



## The effect of mixed oxidants and powdered activated carbon on the removal of natural organic matter

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### ABSTRACT

Present paper studies the influence of electrochemically generated mixed oxidants on the physicochemical properties of natural organic matter, and especially from the disinfection by-products formation point of view. The study was carried out in a full scale water treatment plant. Results indicate that mixed oxidants favor humic to non-humic conversion of natural organic matter. Primary treatment preferentially removes the more hydrophobic fraction. This converted the non-humic fraction in an important source of disinfection by-products with a 20% contribution to the final trihalomethane formation potential (THMFP<sub>F</sub>) of the finished water. Enhanced coagulation at 40 mg l<sup>-1</sup> of polyaluminium chloride with a moderate mixing intensity (80 rpm) and pH of 6.0 units doubled the removal efficiency of THMFP<sub>F</sub> achieved at full scale plant. However, gel permeation chromatography data revealed that low molecular weight fractions were still hardly removed. Addition of small amounts of powdered activated carbon, 50 mg l<sup>-1</sup>, allowed reduction of coagulant dose by 50% whereas removal of THMFP<sub>F</sub> was maintained or even increased. In systems where mixed oxidants are used addition of powdered activated carbon allows complementary benefits by a further reduction in the THMFP<sub>F</sub> compared to the conventional only coagulation–flocculation–settling process.

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### 1. Introduction

Conventional drinking water production includes coagulation–flocculation–settling (CFS) followed by sand filtration and chlorine disinfection. Alternatives to chlorine, such as ozone and chlorine dioxide, have been constantly pursued due to the appearance of harsh microorganisms as well as the formation of chlorinated disinfection by-products of chlorine [1,2]. In order to avoid algae proliferation within treatment plant, pre and intermediate chlorination is usually effected. During these previous oxidation steps, water contains higher loads of organics, rich in dihydroxybenzene type structures, thus formation of chlorinated disinfection by-products (DBP) is favored [3,4].

**Abbreviations:** CFS, coagulation–flocculation–settling; DBP, disinfection by-products; DEAE, diethylaminoethyl cellulose; DOC, dissolved organic carbon; HPIA, hydrophilic acid; HPOA, hydrophobic acid; MW, molecular weight; NOM, natural organic matter; PAC, powdered activated carbon; PACl, polyaluminium chloride; RI, refractive index; RW, raw water; SPTHMFP, simulated plant THMFP; SUVA, specific UV absorbance; THM, trihalomethanes; THMFP, THM formation potential; THMFP<sub>F</sub>, final THMFP; TPHA, transphilic acid; UV, ultraviolet absorbance; WTP, water treatment plant.

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Many researchers [5,6] focused attention to the association of DBPs, and specifically trihalomethanes, with noxious health effects in the carcinogenesis, reproductive and developmental areas. Humans are primarily exposed to trihalomethanes (THMs) through drinking water consumption and also dermal and respiratory pathways from bathing and swimming [7]. Consequently, the health risk associated to DBPs formation is forcing authorities to closely examine and optimize the disinfection procedures in water treatment plants.

Electrochemically produced mixed oxidants are generated in situ by electrolysis of brine. In this reaction chlorine, also known as nascent chlorine, is produced as primary reaction. Ozone and chlorine dioxide are produced as secondary reaction [8,9]. Ozone has a greater disinfection effectiveness than other oxidizers whereas chlorine dioxide is a powerful oxidizer and germicidal agent which does not react with ammonia. Furthermore, it remains in its molecular form in the pH range typically found in natural waters. Previous works [10,11] reported that the nascent chlorine, ozone and chlorine dioxide combination exhibits greater oxidative power (synergy) for selected microorganisms than conventional chlorine. This way it is possible, with a smaller dosage, to eradicate the pathogenic germs and avoid the presence of resistant germs. However, the exact composition of the intermediates produced from these electrochemically mixed oxidants is still not well understood [12].

