



## Evaluation of trihalomethane formation potential in function of oxidation processes used during the drinking water production process

R. Mosteo\*, N. Miguel, S. Martin-Muniesa, Maria.P. Ormad, José L. Ovelleiro

University of Zaragoza, Department of Chemical Engineering and Environmental Technologies. C/María de Luna, 3, 50018. Zaragoza, Spain

### ARTICLE INFO

#### Article history:

Received 23 January 2009

Received in revised form 16 June 2009

Accepted 13 July 2009

Available online 22 July 2009

#### Keywords:

Trihalomethane

Natural organic matter

Advanced oxidation process

### ABSTRACT

The presence of natural organic matter (NOM) in both surface and groundwater supplies produces toxic by-products, mainly trihalomethanes (THMs), during oxidation steps in drinking water production. This research work shows the efficiency of different advanced oxidation processes (AOPs) based on ozone for the degradation of precursors of trihalomethanes in aqueous solutions. Completed treatments comprised different preoxidation processes (chlorination and AOP:  $O_3$ ,  $O_3/H_2O_2$ ,  $O_3/TiO_2$  and  $O_3/H_2O_2/TiO_2$ ), adsorption with PAC (optional operation), coagulation–flocculation and final postchlorination applied to synthetic samples which were prepared by dilution of the soluble fraction of a humic solution. A direct chlorination of synthetic humic samples which display dissolved organic carbon close to  $3\text{ mg l}^{-1}$  produced a THM concentration of around  $1600\ \mu\text{gCl}_3\text{ l}^{-1}$  (measured as THMFP). Comparisons between the trihalomethane formation potential of initial synthetic samples and samples treated by prechlorination and coagulation–flocculation–decantation show that the main factor responsible for THM reduction is the coagulation–flocculation process since a decrease of 90% is achieved. Considering the various completed treatments studied, the most recommendable include preoxidation by ozonation, adsorption by PAC, coagulation–flocculation using aluminium sulphate followed by decantation and final postchlorination.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Chlorine has been used as an oxidant in drinking water treatment over the last 100 years. Although many benefits have been gained using chlorine as an oxidant, there are also disadvantages [1]. One of the most important disadvantages is the formation of organic halogen compounds, such as trihalomethanes (THMs), as a consequence of the reaction of chlorine with the natural organic matter present in both surface and groundwater [2]. The natural organic matter present in water bodies is a complex mixture of organic substances such as humic and fulvic acids, proteins, lipids, hydrocarbons and aminoacids [3]. Furthermore, humic acid substances constitute the major fraction of natural organic matter in water supplies. These substances and more precisely the most soluble fraction of humic matter, which are aromatic compounds with nucleophilic character, react with chlorine generating THMs. They have been known to cause cancer and other toxic effects in human beings. Concerns regarding the potential health effects of these by-products have prompted several industrialized countries to develop a number of regulations [4].

The oxidant by-product regulation in the United States has set maximum concentration levels for total THM species (chloroform, bromodichloromethane, dibromochloromethane and bromoform) and five haloacetic acids species (monochloro-, dichloro-, trichloro-, monobromo- and dibromoacetic acid) of  $80$  and  $60\ \mu\text{g l}^{-1}$ , respectively [5]. European Union regulations limit THMs to  $100\ \mu\text{g l}^{-1}$  [6]. The World Health Organization guidelines are  $200\ \mu\text{g l}^{-1}$  for chloroform,  $60\ \mu\text{g l}^{-1}$  for bromodichloromethane,  $100\ \mu\text{g l}^{-1}$  for dibromochloromethane,  $90\ \mu\text{g l}^{-1}$  for dichloroacetonitrile and  $100\ \mu\text{g l}^{-1}$  for dibromoacetonitrile [7]. Moreover, in accordance with Royal Decree 140/2003 [8] the maximum concentration of THMs in water in Spain is set at  $100\ \mu\text{g l}^{-1}$  as the sum of chloroform, bromoform, bromodichloromethane and dibromochloromethane.

The prechlorination step has been substituted by preoxidation with ozone in many drinking water treatment plants, producing a significant improvement in water quality.

The drinking water supply of Zaragoza city (Spain) is the Ebro River which has high fluctuations in its composition, classified as bad or poor quality according to the EU Water Framework Directive (2000/60/CE). The following can be considered as average values: a pH 8, dissolved organic carbon (DOC) =  $5\text{ mg l}^{-1}$ , conductivity of  $800\ \mu\text{S cm}^{-1}$ , turbidity =  $100\text{ NTU}$ , Chlorine demand (CD) =  $10\text{ mg Cl l}^{-1}$ . Bromide is not detected. The variability of these analysed parameters is remarkable (see more information at

\* Corresponding author. Tel.: +34 976762390; fax: +34 976762142.

