

# Effects of Ozonation on Characteristics of Aquatic Fulvic Acid

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Aquatic fulvic acid (FA) treated with ozone was characterized by physical/chemical (dissolved organic carbon-DOC), spectroscopic (UV/VIS, IR, fluorescence), chromatographic (gel permeation chromatography-GPC) methods. The influence of ozonation on the subsequent water treatment process such as flocculation and chlorination was also examined. The DOC concentration of the 20 min ozonated FA samples was reduced only a small amount (5%) whereas the UV absorption reduced to a higher percent (40%). The IR spectra of ozonated samples showed a moderate attenuation of the double band and aromatic character of FA. Ozonation of the FA caused the fluorescence intensities to increase steadily with ozonation time, whereas it decreased when FA was flocculated after ozonation. Gel chromatographic characterization of FA showed that the high molecular weight (HMW) fractions were eliminated after flocculation followed by ozonation, while the apparent molecular weight (AMW) distribution of ozonated FA changed slightly. The formation potentials of trihalomethane (THMFP) and adsorbable organically bound halogen (AOXFP) were significantly decreased with the increasing ozonation time along with the flocculation process.

## Introduction

The yellow to brown colour of many raw water sources can be attributed to the presence of humic material. Humic substances as natural organic matter (NOM) show no toxic properties<sup>1</sup>. Aquatic humic substances (HS) are thought to have a moderate aromatic character (~25% of the total carbon) with large numbers of carboxyl groups, some phenolic groups, alcoholic OH groups, methoxyl groups, ketones, and aldehydes<sup>2-4</sup>. Fulvic acids have been proven to account for 80-90% of the humic material present in surface water<sup>5</sup>.

Disinfection by chlorine or ozone creates new compounds by chemical reactions between fulvic acids and disinfectant. Today, it is a known fact that humic substances in surface waters will form trihalomethanes (THMs) in the presence of free chlorine<sup>6,7</sup>.

When ozone is applied as a preoxidant in water treatment, it can react rapidly with NOM present in water<sup>8</sup>. Ozonation changes the nature of NOM, which in turn affects the removal of DOC during flocculation, adsorption and chlorination<sup>8,9</sup>. A review of the literature reveals that increasing ozonation is often associated with a reduction of trihalomethane formation potential (THMFP) and adsorbable organically bound halogen formation potential (AOXFP)<sup>11-13</sup>. This research was aimed at expanding our knowledge of the impacts

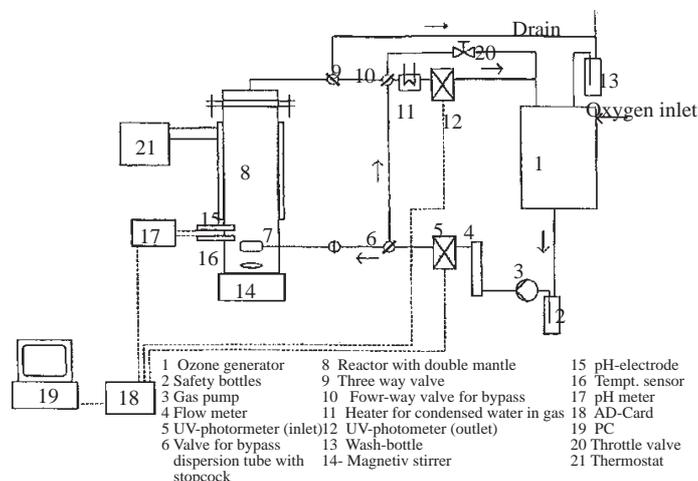
of preozonation on HS. It was expected that the results might have implications for the removal of HS by subsequent processes such as flocculation and chlorination.

## Experimental

**Samples:** The experiments were performed by FA (HO10) isolated from a brown water Lake Hohloh, (HO10), Black Forest, Germany. The isolation of FA was done according to Abbt-Braun and et. al<sup>14</sup>.

The studied final concentration of FA samples was 1.4 mg/L DOC. Before use, the sample was prefiltered through a 0.45  $\mu\text{m}$  polycarbonate membrane. The resulting FA was approximately 50% carbon by weight.

