

ISSN 1996-5052

Current Research in
Chemistry

Characterization of Extracted Fulvic Acids from a Dam in Notsè and the Zio River in Togo

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ABSTRACT

The aim of this study was to analyze the fulvic acid content of water sampled from an artificial lake that is a source of drinking water for the town of Notsè. The same studies were done in the Zio river. This preliminary study done on raw water samples from these hydrological sites showed that both are poor in minerals and have a COD value of about $24 \text{ mg O}_2 \text{ L}^{-1}$. The characterization of the fulvic acid extracted from these samples focused on: (i) The classification of the basis of their molecular weight and chemical components, (ii) The determination of their physical parameters under UV radiation and (iii) The effect of chlorination, 60% of the fulvic acids from the river and 40% from the lake have an apparent molecular weight of 30 kD. Their contents in carbon, hydrogen and nitrogen are similar to the contents of fulvic acids in French surface water. The UV absorbency of their solutions at 100 mg L^{-1} varied from 0.017 to $0.023 \text{ OD AF mg L}^{-1}$. The formation of trihalomethane (THM) is proportional to the concentration of fulvic acid. The result has shown that the reactivity of fulvic acid with chlorine increases with the absorbency of their aqueous solutions. However, in the Notsè sample, the reactivity varies with the apparent molecular weight.

Key words: Fulvic acids, apparent molecular weight, ultra violet radiation, chlorination

INTRODUCTION

In the tropics, surface water is often significantly loaded with natural organic compounds and the majority of these compounds are derived from humus. Jayaganesh and Senthurpandian (2010) reported that the decomposition of plant and animal residues by micro organisms produces humic substances. These humic substances are undesirable because they cause water coloration (Ibrahim *et al.*, 2008), favor the solubility of micro-pollutants such as pesticides and heavy metals and enable the formation of toxic compounds during the chlorination process (Karanfil *et al.*, 2008). Also, these humic substances raise the organic matter content to about 60% in surface waters and therefore, are a major problem in the purification of water for human consumption. Trihalomethanes (THMs) generated in the chlorination process are suspected to be carcinogenic (US EPA; Zazouli *et al.*, 2007a) and mutagenic compounds (Meier *et al.*, 1985). The Maximum Acceptable Concentration (MAC) of THMs in drinking water has recently been established in several countries and regions of the world due to their potential effect on human health. For example, Canadian drinking water quality guidelines (FPSDW, 1996) set the MAC for THMs at $100 \mu\text{g L}^{-1}$.

Surface waters have attracted much attention from water companies because of their greater accessibility than underground waters. In Togo, the company "Togolaise des Eaux" is responsible for drinking water production and distribution. Surface waters are more used for this purpose. The treatment involves flocculation/decantation, filtration with sand and chlorination. The major production of THM occurs during the chlorination stage which the humic substances that were not removed in the flocculation/decantation stage are oxidized.

This study has reported the characterization of fulvic acid at two hydrologic sites in Togo and the effect of chlorination on these waters. Waters from the artificial lake at Notsè and the Zio river were selected for two reasons:

- The artificial lake is used for drinking water production in Notsè town
- There is a future plan to build a dam on the Zio river to increase the supply of drinking water to Lome and its suburbs

MATERIAL AND METHODS

Sampling sites and procedures: The Notsè lake lies at about 90 km to the north of Lome and has a capacity of about 170.000 m³. The samples were collected at the entrance of the treatment plant where the water flows by gravity at a rate of 110 m³ h⁻¹ through a 3 km long pipe.

The Zio river is 15 km from Lome and the samples were collected near a bridge on the Lome-Tsevie road.

Humic substance extraction: The humic substances were extracted using a modified method reported by Thurman and Malcolm (1981). The samples were filtered on cellulose filter paper (Whatman) instead of the reported silver filter. All organic and mineral particles were removed during this process.

The method of extraction consists of adsorption at pH 2 of humic substances on an XAD 8 resin followed by elution with sodium hydroxide. Then, fulvic acids are separated from humic acid at pH 1, purified and freeze dried. The adsorption and elution were carried out in a 3.5 cm diameter, 71 cm long column containing 41 cm of resin. The flow rate was 1.6 L h⁻¹.