Few works have examined the effect of electromechanically generated mixed oxidants on natural organic matter at full scale drinking water utilities. The present paper presents results of the use of this alternative oxidation strategy when used in conjunction with conventional treatment and also with adsorption by powdered activated carbon. The effect of this mixed oxidants system on the content, nature and reactivity to form THMs of the natural organic matter (NOM) has been analyzed.

## 2. Experimental

The selected water treatment plant (WTP) is a small utility that treats 1400 m<sup>3</sup>/day and uses a mixed oxidant generator manufactured by Cetolar to produce nascent chlorine as primary and secondary oxidant. The amount of each species produced depends on several factors such as the electric power supplied during electrolysis of brine. The overall disinfectant dosage is quantified in terms of free chlorine residual (FCR). Treatment includes preoxidation, coagulation–flocculation–settling, intermediate oxidation, sand filtration and disinfection. Alum is added as coagulant in a concentration range from 15 to 20 mg l<sup>-1</sup>. The dosage of oxidant is automatically regulated to ensure a free chlorine residual between 0.5 and 0.8 mg l<sup>-1</sup> at plant outlet stream. For this study, raw, settled and filtered water from the full scale plant were analyzed.

The four THMs species were determined by Gas Chromatography (GC)/Electron Capture Detector (ECD) (HP 5890 Series II). Analysis conditions: injection on-column, volume 0.5 µl; oven temperature 50 °C for 5 min, 50–105 °C at 6 °C/min; carrier gas N<sub>2</sub> at 6 ml min<sup>-1</sup>, make-up gas N<sub>2</sub> at 60 ml min<sup>-1</sup>; detector temperature 300 °C; column HP-1 methyl siloxane 30.0 m × 530 mm × 2.65 mm. Detection and quantification levels (defined as peak height to noise ratio of 3:1 and 10:1, respectively) correspond to 0.15 and 0.50 µg l<sup>-1</sup>, respectively. pH measurements were carried out with a Crison (GLP-22) pH-meter. DOC was measured as Non-Purgable Organic Carbon in a TOC analyzer with non-Dispersive Infrared detector (Shimadzu TOC 5050A). UV absorbance was measured at 254 nm in a Helios-γ (TermoSpectronic) spectrophotometer with 1 cm optical path lengths. Fractionation and quantification of NOM was done by two different procedures: (i) by using two non-ionic macroporous resins in series; amberlite DAX-8 and supelite XAD-4 [13] and (ii) by using a weak ionic exchange resin (DEAE) [14,15]. NOM characterization procedure involves the separation of NOM into hydrophobic acid (HPOA-DAX8), transphilic acid (TPHI), hydrophilic acid (HPIA-XAD) using XAD resins [16]. DEAE resin was used to obtain the so-called HPOA-DEAE and HPIA-DEAE fractions. Both procedures were applied in parallel to fractionate NOM in water samples. Precursor concentration in this study was quantified as UV absorbance, dissolved organic carbon and by standardized chlorination tests. Chlorination tests, namely THM formation potential tests, were done according to Standard Methods [14]. THMFP<sub>F</sub> denotes final or maximum THMs that can be formed. Chlorination conditions were 22 °C, initial chlorine concentration 78 mg l<sup>-1</sup>, contact time 7 days, pH 7.0 units. SPTHMFP refers to simulated plant formation potential. Chlorination occurs at similar conditions to those set at WTP. Chlorination conditions were 10 °C, initial chlorine concentration 15 mg l<sup>-1</sup>, contact time 15 h, pH 8.0 units. THMs were determined by Gas Chromatography (GC)/Electron Capture Detector.