E-mail address: [mosteo@unizar.es](mailto:mosteo@unizar.es) (R. Mosteo).

[www.chebro.es](http://www.chebro.es)). The drinking water treatment plant at Zaragoza (750,000 inhabitants) treats waters from the Ebro river by means of an intensive process, using sodium hypochlorite in the oxidant steps, aluminium salts as coagulant in the coagulation process and adsorption onto activated powdered carbon in the extended treatment step [9].

Advanced oxidation processes (AOPs) are an alternative to conventional preoxidation using chlorine. These processes are based on the generation of highly reactive hydroxyl radicals which do not produce any toxic by-products with the exception of organobromates. These sub-products are identified in the treatment of waters that contain bromide. Ozone has a high oxidant power and, if there is no bromide in the waters, does not generate hazardous organohalogenated by-products, such as THMs [10,11]. Ozone may react with the organic matter present in the water via two distinct mechanisms: a direct reaction and an indirect or oxidation reaction. The direct reaction is produced by different reactions: cycloaddition, nucleophilic and electrophilic. The indirect reaction takes place via radicals generated in the decomposition of ozone (hydroxyl, superoxide, ozonide and hydroperoxide radicals) and it is helped by different agents such as a basic pH, the presence of hydrogen peroxide and of titanium dioxide [9].

On the basis of previous studies [1,12,13], the advanced oxidation processes selected for this research work were  $O_3$ ,  $O_3/H_2O_2$ ,  $O_3/TiO_2$  and  $O_3/H_2O_2/TiO_2$  working at pH 8. In general, nowadays the economic costs of hydrogen peroxide and titanium dioxide are high ( $TiO_2 = 1740$  euros/Tm (Ercros);  $H_2O_2 = 177$  euros/Tm (Hunstman)), implying a significant financial investment in the applied treatment. The use of these reagents is therefore only justified when a considerable improvement in water quality is produced.

The aim of this report, therefore, is to apply different advanced oxidation processes based on ozone and compare them with conventional preoxidation. These oxidation processes, both AOPs and chlorination, are carried out in the whole of the drinking water production treatment. The effectiveness of the different processes is evaluated by different physical–chemical parameters, of which the trihalomethane formation potential (THMFP) is the most important.

## 2. Material and methods

### 2.1. Sample and reagents

In this study, synthetic samples were prepared due to the high variability of water from the Ebro River in Zaragoza (Spain), in order to have a reproducible sample. These synthetic samples were obtained by the dilution of humic solution, and the procedure is described briefly. A humic stock solution was prepared by dissolving 2 g of humic acid (Fluka, Switzerland) in 100 ml of distilled deionized water (Milli-Q) at pH 10, obtained by adding 0.1N NaOH. The solution was stirred with a magnetic stirring bar for 45 min. The solution was then centrifuged, decanted and re-centrifuged. The supernatant was filtered through a 0.45 nm microfilter (Millipore) with the aim of isolating the soluble organic matter fraction. This stock solution was placed in a brown bottle and stored at 4 °C [14]. The dissolved organic carbon (DOC) present in this stock solu-

**Table 1**

Analytical conditions of organic volatile compounds.

Automatic injector HS 2000	
Temperature of incubation	250 °C
Time of incubation	30 min
Gas chromatographer TRACE GC 2000 (ThermoFinnigan)	
Column	DB624 (J&W, 30 m, 0.32 mm, 1.8 μm)
Program of temperature	45 °C (11 min)–3 °C min <sup>-1</sup> –75 °C (6 min)–3 °C min <sup>-1</sup> –95 °C–8 °C min <sup>-1</sup> –165 °C–20 °C min <sup>-1</sup> –225 °C (5 min)
Temperature of injector	250 °C
Volume of injection	2 μl, split
Carrier gas	He (N55), 1 ml min <sup>-1</sup>
Mass spectrometer POLARIS (ThermoFinnigan)	
Energy of ionization	70 eV
Mode of acquisition	SIM
Velocity of screening	1 scan s <sup>-1</sup>
Time of acquisition	45 min

tion was approximately 600 mgC l<sup>-1</sup>. Dilutions of the stock solution were made up prior to each experiment to render a final organic matter concentration (measured as DOC) of 3 mgC l<sup>-1</sup>, a similar concentration to that detected in the Ebro river. Additionally, synthetic samples with the following DOC (6 mgC l<sup>-1</sup>, 15 mgC l<sup>-1</sup>, 30 mgC l<sup>-1</sup> and 60 mgC l<sup>-1</sup>) were prepared in order to evaluate the THMFP parameter.