Chemical and physical characterization: The characterization was carried out at the Pierre et Marie University in Paris according to French Norms AFNOR. Fulvic acid concentration in the stock solution was 100 mg L⁻¹. An UV-Visible spectrophotometer (spectronic 6001) was used to measure molecular absorption. We measured the absorption of total fulvic acid (100 mg L⁻¹) and four fractions of fulvic acid based on their molecular weights. The measurements were carried out at a single wavelength of 254 nm for total fulvic acid while a wavelength range of 200 to 400 nm was used for the four fractions of fulvic acid.

The chlorination of fulvic acid was done at room temperature (about 30°C) in a phosphate buffer (pH = 6.9, ionic strength J = 0.02) by addition of 15-20 Cl₂ mg L⁻¹. To stop the reaction, excess sodium sulphite is added to the solution. THMs were then extracted from the samples by addition of 3 mL of pentane to 60 mL of the obtained solution and then quantified using gas chromatography (Varian 4400) in a glass column (2 m long and a diameter of 1/4 inch) filled with 1.5% OV 101 and 6% OV 201 on a chromosorb WHP 80-100 under the operating conditions indicated in Table 1.

RESULTS

Surface water characteristics in Togo: Different characteristics obtained from the analysis of the sampled surface waters are summarized in Table 2. The pH values ranged from 7.0 to 7.8 and are similar to those generally reported for natural surface waters (Teksoy *et al.*, 2008; Rodriguez *et al.*, 2004; Zazouli *et al.*, 2007b). Our analysis showed that conductivity was low for all samples.

Organic matter was quantified on the basis of the permanganate index and Chemical Oxygen Demand (COD).

Humic substances extracted: The results of the extraction of humic substances (fulvic acid) are indicated in Table 3. The concentration of fulvic acid extracted from the Notsè samples varied between 2.32 and 2.63 mg L⁻¹. There was a significant variation of concentration in the fulvic acid in the samples from the Notsè dam in dry and rainy seasons.

Physical and chemical characteristics of the fulvic acids: Our studies were focused on the elementary composition and absorption at 254 nm of fulvic acid extracted from the river Zio and the artificial lake at Notsè. The results of elementary composition obtained for two extracts of fulvic acid from the river Zio and three extracts of fulvic acid from the lake at Notsè are shown in Table 4. The most important components of extracted acids are carbon (50%), hydrogen (4-5%) and nitrogen (1.1-1.3%).

The result of absorption measurement showed that the absorption of the sample from the Zio river varied from 0.54 to 0.90 OD FA mg L⁻¹. Similar values were obtained for the sample from

Table 1: Operating conditions of chromatography

Parameters	Values
Oven temperature (°C)	50
Injector temperature (°C)	200
Detector temperature (°C)	250
Gas vector N ₂	30 mL min ⁻¹
Injection volume	1 µL

Table 2: Physical and chemical characteristics of the samples

	Zio water	Notsè dam water
Temperature (°C)	24.0-28.0	24.0-30.0
pH	7.0-7.7	7.0-7.8
TAC (meq L ⁻¹)	1.0-1.2	1.1-1.6
Ca ²⁺ (mg L ⁻¹)	7.6-9.2	9.6-12.8
Mg ²⁺ (mg L ⁻¹)	6.1-11.0	6.1-9.9
Total Fe (mg L ⁻¹)	2.8-3.8	0.7-1.9
Conductivity (µS cm ⁻¹)	98.0-122.0	112.0-140.0
Cl ⁻ (mg L ⁻¹)	2.5-3.8	3.0-4.0
SO ₄ ²⁻ (mg L ⁻¹)	9.1-13.1	3.6-4.0
NO ₃ ⁻ (mg L ⁻¹)	1.8-3.0	0.9-1.2
COD (O ₂ mg L ⁻¹)	Dec-34	18.0-28.0
permanganate index (O ₂ mg L ⁻¹)	5.0-11.9	5.9-7.0
SiO ₂ (mg L ⁻¹)	14.2-23.0	12.0-14.0
Phosphorus (P ₂ O ₅ mg L ⁻¹)	0.2-0.4	0.2-0.5

Table 3: Humic substance extraction yields

Sites	Extracts	Quantity of fulvic acids extracted per liter of water used (mg L ⁻¹)
Zio river	FAZ ₁	4.72
	FAZ ₂	2.58
	FAZ ₃	3.70
	FAZ ₄	4.65
	FAZ ₅	1.36
	FAZ ₆	1.32
Notsè dam	FAN ₁	2.47
	FAN ₂	2.63
	FAN ₃	2.49
	FAN ₄	2.39
	FAN ₅	2.37
	FAN ₆	2.36

