

Irradiation wavelength, nm	Flow, L/h	Initial [H_2O_2], ppm	Final [H_2O_2], ppm	Initial THMFP, ppb	THMFP reduction, %	Initial TOC, ppm	TOC reduction, %
185	100	19	3	156	8.5	2	18
	100	44	4.5	192	41	1.2	49
	200	38	7	82	11	1.7	27
	300	50	13	104.9	10	1.7	17
	300	77	21	72.7	28.8	1.9	17.5
	400	17	4.5	88.9	2.1	2.1	12.3
254	100	34	5	34.4	0	1.3	27
	100	56	10	66	11	1.2	40
	150	231	61	83.9	29.8	1.5	25.5
	200	231	89	83.9	29.8	1.5	10.6
	200	52	10	53.4	9	1.6	16
	300	58	15	54.2	0	1.3	40

high H_2O_2 residual concentration at the exit of the photoreactor. For this reason it is necessary to reach a balance between high flow rates and reasonable H_2O_2 dosage. In addition, it is known that there is an optimum in the H_2O_2 dosage for UV/H_2O_2 treatments of pollutants and in some cases high H_2O_2 dosage may even decrease the efficiency of the advanced oxidation process [18].

As can be seen in Figs. 2 and 3 and Table 2, the photochemical treatment led in many cases to a significant reduction in the THMFP, the main water quality parameter that may force to stop pre-chlorination in industrial potabilization processes. Since the experiments are carried out with natural waters whose TOC and THMFP values fluctuate, it is the percentage of reduction of the THMFP value of the untreated and treated water measured at the same time, the parameter to be considered to rank the efficiency of the photochemical treatment. Thus, we notice that under the best conditions attained for each set of lamps the improvement of the water quality parameters, and particularly the reduction of the THMFP values, using 254 nm lamps was much less as compared to 185 nm lamps (see highlighted rows in Table 2). Thus with 254 nm lamps working at a flow rate of 100 L/h and 56 ppm H_2O_2, a 40% and 11% reduction of TOC and THMFP, respectively, was obtained. In contrast, using 185 nm lamps and operating at a flow rate of 100 L/h with 44 ppm H_2O_2, the reduction in TOC and THMFP were 49% and 41%, respectively. These values exemplify the influence of the irradiation wavelength and the better performance of the 185 nm lamps in spite of the much lower (about five-fold) intensity flux of the 185 nm lamps (see Experimental).

It is known that the wavelength strongly influences the penetration depth of photons into the static aqueous solution and the nature of the photochemical processes that can occur. Thus, using 254 nm wavelength the irradiation in static solutions can occur at much longer distances from the lamps than using 185 nm excitation light since the transparency of the water at 254 nm is very high (transmittance >95%). On the other hand, 254 nm can only excite marginally hydrogen peroxide (extinction coefficient of H_2O_2 at 254 nm is 19.6 M^{-1} cm^{-1}, quantum yield of $OH^\bullet$ generation of unity). Although the fluid regime in the photoreactor is turbulent due to the forced air stream, we also assume that the penetration depth of the photons is not much altered with respect to experiments under static conditions. Therefore, a more uniform distribution of hydroxyl radicals throughout the photoreactor can be expected. The remarkable H_2O_2 concentration reduction upon 254 nm irradiation indicates that this wavelength is also able to produce the homolytic splitting of H_2O_2 in our photoreactor. Other processes that can take place upon irradiation at 254 nm include photosensitization by natural aromatic compounds present in the raw water, the occurrence of some photo-Fenton processes due to the iron ions present in the natural water or the H_2O_2 interception by other intermediates and reactive species generated photochemically. A control in which a H_2O_2 was added to the raw water shows that no dark reaction leading to H_2O_2 depletion occurs in the absence of light.