### 2.2. Analytical methodology

#### 2.2.1. Physical–chemical parameters

The pH was checked by a pHmeter (Crison 507) and the conductivity by a conductimeter (Crison Basic 30). The  $H_2O_2$  concentration in the solution was controlled using a Merck peroxide test ( $O_2^{2-}$ ) (0–25 mg $H_2O_2$  l<sup>-1</sup>). The turbidity was checked by Hanna Turbidimeter (2130-B Standard Method [15]). The chlorine demand (CD) was measured by the 2350 B Method [15] and the residual chlorine and ozone were determined by the 4500-Cl and 4500-B Methods [15] respectively.

To determine the Dissolved Organic Carbon (DOC) of the samples, an analyser of Total Organic Carbon Shimadzu TOC-VCHS was used according to method 5310 B of Standard Methods [15]. The samples were previously filtered.

#### 2.2.2. Analysis of trihalomethanes

The THMFP was measured by Standard Method 5710B [15], the samples were buffered at pH 7, chlorinated with an excess of free chlorine (chlorine demand + 1 mg/l) and stored at 25 °C for 7 d to allow the reaction to approach completion.

The THMs analysis was carried out by EPA Method 524.2 [16] based on HS/GC/MS. The chromatographic conditions employed are shown in Table 1 and validation results of the analytical methodology are reflected in Table 2.

### 2.3. Applied treatments

The experimentation was carried out at lab-scale and in batch mode and the applied treatments are shown in Table 3.

**Table 2**

Main features of the validation methodology of THM measurement.

Compounds	Retention time	Characteristic mass (m/z)	Reproducibility (% variability coefficient)	Repeatability (% variability coefficient)
CHCl <sub>3</sub>	5.97	83.85	16.4	9.5
CHBrCl <sub>2</sub>	11.73	83.85	11.6	6.6
CHBr <sub>2</sub> Cl	19.02	127.129	11.1	6.6
CHBr <sub>3</sub>	26.90	173.252	15.2	10.8

Quantification limit: 5 μg l<sup>-1</sup> Detection limit: 1 μg l<sup>-1</sup> Linear range: 5–100 μg l<sup>-1</sup>.

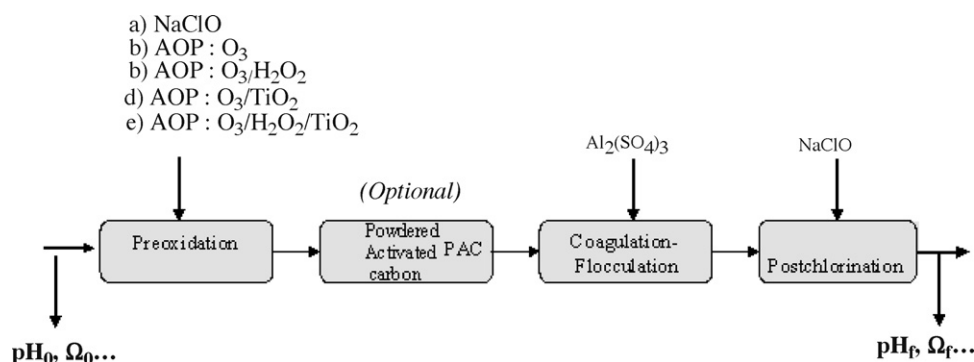


Fig. 1. Diagram of the drinking water treatment and measurement points.

Table 3

Main features of the drinking water production processes.

Experiment	Preoxidant agent	PAC	Coagulation–flocculation [Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ]	Postchlorination
Process 1	NaClO (CD)	10 mg l <sup>-1</sup>	100 mg l <sup>-1</sup>	NaClO (1 mg Cl <sub>2</sub> l <sup>-1</sup> )
Process 2	O <sub>3</sub>	10 mg l <sup>-1</sup>	100 mg l <sup>-1</sup>	NaClO (CD + 1 mg Cl <sub>2</sub> l <sup>-1</sup> )
Process 3	O <sub>3</sub>	–	100 mg l <sup>-1</sup>	NaClO (CD + 1 mg Cl <sub>2</sub> l <sup>-1</sup> )
Process 4	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	10 mg l <sup>-1</sup>	100 mg l <sup>-1</sup>	NaClO (CD + 1 mg Cl <sub>2</sub> l <sup>-1</sup> )
Process 5	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	–	100 mg l <sup>-1</sup>	NaClO (CD + 1 mg Cl <sub>2</sub> l <sup>-1</sup> )
Process 6	O <sub>3</sub> /TiO <sub>2</sub>	10 mg l <sup>-1</sup>	100 mg l <sup>-1</sup>	NaClO (CD + 1 mg Cl <sub>2</sub> l <sup>-1</sup> )
Process 7	O <sub>3</sub> /TiO <sub>2</sub>	–	100 mg l <sup>-1</sup>	NaClO (CD + 1 mg Cl <sub>2</sub> l <sup>-1</sup> )
Process 8	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /TiO <sub>2</sub>	10 mg l <sup>-1</sup>	100 mg l <sup>-1</sup>	NaClO (CD + 1 mg Cl <sub>2</sub> l <sup>-1</sup> )
Process 9	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /TiO <sub>2</sub>	–	100 mg l <sup>-1</sup>	NaClO (CD + 1 mg Cl <sub>2</sub> l <sup>-1</sup> )