FAZ: Fulvic acids from Zio river, FAN: Fulvic acids from Notsè dam

Table 4: Primary composition of fulvic acids extracted

Extracts	Carbon (%)	Nitrogen (%)	Hydrogen (%)
FAN ₁	50.24	4.81	1.14
FAN ₂	50.20	4.81	1.18
FAN ₃	51.01	4.88	1.21
FAZ ₁	49.00	4.66	1.29
FAZ ₂	49.39	4.22	1.27

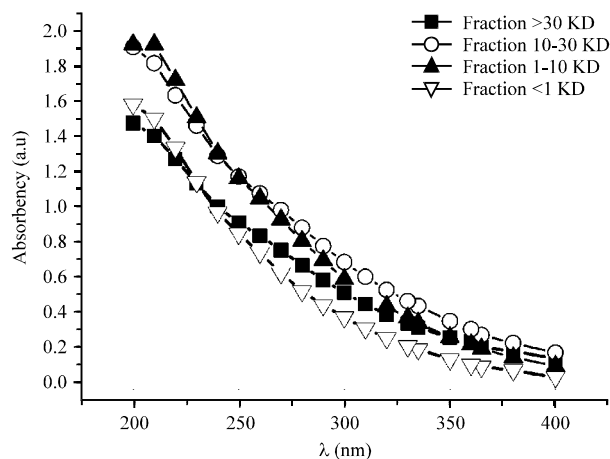


Fig. 1: Absorbency values as a function of wave length (200-400 nm)

the artificial lake (0.61 to 0.77 OD FA mg L⁻¹). The absorption values decreased in for the four fractions of fulvic acid solution between 200-400 nm (Fig. 1). The same decrease was observed in the absorption values for total fulvic acid.

The results of chlorination are shown in Table 5. From these values we noticed that reactivity with chlorine was proportional to the absorption at 254 nm. The relationship between UV absorbance at 254 nm and chlorine demand is shown in Fig. 2.

Table 5: Result of chlorine demand, absorbance and permanganate index

Samples of fulvic acid (100 mg L ⁻¹)	Chlorine demand (Cl ₂ mg L ⁻¹)	Absorbance at 254 nm (OD AF mg L ⁻¹)	Permanganate index (O ₂ mg L ⁻¹ AF mg L ⁻¹)
FAZ1	0.90	0.023	0.61
FAZ2	0.75	0.020	0.49
FAZ3	0.78	0.021	0.50
FAZ4	0.82	0.022	0.57
FAZ5	0.68	0.019	0.44
FAZ6	0.54	0.018	0.43
FAN1	0.77	0.022	0.44
FAN3	0.75	0.021	0.49
FAN4	0.70	0.020	0.47
FAN5	0.65	0.020	0.47
FAN6	0.62	0.019	0.43

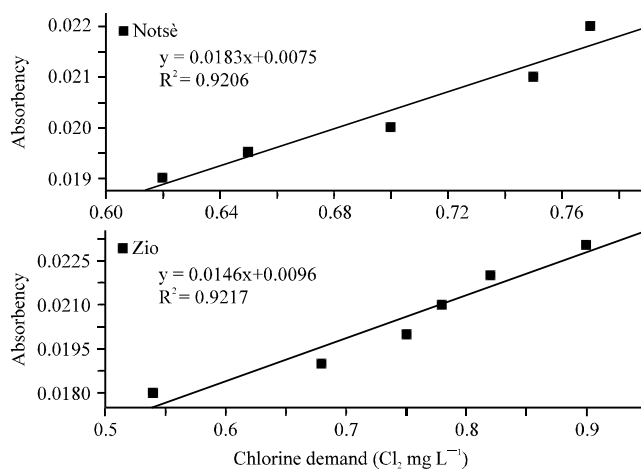


Fig. 2: Relationship between chlorine demand and absorbance at 245 nm

The extracted fulvic acids have sites that react with chlorine and potassium permanganate and the chlorine reactive sites were quantified based on the amount of chlorine required.