**Ozonation:** The applied ozone concentration (7 mg/L) was generated by Anseros (Type Com/R) ozone generator, which was fed with oxygen gas. Ozonation was carried out in a 1.000 mL glass cylindrical vessel which has a glass cover containing inlets for feeding the gas, temperature and pH measurements, sampling and venting. A stirrer kept the liquid phase mixed. The data for ozone concentrations, temperature and pH was continuously monitored with a PC connected to the system. Details of the ozonation system are shown in Figure 1. The ozone concentration in the gas flow was measured at the reactor in- and outlet by UV detector at 253.7 nm with two-second intervals. The absorbed amount of ozone was calculated by integration of the difference of the inlet and outlet ozone concentrations over small intervals. The sample contact times were 5 min and 20 min and the concentrations of absorbed ozone these durations were 3.44 mg/L and 10.88 mg/L, respectively. pH values of FA solutions were 4.3 - 4.5. In the experiments, the temperature of the solution and gas flow rate was fixed at 10°C and 41 L/h, respectively.



**Figure 1.** Schematic diagram of the ozonation system

**Dissolved Organic Carbon (DOC):** DOC measurements were made by the persulfate-ultraviolet oxidation method (APHA, 1992). The DOC Analyzer (Dohrman Model DC 80) was calibrated with a 10 mg/L (as carbon) potassium hydrogen phthalate (KHP) standard before each run of sample. Measurements were conducted in triplicate. Error of the method was  $\pm 1\%$ .

**Spectroscopic Characterization:** UV/Vis specific spectral absorption coefficient (SAC) that is ratio of absorbance units ( $\text{m}^{-1}$ ) to DOC (mg/L) was determined by measuring UV absorption at  $\lambda=254$

nm (SAC<sub>254</sub>) and Vis-Absorption at  $\lambda=436$  nm (SAC<sub>436</sub>) by using 1 cm quartz cell at pH 6.8 with a Perkin Elmer-Lambda 5 spectrophotometer.

**Fluorescence:** The fluorescence of FA was recorded with a fluorescence spectrometer (Perkin Elmer LS 50 B) using an excitation wavelength of 330 nm. The emission spectra were measured between  $\lambda=350$  nm and 550 nm at an angle of 90° versus the position of the excitation beam. The bandwidth of the slits was 5 nm. pH and DOC concentration of FA solution were 6.8 and 5.0 mg/L for the measuring of fluorescence, respectively.

**IR-spectra:** The IR- spectra were recorded in the range from 4000 to 500  $\text{cm}^{-1}$  with a resolution of 8  $\text{cm}^{-1}$  with a FTIR Spectrometer (Bruker Equinox 55) using KBr pellets of freeze dried FA samples.

**Gel Chromatography:** The nominal mass distribution was determined on a polyacrylate gel (particle size, 40  $\mu\text{m}$ ; pores, 40-80 nm range) TSK-HW-40S column (21 cm length, 1.6 cm diameter) with a simultaneous quantification of UV-Detection ( $\lambda=254$  nm) (Gamma Analysen Technik GmbH, GAT-PHD601) and DOC-Detection (Gräntzel, Thinfilm-UV-TOC with IR-Detector Siemens, Ultramat 5E). Samples with 5.0 mg/L of DOC after filtrating with 0.45  $\mu\text{m}$  polycarbonate filter were chromatographed with 0.028 M phosphate buffer as mobile phase with a flow rate of 1.0 mL/min. All the data collected are recorded on a PC. Details of chromatographic system were presented elsewhere<sup>15,16</sup>.

**Chlorination:** The solutions of FA (3.0 mg/L) were reacted with hypochlorite solution (as 10 mg  $\text{Cl}_2/\text{L}$ ) at pH=7.0. The reactions were completed by adding of  $\text{Na}_2\text{S}_2\text{O}_3$  after 48 h. The adsorbable organically bound halogens (AOXs) were analysed according to German standard methods<sup>17</sup>. The effect of ozone on organic halide formation of FA was investigated with respect to chloroform. Quantitative analysis of THM was done on a GC/ECD- System (Chrompack CP 900). Error of the method was  $\pm 8\%$ .

**Flocculation:** Flocculation is performed with polyaluminiumchloride (PAC) at a dosage of 3.0 mg Al/L. The DOC concentration of samples was 4.0 mg/L. The experiments were carried out following the standardized procedure in Engler-Bunte-Institute<sup>18</sup>. After allowing the flocks to grow for 24 h, the solutions were filtered using 0.45  $\mu\text{m}$  polycarbonate filter. The aluminium remaining in solution was determined by electrothermal AAS.