The sequence of operations employed in the combined treatments was preoxidation, adsorption, coagulation–flocculation–decantation and postchlorination. In some experiments, the coagulation treatment was carried out directly after preoxidation without using the adsorption operation (Fig. 1).

### 2.3.1. Preoxidation

The preoxidation is carried out by the different options described below:

- Preoxidation by chlorine using NaClO (MERK) as the oxidizing agent. The amount of NaClO added to the sample was exactly the same amount corresponding to its chlorine demand (CD) measured by the 2350 B Method [15].
- Preoxidation by ozone using a dose of 3 mg l<sup>-1</sup>, usually used in drinking water plants in Spain and established previously by other authors [17,18,19]. Ozone based treatments were carried out at pH 8. The equipment used to produce ozone was a corona discharge generator (Fisher). The generator is connected to a closed glass reactor and the ozone is transferred to the sample by a porous diffuser. This reactor was connected to three washing bottles which contain potassium iodide at 2% and absorb the unconsumed ozone. A diagram of the system is shown in Fig. 2.

The generator produced 12 mg O<sub>3</sub> min<sup>-1</sup>, which was moved through 1 l of sample for 15 s. Therefore 3 mg O<sub>3</sub> l<sup>-1</sup> were applied. Ozone that was not consumed or removed in gas phase (O<sub>3</sub>-noconsumed) was absorbed in two serial gas washing bottles containing IK 2%. O<sub>3</sub>-noconsumed was calculated by valuate of IK, resulting in 0 mg O<sub>3</sub> l<sup>-1</sup> in all cases. The waste dissolved ozone was measured with a Test of Ozone Spectroquant® (MERCK) resulting in <0.01 mg O<sub>3</sub> l<sup>-1</sup>. Therefore the consumed ozone was 3 mg O<sub>3</sub> l<sup>-1</sup>, according to the equation:

$$O_3\text{consumed} = O_3\text{applied} - O_3\text{-noconsumed} - O_3\text{waste-dissolved}$$

(c) Preoxidation by ozone combined with hydrogen peroxide and titanium dioxide using 3 mg O<sub>3</sub> l<sup>-1</sup> and adding 1.5 mg l<sup>-1</sup> of hydrogen peroxide (30% (v/v), Carlo Erba) and/or 1 mg l<sup>-1</sup> of Titanium dioxide P25 (Degussa) before starting the reaction. Previous results obtained by our research group [20] were taken into account to select the hydrogen peroxide concentration. The TiO<sub>2</sub> dose employed in this study was selected due to experience of previous studies by our research group [21,22] and because research has shown that it is the optimum concentration for disinfection stages, which is the main objective of the oxidation operation in the process of drinking water production [23].

### 2.3.2. Adsorption onto activated carbon (Optional operation)

Adsorption onto powdered activated carbon (PAC) treatment was carried out using 10 mg l<sup>-1</sup> powdered activated carbon (the amount usually employed at the water treatment plant in Zaragoza). The powdered activated carbon (CHIEMIVALL Plus) was introduced into the sample and gently shaken for 5 min, being removed before analysis by filtration. This powdered activated car-

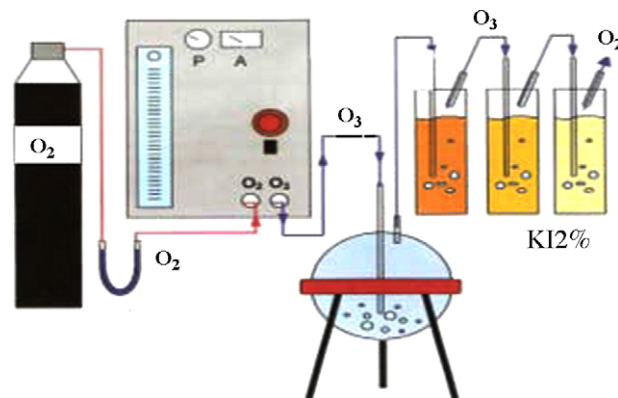


Fig. 2. Diagram of ozone generator.