Jar-test experiments were performed using a laboratory jar-test device (flocumatic). A commercial coagulant was used, polyaluminium chloride (PACl) (ref. PA/18.B, Al<sub>2</sub>O<sub>3</sub> 17.5%, 40% basicity). An anionic polyacrylamide based flocculant (Flocusol-AP/1) was used in all experiments. Jar-test mixing conditions were as follows: water samples (0.5 l) and coagulant were flash mixed (80 rpm) for 2 min. Anionic flocculant was added (10 mg l<sup>-1</sup>) just before flash mixing terminates followed by slow mixing (20 rpm) for 30 min. Flocs were allowed to settle for 1 h. Water samples from each jar were vacuum filtered through 0.45 µm PTFE filter. pH was adjusted with sulphuric acid (0.1 M). When needed PAC was added and rapid mixing at 100 rpm was maintained for 5 min. Then, coagulant was added and the previously described procedure was followed (2 min 80 rpm, flocculant addition, 30 min 20 rpm, 0.45 µm PTFE). 15% of jar-test experiments (randomly selected) were duplicated in order to check for reproducibility. The measured average standard deviation was below 10%.

Physical and chemical properties of PAC are presented in Table 1. A porosimeter system (ASAP 2010, Micromeritics) was used to determine the textural properties. The total pore volume was calculated from the adsorbed volume of gas near the saturation point ( $P/P_0 = 0.98$ ). The  $S_{micr}$ ,  $S_{mes}$  and  $dp$  were determined using density functional theory (DFT) by assuming the graphite model with slit shape geometry. Surface area was calculated from the BET method. The determination of the  $pH_{pzc}$  was done by the bottle-point method. The pH within each flask (20 ml) was adjusted to a value between 2 and 12 by adding HNO<sub>3</sub> 0.1 M or NaOH 0.1 M. Then 0.1 g of carbon was added to each flask, and the final pH was measured after 24 h under agitation at room temperature. The amount of acidic and basic functional groups on carbon surface was measured from titration techniques [17]. 65 ml vials were filled with 0.1 g of carbon and 20 ml of 0.05 N NaOH or 0.05 N of HCl. Vials without carbon and containing either acid or base were prepared as blanks. Samples and blanks were shaken at 200 rpm for 48 h at room temperature. Finally, samples were filtered (0.45 µm) and 15 ml of the solution was titrated with 0.05 N of either NaOH or HCl solution.

Molecular weight distribution of NOM was determined by HPLC-UVA/RI. Calibration standards were polyethylene glycol and polyethylene oxide. Analytical conditions were as follows: column TSK α-3000, column temp. 40 °C, injection volume 150 µl, mobile phase phosphate buffer 0.004 M (pH 6.8), Na<sub>2</sub>SO<sub>4</sub> 0.0025 M, ionic strength 0.1 M, flow rate 1.0 ml min<sup>-1</sup>. Experimental set-up consists of a HPLC system with a RI and UV detectors in series. Retention time of standard solutions was determined using refractive index detector (detector temp. 40 °C) whereas NOM in samples was quantified using UV absorbance detector (254 nm).

## 3. Results and discussion

THMs precursor content of raw water that supplied WTP, measured as THMFP<sub>F</sub> was 113 µg l<sup>-1</sup>, which exceeds maximum contaminant level of 100 µg l<sup>-1</sup> established by European Directive [18]. SUVA value (2.41 mg<sup>-1</sup> m<sup>-1</sup>) denotes low to moderate aromaticity of NOM in sample. The variation in distribution of hydrophobic and hydrophilic fractions in NOM throughout the plant is shown in Fig. 1. Based on THMFP<sub>F</sub> measurements DEAE absorbed 92% of raw water values whereas the sum of DAX8 and XAD4 extracts accounted for 57% of raw water. When UV absorbance was used for quantification these fractions accounted for 72% and 77% or

**Table 1**  
Physical and chemical properties of powdered activated carbon.

	Origin	$\rho$ (g cm <sup>-3</sup> )	$V_T$ (cm <sup>3</sup> g <sup>-1</sup> )	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{micr}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{mes}$ (m <sup>2</sup> g <sup>-1</sup> )	$dp$ (Å)	$pH_{pzc}$	Surface acidity (meq g <sup>-1</sup> )	Surface basicity (meq g <sup>-1</sup> )
F-400	Coal	0.425	0.483	852	639	43	10.1	10.5	0.10	0.29

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