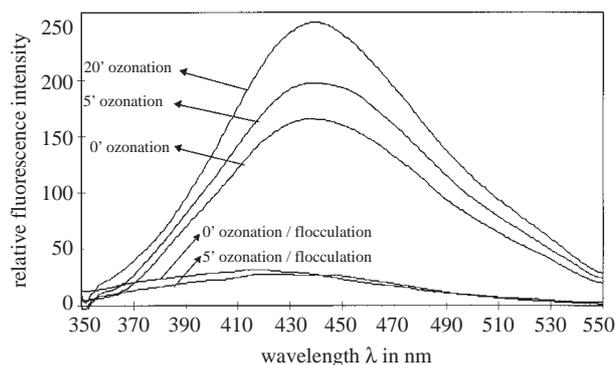
## Results and Discussion

**Physical/Chemical and Spectroscopic Characterization of Ozonated FA:** After ozonation, decrease in DOC concentration was small (Table 1). The results showed that ozonation of FA led to a much larger decrease in UV absorbance with compare to the removal of DOC. The decrease of UV/Vis absorbance at 254 nm and at 436 nm with increasing ozone concentration can be attributed to the degradation of the double bonds and oxidation of reactive chromophoric groups such as  $-\text{C}=\text{O}$  and  $-\text{NO}_2$ <sup>19</sup>.

**Table 1.** Effects of ozonation on DOC and on specific spectral absorbance coefficients at  $\lambda= 254$  nm (SAC<sub>254</sub>) and at  $\lambda= 436$  nm (SAC<sub>436</sub>)

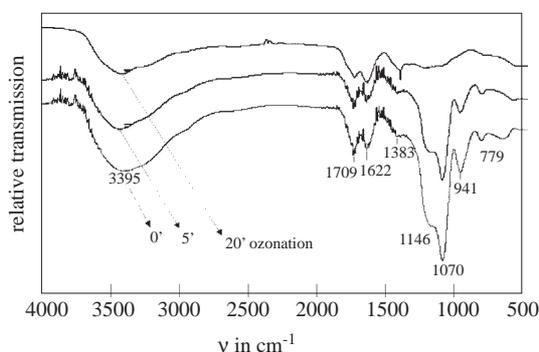
parameters	before O <sub>3</sub>	5 min O <sub>3</sub>	20 min O <sub>3</sub>
DOC - elimination grade (%)	0	1.5	5.0
SAC <sub>254</sub> - elimination grade (%)	0	10	40
SAC <sub>436</sub> - elimination grade (%)	0	23	53

Fluorescence is a typical property of humic and fulvic acids. The fluorescence intensities of unozonated and ozonated (18.94% and 51.52% for 5 and 20 min ozonation times) FAs showed that ozonation caused to increase of the fluorescence intensities in both ozonation times (Figure 2). The increase of fluorescence of ozonated samples can be attributed to the association of the fluorescent structures, which may be produced by the partial oxidation of nonfluorescent chromophores with ozone. The flocculation of FA resulted in significant reductions of fluorescence intensities in both ozonated (86%) and unozonated (84%) samples and positions of emission maximum exhibited a blue shift.



**Figure 2.** Fluorescence emission spectra of ozonated and ozonated/flocculated FA

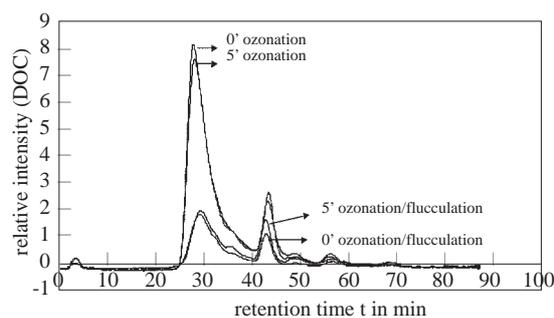
The functional groups of FAs were determined by infrared spectroscopy. Absorption bands of FA were compared with the data of aquatic HS collected by Abbt-Braun<sup>20</sup>. The broad bands around  $3400\text{ cm}^{-1}$  are due to O-H stretching bonds of phenolic structures and alcohols and N-H stretching band of amines and amides (Figure 3). The absorption band at  $1709\text{ cm}^{-1}$  is very likely caused by the C=O stretch vibration of acids, esters, aldehydes and ketones. The second band at  $1622\text{ cm}^{-1}$  is typical for the bog water FA, which is due to C=C stretching vibration of unsaturated (conjugated ketones) and aromatic structures (conjugated phenyl group). The C=O stretching frequency (around 1620) is characteristic in amides or quinonoid structures of FA. The C-O stretching bands of polysaccharide structures appear around  $1070\text{ cm}^{-1}$ . The intensities of absorption bands of FA decreased with increasing ozonation time. It can be shown by IR-spectra of ozonated samples that ozonation leads to decrease of the double-bond character and the aromatic character but not strong as much as C-O stretching bands of polysaccharides.