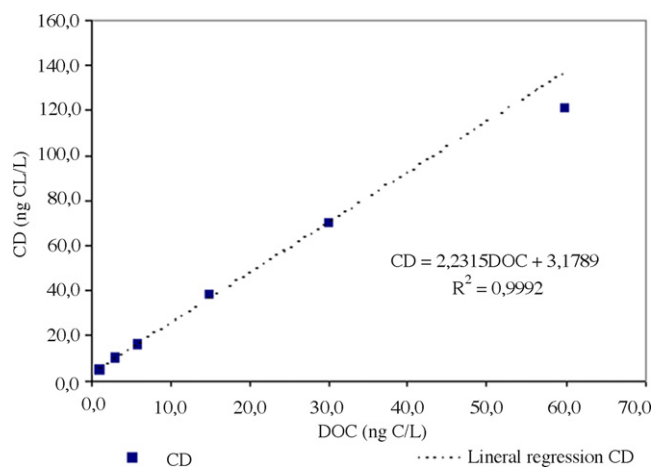


Fig. 3. Chlorine demand for different synthetic samples.

bon has a superficial area of  $1000 \text{ m}^2 \text{ g}^{-1}$  and a particle size of  $40 \mu\text{m}$ .

### 2.3.3. Coagulation–flocculation process

Coagulation–flocculation–decantation experiments were carried out using a dosage of aluminium sulphate (PANREAC) as the coagulating agent of  $100 \text{ mg l}^{-1}$ . A Jar-Test was used to first produce rapid agitation (200 rpm) for 5 min, during which time destabilization of the colloids occurred. After that slow agitation (40 rpm) took place for 20 min, thus allowing the formation of flocs and their later decantation after 2 h.

### 2.3.4. Final oxidation

For the purpose of knowing the THMFP of treated samples and taking into account the procedure used in real drinking water treatment plants, a final oxidation was carried out by the addition of NaClO until achieving residual chlorine of  $1 \text{ mg l}^{-1}$  in the samples. The use of this reagent is due to the fact that chlorine is the only disinfectant agent with residual effect.

## 3. Results and discussion

### 3.1. Chlorine demand and THMFP of synthetic samples

The chlorine demand and THMFP of synthetic samples with different contents of dissolved organic carbon were analysed. Figs. 3 and 4 show the results obtained for both parameters in function of dissolved organic carbon.

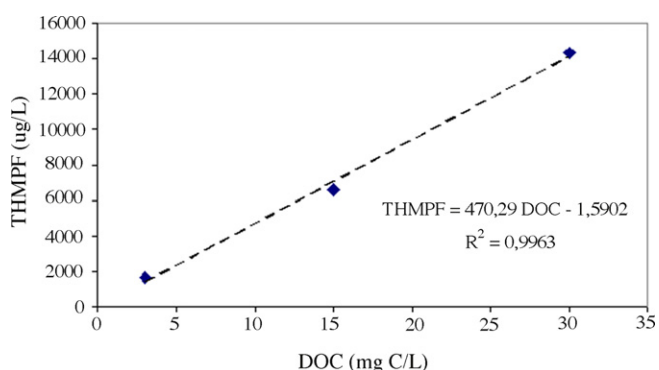


Fig. 4. THMFP for synthetic samples in function of concentration of organic matter (measured as DOC).

Table 4

THM concentration in samples using NaClO as oxidant agent.

Organic matter concentration (measured as DOC)	$3 \text{ mgCl}^{-1}$	$15 \text{ mgCl}^{-1}$	$30 \text{ mgCl}^{-1}$
$\text{CHCl}_3$ ( $\mu\text{g l}^{-1}$ )	1650	6600	14300
$\text{CHBrCl}_2$ ( $\mu\text{g l}^{-1}$ )	5	5	4
$\text{CHBr}_2\text{Cl}$ ( $\mu\text{g l}^{-1}$ )	2	1	1
$\text{CHBr}_3$ ( $\mu\text{g l}^{-1}$ )	1	1	1
THMFP ( $\mu\text{gCCl}_3 \text{ l}^{-1}$ )	1655	6605	14304

As expected, an increase in the humic content in the samples (measured as DOC) produces an increase in the chlorine demand (CD) (Fig. 3) and in the quantity of THMs generated after chlorination (Fig. 4). In the same way, both Chlorine Demand and THMFP have linear dependence in function of the dissolved organic concentration present in the samples (Figs. 3 and 4). Furthermore, the results show a production of THMs in concentrations higher than those determined by other authors [24] due to the fact that synthetic samples prepared by dilution of a humic solution (THM precursor) were used in this study instead of real samples. The dissolved organic concentration in real surface waters is a contribution of different organic compounds and some substances are not THM precursors.