The chlorine demand was established for a 72 h period. The quantity of chlorine required varied from 0.62-0.77 Cl₂ mg L⁻¹ FA (Notsè) and from 0.54-0.9 Cl₂ mg⁻¹ FA (Zio). Chlorine demand was higher for fulvic acid extracted during the rainy season (FAZ1→6, FAN1→4).

As for chlorine demand, we also observed that the number of oxidable sites indicated by the permanganate index was also proportional to the absorption values (Table 5).

Chlorination of fulvic acid samples from Notsè dam: Solutions of 1-20 mg L⁻¹ of fulvic acid extracted from the sample from the artificial lake were treated with chlorine at room temperature (about 30°C). Trihalomethanes and bromoform were monitored.

Figure 3 shows the kinetics of the formation of THM for chlorination experiment on fulvic acid extracted from the Zio river and Notsè dam. After 5 h, the concentration of THMs was 13 µg L⁻¹. Thereafter, THMs were produced slowly during 5 days reaching a plateau thereafter. In the same conditions, more THMs were produced from fulvic acid from the Zio.

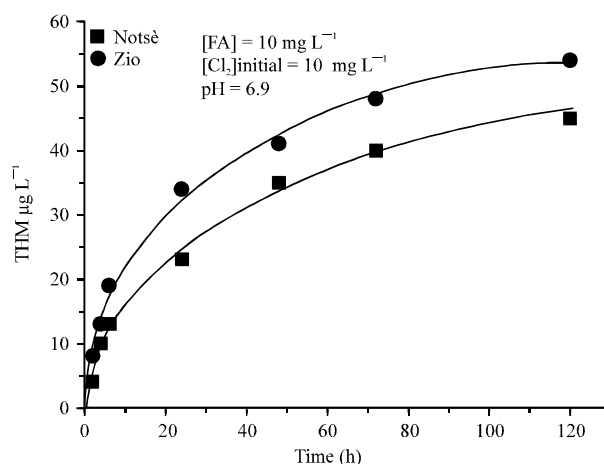


Fig. 3: Formation of THM from chlorination of fulvic acid material extracted from Notsè dam and the Zio river

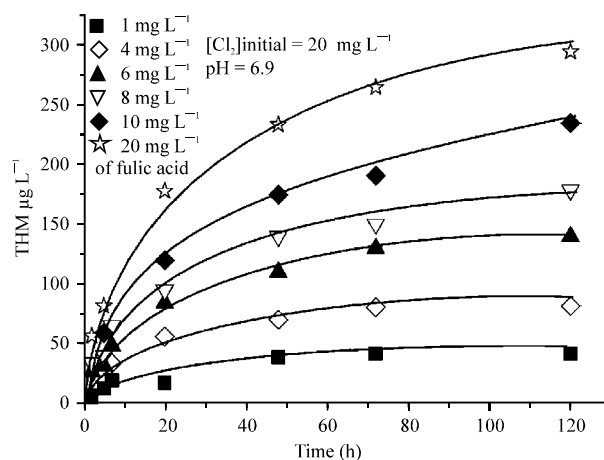


Fig. 4: Kinetics of THM production at different concentrations of fulvic acid

The evolution of THM production as a function of time at different fulvic acid concentrations is shown in Fig. 4. After 50 h, there was no significant increase in THM production when the fulvic acid concentration was varied from 1 to 6 mg L⁻¹. The addition of 20 mg L⁻¹ chlorine was probably sufficient to transform, over a 50 h period, all the THM precursors in a solution containing up to 6 mg L⁻¹ of fulvic acid. However, the addition of the same amount of chlorine (20 mg L⁻¹) was not sufficient to transform the THM precursor in a solution containing more than 8 mg L⁻¹ of fulvic acid.

The estimation of the amount of bromoform produced was achieved with a 20 mg L⁻¹ fulvic acid solution. The results obtained are presented in Fig. 5. The production of bromoform was low for the fulvic acids extracted from all samples compared to THM produced. Less than 7 µg L⁻¹ of bromoform was produced over a period of 120 h. For the chlorination of fractionated fulvic acids, 20 mg L⁻¹ of chlorine was added to a volume containing 10 mg L⁻¹ of fulvic acid from each of the four fractions. Figure 6 shows the result of this study.