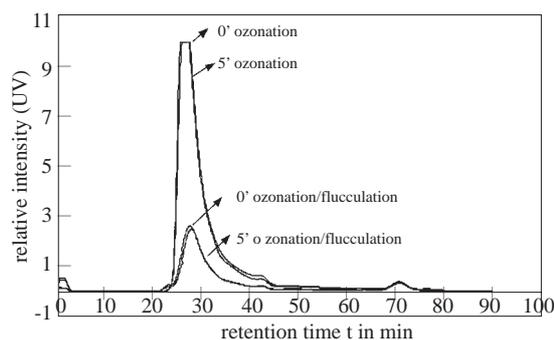
**Figure 3.** IR-spectra of HO10 FA

**Chromatographic Characterization of Ozonated FA:** The characterization of the DOC after ozonation and ozonation/flocculation was done by gel permeation chromatography. The apparent molecular

weights (AMWs) of FA fractions were determined with integrated areas under gel chromatograms and calibrated with polyethyleneoxides (PEOs). In gel chromatograms, the fractions of FA with high molecular weight (HMW) ( $t_R= 23$  min to about 38 min) show a relatively sharp peak, whereas the low molecular weight (LMW) fractions were broadly distributed. As the retention time increased, the distribution of DOC shifted from HMW fractions toward intermediate and smaller ones due to elution procedure of gel chromatography (Figure 4)<sup>21</sup>. A similar chromatogram was seen in the UV-detection (Figure 5). The pronounced sharp peaks having  $t_R= 45$  min (Figures 4,5) are LMW organic matters which are UV-inactive. In Table 2, the results of the ozonated and unozonated FAs obtained by gel chromatograms are summarized. After 20 min of ozonation, a significant part of the high molecular weight substances were broken down into smaller molecules (AMW: 709 g/mol), which were seen at higher retention times in the LC/DOC chromatogram as stated elsewhere<sup>16</sup>. There is a loss of organic carbon from all molecular size fractions, which can be attributed to organic carbon oxidation to produce either volatile organics or CO<sub>2</sub>. The LC/UV chromatogram of 20 min ozonated FA has a weaker shoulder than 5 min ozonated FA<sup>16</sup>. Initial results compared to UV spectral absorbances indicated that about 85.6% SAC<sub>254</sub> was diminished after 20 min ozonation (Table 2). The decrease in the UV absorbance at 254 nm can be interpreted as being due to the destruction of the HMW fraction of FA containing double bonds and the chromophores.



**Figure 4.** LC/DOC chromatogram of ozonated and ozonated/flocculated FA



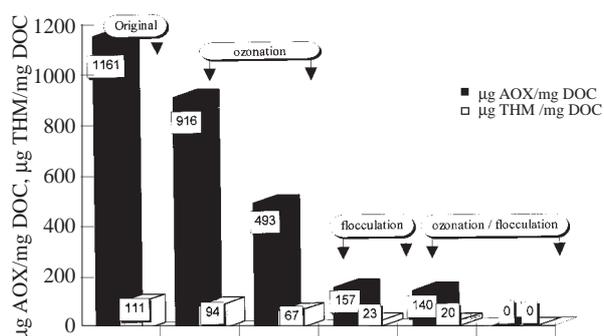
**Figure 5.** LC/UV chromatogram of ozonated and ozonated/flocculated FA

Ozone leads to changes in the high molecular weight fraction by breaking down the molecules to smaller pieces and by the introduction of polar carboxylic groups that do not contribute to reaction with aluminium<sup>22</sup>. The results in Figure 4 reveal that the DOC removal may be reduced by flocculation of ozonated samples, but UV reduction of ozonated samples by flocculation was better than unozonated ones (Figure 5).

**Table 2.** The results of the gel chromatograms of FA with DOC and UV detections.

Parameters	0 min ozonation	5 min ozonation	20 min ozonation
HMW fraction			
$t_R$ (min)	28.46	28.86	29.79
DOC (mg/L)	3.45	3.05	1.77
% of cDOC	51	45	41.5
SAC <sub>254</sub> (1/m)	58.32	56.63	8.39
% of cSAC	80	81	77
MW (g/mol)	926.8	855.13	709
LMW fraction			
$t_R$ (min)	44.68	44.53	43.88
DOC (mg/L)	0.66	0.69	0.34
% of cDOC	10	10	8
SAC <sub>254</sub> (1/m)	2.86	2.90	0.91
% of cSAC	4	4	8.3
MW (g/mol)	35.5	36.6	41.7

**Effect of Preozonation on AOXFM and THMFP:** AOXFM and THMFP were significantly reduced by flocculation following ozonation or flocculation alone with increasing ozonation time (Figure 6). This might be due to the oxidation of hydroxylated aromatic rings with two free meta-positioned OH-groups during ozonation. These kind functional groups are potential active sites for haloform formation<sup>8</sup>.