Concentrations of each trihalomethane after chlorination of synthetic samples ( $3 \text{ mgCl}^{-1}$ ,  $15 \text{ mgCl}^{-1}$  and  $30 \text{ mgCl}^{-1}$ , measured as COD) are shown in Table 4.

As is observed in Table 4, the main compound formed in the chlorination is chloroform. In fact, this trihalomethane is the compound that presents a linear tendency with the COD of synthetic samples. Concentrations of  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  are not modified by the COD of synthetic samples, so there is no dependence with the initial humic content of the samples. As a consequence, it can be ensured that there is no bromine in the synthetic samples and the presence in chlorinated samples is due to the NaClO reagent used in which the bromine is an impurity.

### 3.2. Efficiency of applied treatments

Table 5 shows the main features of the synthetic samples used in the different treatments.

Table 6 summarizes the physical–chemical parameters analysed after the completed experiments (Process 1, 2...9) indicated in Table 3.

In general, as can be observed in Tables 5 and 6, all the completed treatments applied to the synthetic samples were very effective in

Table 5

Main features of initial synthetic samples.

pH	DOC	CD	THMFP	Conductivity	Turbidity
8.1	$3 \text{ mg l}^{-1}$	$10 \text{ mg l}^{-1}$	$1655 \mu\text{gCCl}_3 \text{ l}^{-1}$	$9.0 \mu\text{S cm}^{-1}$	0.7 NTU

Table 6

Physical–chemical characterization after the completed process.

Experiment	$\text{DOC}_f$ (mgCl)	$\text{pH}_f$	$\Omega_f$ ( $\mu\text{S cm}$ )	Turbidity <sub>f</sub> NTU	THMFP ( $\mu\text{gCCl}_3 \text{ l}^{-1}$ )
Process 1	<1	7.8	116	0.3	112
Process 2	<1	7.7	204	0.3	20
Process 3	<1	7.8	199	0.3	35
Process 4	<1	7.5	203	0.4	57
Process 5	<1	7.5	205	0.4	60
Process 6	<1	7.2	203	12.3	99
Process 7	<1	7.4	204	15.8	126
Process 8	<1	7.8	192	16.2	12
Process 9	<1	7.7	179	10.3	25



terms of dissolved organic matter removal and in the reduction of THMs generated at the end of the process.

Furthermore, Tables 5 and 6 show that the turbidity is reduced in those completed treatments in which  $\text{TiO}_2$  is not employed (process 1–5) although an important increase of this parameter is produced in photocatalytic processes, achieving values of 10–15 NTU in the treated samples. After applying each completed treatment the pH is maintained constant and the conductivity increases considerably (from  $9 \mu\text{S cm}^{-1}$  to  $100\text{--}200 \mu\text{S cm}^{-1}$ ) due to the addition of coagulant ( $\text{Al}_2(\text{SO}_4)_3$ ).

As indicated previously, the production of THMs is clearly reduced because the THMFP of the initial synthetic samples is  $1655 \mu\text{gCCl}_3 \text{ l}^{-1}$  while at the end of the different processes, summarized in Table 3, the THMFP of the treated samples is about  $12\text{--}126 \mu\text{gCCl}_3 \text{ l}^{-1}$ . It can be said that the applied treatments produce THM reductions close to 90%. Of the different treatments, the use of the  $\text{O}_3/\text{H}_2\text{O}_2/\text{TiO}_2$  process, PAC adsorption, coagulation–flocculation–decantation and final oxidation generates the lowest quantities of THMs in the treated samples. On the other hand, the process of prechlorination, coagulation–flocculation–decantation and final oxidation produces the highest concentration of THMs in the treated samples. If the THMFP obtained after process 2 (prechlorination and coagulation–flocculation–decantation) is compared with the THMFP of the initial synthetic sample (evaluated by direct chlorination of the synthetic sample), it can be observed that coagulation–flocculation–decantation is the most important part of the process responsible for this substantial reduction compared to activated carbon addition or the oxidant agent.