In contrast to the use of 254 nm as excitation wavelength, the use of 185 nm light limits the volume in which the photochemical reactions occur to a very thin layer around the irradiation lamps. The penetration power of 185 nm light is estimated in less than 1 mm since water has a significant molar absorptivity at this wavelength (transmittance at 200 nm <0.5%) [19,20]. Therefore, the most reasonable hypothesis to understand the beneficial influence of 185 nm irradiation on the water quality parameters is that direct excitation of hydrogen peroxide by 185 nm photons produces the homolytic cleavage of the hydroperoxy bond leading to the generation of hydroxyl radicals [21] These hydroxyl radicals will be formed in a thin layer around the sleeve walls and would attack to the organic material dissolved in the water generating secondary much longer lived carbon centred radicals [22]. These secondary radicals will diffuse to longer distances from the photoreactor walls. These carbon-centred radicals can be at some stage intercepted by ambient oxygen dissolved in water, giving rise to peroxy radicals and initiating advanced oxidation processes [22]. The occurrence of this advanced oxidation is manifested by the fact that the photochemical treatment leads to a notable reduction on the initial concentration of H_2O_2 as well as the TOC. We notice that in addition to H_2O_2 185 nm irradiation also can effect the direct splitting photolysis of water to form hydroxyl radicals. Also 185 nm [23] in the presence of oxygen could generate ozone, a species that could lead to a reduction in THMFP. However, this possibility can be disregarded since no reduction in TOC or THMFP was observed in the absence of hydrogen peroxide and, therefore, is clear that the effects in the water parameters are caused by H_2O_2.

The beneficial influence of this photochemical process on the reduction of THMFP seems to indicate that those groups that later will be responsible for the generation of THMs are those being destroyed in the photooxygenation process mediated by the carbon centred radicals (185 nm) rather than be hydroxyl radicals (254 nm). Thus, although poorly understood with the current knowledge about THM formation, a possible explanation to justify the higher efficiency of 185 nm irradiation would be that localized generation of hydroxyl radicals in a small volume of the photoreactor is more favourable for the reduction of THMFP than a uniform generation of unselective hydroxyl radicals all over the reactor tank. Thus, for instance, it has been shown that although, in general, UV/H_2O_2 is useful to reduce THMFP, in some cases, this treatment may increase the THMFP value even with reduction of TOC. This is due to the transformation of the organic matter and the different tendency of the evolved products to form THMs upon UV/H_2O_2 treatment.

Based on the current knowledge on advanced oxidation processes [22], Scheme 1 summarizes the chemical processes that are believed to produce these variations in the TOC and THMFP values.

- Scheme 1. Pathway for degradation of organic compounds:

$H_2O_2 + h\upsilon \rightarrow 2\,OH^\bullet$

$R{-}H + {}^\bullet OH \rightarrow R^\bullet + H_2O$
(longer-lived, diffusion through the photoreactor)

$2\,OH^\bullet \rightarrow H_2O_2$

$R^\bullet + O_2 \rightarrow R\text{-}O\text{-}O^\bullet$ (long-lived radicals)

$R^\bullet + H_2O_2 \rightarrow ROH + {}^\bullet OH$

$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$

ROOH and $ROO^\bullet$ → degradation products (several steps leading to mineralization; THMFP reduction)

It is worth noting that while both 185 and 254 nm wavelengths in the presence of hydrogen peroxide produce a significant decrease of TOC, performance with respect to THMFP reduction is very different. In other words, it is not possible to correlate directly a decrease on TOC (ppms going to CO_2) or the variation in the UV at 254 nm with THMFP (ppb arising from the reaction of chlorine). For instance, using 254 nm lamps and working at a flow of 100 L/h with an initial H_2O_2 concentration of 34 ppm, the optical density of the initial water (0.13 units) is reduced upon treatment to a value of 0.06; however, the percentage of THMFP reduction is 0. In addition, possible variations in the nature of dissolved organic matter among different runs makes uncertain a more detailed rationalization of the differences in the effectiveness of the 185 and 254 nm irradiations. One of the possible reasons for the lack of correlation between reduction of THMFP and the organic content could be the low TOC levels of the raw water. The reason for this must be the complexity of chemical processes from which THMs are originated from the mixture of organic compounds present in the natural water. Thus, we can envision that while organic molecules are being destroyed (perhaps in several molecules) and the TOC decreases (due to the formation of some CO_2), the degradation intermediates, most probably having a higher content on oxygenated functionalities, can be more prone to generate higher ppbs of THMs by reaction with chlorine than the original starting organic compounds. More clearly, low concentrations of some organic compounds can give rise to higher amounts of THMs if they are more reactive with chlorine than the initial precursors towards chlorine.

Precedents reporting the lack of correlation between TOC and THMFP can be found in the literature [24,25]. It is interesting to note that the higher efficiency of 185 nm with respect to THMFP is observed in spite of the lower photonic flux of these lamps (4 mW/cm^2) with respect to the 254 nm lamp (19 mW/cm^2). In fact, 254 nm lamps have higher efficiency with respect to the electricity to light conversion, but lower efficiency with respect to THMFP reduction.