**Figure 6.** Effect of preozonation and flocculation on the formation potential of AOX and THM

## Conclusions

The results of this study can be concluded as follows:

After ozonation, the DOC concentration was reduced to a small extent. The UV/VIS absorbance was decreased to a greater extent. These results and IR spectra show that the reactive functional groups like ketones, aldehydes and double bonds are slightly oxidized by ozone.

Ozonation produced moderate changes in the molecular weight distribution of FA. The apparent molecular weight distribution of ozonated FA changed slightly, whereas the high molecular weight fractions were eliminated after flocculation followed ozonation.

Ozonation reduced the concentration of chlorination byproduct precursors in HS. The AOXFP and THMFP were significantly decreased in ozonated samples. This might be due to the oxidation of hydroxylated aromatic rings with two free meta positioned –OH groups during ozonation. The remaining DOC of the ozonated samples showed less AOXFP and THMFP when subsequent flocculation was carried out.

Therefore, it can be assumed that the high molecular weight fractions contribute to a high extent to the THM and AOX formation.

Fulvic acids are resistant to ozonation. Some functional groups were oxidized. The complete elimination of FA is not possible by using only ozone.

## Acknowledgement

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## References

1. A. N. Breemen, T. J. Niewstand and G. C. Meent-Olieman, **Wat. Res.** **13**, 771-779 (1979).
2. M. Schnitzer and S. H. Kahn, "Humic Substances in the Environment", M. Dekker, New York, 1972.
3. F. J. Stevenson, "**Humic Chemistry, Genesis, Composition, Reactions**", Wiley-Interscience, New York, 1982.
4. F. H. Frimmel and R. F. Christman, "**Humic Substances and Their Role in the Environment**" in Dahlem Workshop Reports, John Wiley & Sons, Chichester, 1988.
5. E. M. Thurman, "**Organic Geochemistry of Natural Waters**", Martinus Nijhoff/Dr. W. Junk Publishers, Dordrecht, 1985.
6. J. N. Veenstra, J. B. Barber and P. A. Khan, **Ozone: Sci. Eng.** **5**, 225-244 (1983).
7. D. A. Reckhow, P. C. Singer and R. L. Malcolm, **Environ. Sci. Technol.** **24**, 1655-1664 (1990)
8. J. J. Rook, **Environ. Sci. Technol.** **11**, 478-482 (1977).
9. M. M. Edwards, J. E. Benjamin and J. Tobiason, **J. AWWA.** **86**, 105-116 (1994).
10. D. M. Owen, G. L. Amy, Z. K. Chowdhury, R. Paode, G. McCoy and K. Viscosil, **J. AWWA.** **87**, 46-63. 1995.
11. R. G. Rice, **Ozone: Sci. Eng.** **2**, 75-99 (1980).
12. B. Legube, J. P. Croué, J. De Laat and M. Doré, **Ozone: Sci. Eng.** **11**, 69-92 (1989).
13. P. Bose, B. K. Bezbarua and D. A. Reckhow, **Ozone: Sci. Eng.** **16**, 89-112 (1994).
14. G. Abbt-Braun, F. H. Frimmel and P. Lipp, **Z. Wasser- Abwasser-Forsch.** **24**, 285- 292 (1991).
15. S. A. Huber, and F. H. Frimmel, **Vom Wasser**, **86**, 277-290 (1996).
16. S. Gül, G. Abbt-Braun and F. H. Frimmel, **Intern. J. Environ. Anal. Chem.** **75(3)**, 275-284 (1999).
17. **DIN 38 409**, 1991. Summarische Wirkungs- und Stoffkenngrößen (Gruppe H). Bestimmung der adsorbierbaren organisch gebundenen Halogene (AOX) (H 14).
18. M. R. Jekel, **Ozone: Sci. Eng.** **5**, 21-35 (1983).
19. L. J. Anderson, J. D. Johnson and R. F. Christman, **Environ. Sci. Technol.** **20**, 739-742 (1986).
20. G. Abbt-Braun, **Vom Wasser** **77**, 291-302 (1991).
21. R. Beckett, Z. Jue and J. G. Giddings, **Environ. Sci. Technol.** **21**, 289-295 (1987).
22. M. Jekel, **Vom Wasser.** **61**, 349-361 (1983).