An analysis of the results obtained in this research work demonstrates that:

- The addition of activated carbon reduces the final concentration of THMs although there is no total removal (process 2 versus process 3; process 4 versus process 5; process 6 versus process 7 and process 8 versus process 9).
- The use of chlorination in the preoxidation operation has an effect similar to that of the  $\text{O}_3/\text{TiO}_2$  process in relation to the final concentration of THMs.
- Preoxidation by ozone has a positive effect in the control of THMs. The combination of ozone with  $\text{H}_2\text{O}_2$  or  $\text{TiO}_2$  does not improve the THM reduction so these reagents have a low negative effect on the control of THMs. Despite the fact that several authors have indicated that  $\text{H}_2\text{O}_2$  increases the effectiveness of ozonation [25,26], in this case this effect is not produced, a result also obtained by Oguz and Keskinler [27]. This is due to the working pH (pH 8) since at this pH the hydrogen peroxide is in excess with respect to the conjugated base and the scavenger effect is produced. With respect to  $\text{TiO}_2$  addition, it can be said that this reagent improves the ozonation process at acid pH in the range of 5.6–6.4 and an inhibition takes place at higher pH [28].
- However, the simultaneous addition of  $\text{H}_2\text{O}_2$  and  $\text{TiO}_2$  to ozonation produces a synergic effect since a lower production of THMs at the end of the treatment is obtained. References to this technique have not been found, so this will be the subject of future research by our group.

#### 4. Conclusions

From the results obtained in this research work the following conclusions may be drawn.

- A direct chlorination of synthetic samples, prepared by diluting humic stock solution in distilled water, with a dissolved organic carbon close to  $3 \text{ mg l}^{-1}$  produces a THM concentration of around  $1600 \mu\text{gCCl}_3 \text{ l}^{-1}$  (measured as THMFP).

- The employment of treatments composed of preoxidation, coagulation–flocculation–decantation and postchlorination on synthetic samples, which present a concentration of organic matter (measured as DOC) around  $3 \text{ mgCl}^{-1}$ , generates a final concentration of THMs in the range from  $12 \mu\text{gCCl}_3 \text{ l}^{-1}$  to  $126 \mu\text{gCCl}_3 \text{ l}^{-1}$ . The process in which the preoxidation is carried out by chlorine or by the  $\text{O}_3/\text{TiO}_2$  process produces the highest THM concentration in the treated sample. On the other hand, the process with  $\text{O}_3/\text{H}_2\text{O}_2/\text{TiO}_2$  preoxidation generates the lowest quantity of these compounds.
- Taking into account all the studied processes, it can be said that the process mainly responsible for THM reduction is coagulation–flocculation.
- Considering the different completed treatments studied, the most recommendable drinking water production process, taking into account health and economic criteria, is preoxidation by ozonation, adsorption by PAC, coagulation–flocculation using aluminium sulphate followed by decantation and final postchlorination.

#### Acknowledgements

The authors wish to acknowledge financial support for this work from the Ministerio de Ciencia y Tecnología, Gobierno de Aragón and Fundación Caixa Cataluña (Project CTM 2005-04585) and from the CTM 2008-01876/TECNO project: “Regeneración de aguas depuradas mediante procesos de oxidación avanzada”.

#### References

- [1] A.M. Alsheyab, A.H. Muñoz, Comparative study of ozone and  $\text{MnO}_2/\text{O}_3$  effects on the elimination of TOC and COD of raw water at the Valmayor station, *Desalination* 207 (2007) 179–183.
- [2] J.B. Sérodes, M.J. Rodríguez, H. Li, C. Bouchard, Occurrence of THMs and HAAs in experimental chlorinated waters of the Quebec City area (Canada), *Chemosphere* 51 (2003) 253–263.
- [3] Alejandro Moncayo-Lasso, Cesar Pulgarin, Norberto Benitez, Degradation of DBP's precursors in river water before and after sand filtration by photo-Fenton process at pH 5 in a solar CPC reactor, *Water Res.* 42 (2008) 4125–4132.
- [4] Vedat Uyak, Ismail Koyuneu, Ibrahim Oktem, Mehmet Cakmakci, Ismail Toroz, Removal of trihalomethanes from drinking water by nanofiltration membranes, *J. Hazard. Mater.* 152 (2008) 789–794.
- [5] P.C. Singer, Formation and control of disinfection by-products in drinking water, AWWA, Denver (1999).
- [6] USEPA, National primary drinking water regulations: Stage 2 disinfectants and disinfection by-products, Final rule 68 (159), 2003.
- [7] EEC Directive (European Economic Community Directive). Amended proposal for a Council Directive concerning the quality of water intended for human consumption—common position, in: Proceedings of the Council of the European Union Directive 80/778/ECC, Com (97) 228 final 95/0010 SYN, Brussels 1998.
- [8] Royal Decree 140/2003 of 7 of February of 2003, laid down the Sanitary Criteria for the Quality of Water for Human Consumption. Bulletin Official of State (BOE), 45, 21 of February of 2003.
- [9] M.P. Ormad, N. Miguel, A. Claver, J.M. Matesanz, J.L. Ovelleiro, Pesticides removal in the process of drinking water production, *Chemosphere* 71 (2008) 97–106.
- [10] U. Von Gunten, Ozonation in drinking water. Part I: Oxidation kinetics and product formation, *Water Res.* 37 (2003) 1443–1467.
- [11] S. Sorlini, C. Collivignarelli, Trihalomethanes formation during chemical oxidation with chlorine, chlorine dioxide and ozone of ten Italian natural waters, *Desalination* 176 (2005) 103–111.
- [12] B. Langlais, D.A. Reckhow, D.R. Brink, Ozone in water treatment. Application and Engineering, in: American Water Works Association Research Foundation, Lewis Publishers, USA, 1991.
- [13] R. Gracia, S. Cortés, J. Sarasa, P. Ormad, J.L. Ovelleiro,  $\text{TiO}_2$  catalysed ozonation and photocatalysis, *Ozone-Sci. Eng.* 25 (1999) 497–505.
- [14] R. Gracia, J.L. Aragiies, J.L. Ovelleiro, Study of the catalytic ozonation of humic substances in water and their ozonation by-products, *Ozone-Sci. Eng.* 18 (1996) 195–208.
- [15] L.S. Cleresci, A.E. Greenberg, R.R. Trussell, Standard Methods for the Examination of waste water, 21th Edition, American Public Health Association, Maryland, USA, 2005.
- [16] EPA Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry—Revision 4.0 EPA Method 524.2.