The fact that the origin of the photochemical processes is direct irradiation of hydrogen peroxide is clearly demonstrated by comparing the water quality parameters at various concentrations of hydrogen peroxide or in its absence. The results indicated in Table 2 show that irradiation using hydrogen peroxide concentrations below 20 ppm have only a very marginal influence on the THMs content. In contrast, when the irradiation is carried out using H_2O_2 concentrations between 30 and 70 ppm the photochemical treatment results in a remarkable influence on the water quality parameters. When using hydrogen peroxide, one issue of concern is the residual concentration after the treatment. Since hydrogen peroxide reacts quantitatively with chlorine, it is convenient to achieve after the photochemical treatment the lowest possible residual concentration of H_2O_2. We point out in this regard that there are efficient catalysts able to effect the decomposition of H_2O_2 into H_2O and O_2 before chlorination, avoiding the unnecessary consumption of chlorine.

On the other hand, it is obvious that the efficiency of the catalytic treatment depends on the irradiation time and, therefore, on the residence time inside the photoreactor. For a given photon flux and photoreactor volume (100 L), higher flow rates decrease the residence time reducing proportionally the total number of photons at which a certain volume of water is exposed. Accordingly, Table 2 shows that the highest flow (30 min retention time) gave lower percentage of THMFP and TOC reductions as compared to lower flows rate (60 min retention times), although the volume of water treated was obviously five-fold that working at lower flow rates. A compromise on between flow rate and percentage of THMFP reduction should also be reached to operate under optimal conditions.

The photochemical treatment is neutral for most of the other water quality parameters that we have controlled such as pH, conductivity, turbidity, and concentration of nitrates and ammonia. These invariable values are not given in Table 2 for clarity and are about the average as shown in Table 1. In particular, no detectable changes in pH and nitrate and ammonia concentrations were observed. The only water quality parameter change in addition to TOC and THMFP that deserves a special comment due to its potential negative influence on the water quality is the evolution of nitrite concentration that increases in ppb significantly upon the treatment depending on the hydrogen peroxide concentration and lamp wavelength. There are precedents in the chemical literature which have also observed nitrite formation by UV light irradiation of natural waters [26].

Given that irradiation in the presence of hydrogen peroxide leads to oxidation processes and that no variation in ammonium content is observed, the most reasonable explanation to account for the increase in the nitrite concentration is the direct photochemical partial deoxygenation of nitrate. Although nitrogen-containing organic matter could give rise under some conditions to nitrite, under strong oxidizing conditions in the presence of an excess of H_2O_2, organic matter is a less likely precursor for nitrite. On the other hand, the transformation of nitrate in nitrite is a well known photochemical process that in our case occurs mainly upon irradiation of 185 nm, but also to a lesser extent upon irradiation at 254 nm. This influence of irradiation wavelength also supports that nitrite is being generate by direct irradiation of nitrate that absorbs strongly below 230 nm. In this context it is worth noting that the raw water has a high concentration of nitrates of about 22 ppm whose origin is mainly lixiviation of fertilizers from the orchards surrounding the Turia River bed and that nitrate is determined by measuring the absorbance at 220 nm (see Experimental section for details). In the worst case, after the treatment at 200 L/h with 185 nm and 38 ppm of H_2O_2, the nitrite concentration varies from 3.7 to 55 ppb. Nevertheless, it has to be mentioned that the presence of nitrite in ppb after the photochemical treatment does not constitute a real problem since, during the final chlorination at the plant before pumping, the water into the pipeline nitrites will be fully oxidized to nitrates by chlorine.

4. Conclusions

Working on a pre-industrial pilot plant with raw natural waters, we have demonstrated that irradiation at 185 nm adding 40 ppm of hydrogen peroxide with a residence time of 1 h is able to reduce significantly the TOC value and more importantly the THMFP of the water without altering the rest of parameters, except nitrite concentration that increases in at ppb levels. This indicates that formation of hydroxyl radicals in a localized zone of the photoreactor is very effective to produce THMFP reduction. In contrast, longer wavelengths such as 254 nm that are able to produce the homolytic cleavage of hydrogen peroxide in all the reactor volume are less effective for the reduction of THMFP, although large percentages of TOC value reduction are attained.

Acknowledgments

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