- [17] T.E. Agustina, H.M. Ang, V.K. Vareek, A review of synergistic effect of photocatalysis and ozonation on wastewater treatment, *J. Photochem. Photobiol.* 6 (2005) 264–273.
- [18] A. Kerc, M. Bekbolet, A.M. Saatci, Sequential oxidation of humic acids by ozonation and photocatalysis, *Ozone-Sci. Eng.* 25 (2003) 497–505.
- [19] F.J. Rodríguez, A. Pérez, B. Orozco, M<sup>á</sup>.C. Sanllorenzo, M<sup>á</sup>.V. Ibeas, Efectos de la ozonización sobre la formación de trihalometanos durante la desinfección final del agua potable con cloro, *Tecnología del agua* 218 (2001) 60–66.
- [20] M.P. Ormad, S. Cortés, A. Puig, J.L. Ovelleiro, Degradation of organochlorine compounds by O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, *Water Res.* 31 (1997) 2387–2391.
- [21] M. Lanao, M.P. Ormad, C. Ibarz, N. Miguel, J.L. Ovelleiro, Bactericidal Effectiveness of O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/TiO<sub>2</sub> on *Clostridium perfringens*, *Ozone-Sci. Eng.* 30 (2008) 431–438.
- [22] N. Miguel, M.P. Ormad, M. Lanao, C. Ibarz, J.L. Ovelleiro, Personal communication. International Conference & Exhibition: Sustainable agri-food industry. Use of ozone & related oxidants. Valencia, Spain, 2007.
- [23] D. Gummy, A.G. Rincón, R. Hajdu, C. Pulgarin, Solar photocatalysis for detoxification and disinfection of water: Different types of suspended and fixed TiO<sub>2</sub> catalysts study, *Sol. Energy* 80 (2006) 1376–1381.
- [24] V. Uyak, S. Yavuz, I. Toroza, S. Ozaydin, E. Ates, Disinfection by-products precursors removal by enhanced coagulation and PAC adsorption, *Desalination* 216 (2007) 334–344.
- [25] W. Chen, M. Elovitz, K. Linden, I. Buffet, Reactions of thiocarbamate, triazine and urea herbicides, RDX and benzenes on EPA contaminant candidate list with ozone and with hydroxyl radicals, *Water Res.* 42 (2007) 137–144.
- [26] J. Wu, J. Yang, M. Muruganandham, C. Wu, The oxidation study of 2-propanol using ozone-based advanced oxidation processes, *Sep. Purif. Technol.* 62 (2008) 39–46.
- [27] E. Oguz, B. Keskinler, Removal of colour and COD from synthetic textile wastewaters using O<sub>3</sub>, PAC, H<sub>2</sub>O<sub>2</sub> and HCO<sub>3</sub><sup>-</sup>, *J. Hazard. Mater.* 151 (2008) 753–760.
- [28] A. Rosal, A. Rodríguez, M. Gonzalo, E. García-Calvo, Catalytic ozonation of naproxen and carbamazepine on titanium dioxide, *Appl. Catal. B Environ.* 84 (2008) 48–57.