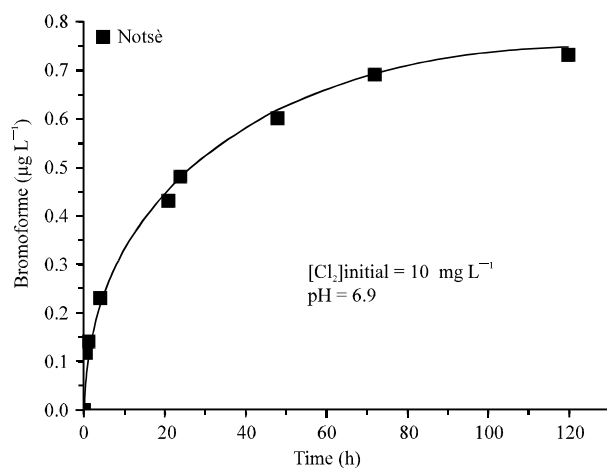


Fig. 5: Kinetics of bromoform production

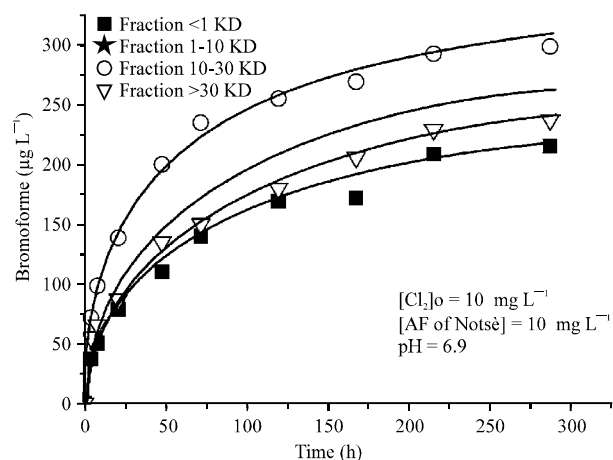


Fig. 6: Kinetics of THM production as a function of molecular weight of fulvic acids

DISCUSSION

Conductivity is lower for all samples confirming the low mineral content of these waters as supported by the low concentrations of different ionic compounds.

The COD values were similar for the samples collected in the artificial lake at Notsè but they are slightly different from COD values of the samples collected in the Zio river. The COD values are two to four times higher than the permanganate index. The concentration of silica present as SiO₂ is high in samples collected from the Zio river probably because of the influence of gravel quarries along the river.

The amounts of fulvic acid in samples collected in the Zio River during the dry season (FAZ5, 6) are significantly lower than the corresponding amounts obtained from samples collected during the rainy season (FAZ1, 2, 3, 4). This difference can be explained by the large quantity of humic matter brought in by stream water in the rainy season. In the case of the lake samples, we assumed that the low concentration of fulvic acid, even in the dry and rainy seasons, is caused by the decantation that removed a significant part of organic compounds from the

water during transit from the dam to the treatment plant. This explains the lower concentration of humic substances in these samples compared to the Zio river samples.

According to the result of the elementary composition, the molecular weight ratios between carbon and hydrogen, carbon and nitrogen are similar to the values reported for surface waters in Europe (Legube *et al.*, 1990).

When the fulvic acids were separated according to their molecular weights, we noticed that absorption at 254 nm mainly depends on molecular weight and this absorption is more significant for the fraction with molecular weight between 10 and 30 kD (Fig. 1).

The relation between absorption and chlorine reactivity suggests that the Optical Density (OD) values could be used as an indicator of the amount of chlorine required during sample treatment. As depicted in Fig. 3, the initial THM formation potential corresponds to the fast reacting THM precursors (Gallard and von Gunten, 2002; Von Guten *et al.*, 2001) probably in aromatic form reacting during the first hours (Grulois *et al.*, 1989). The kinetics of chlorine reactivity suggests that there are two sites of THM precursors: the fast reacting THM sites and the slow reacting sites. Boukari *et al.* (1999) reported that the fast chlorine consumption during the first minute's period of time is caused by some aromatic rings such as resorcinol they found in fulvic acid structure extracted in some waters of Togo.

Analyzing Fig. 4, we noticed that the potential for THM production depends on the molecular weight of the fulvic acids. Fulvic acids with 10-30 kD have a greater potential for THM production than those with 1 kD. However, the potential for THM production was also significant when molecular weight was varied from 1-10 kD.

CONCLUSION

Fulvic acids were extracted from samples collected at two locations in Togo where surface water is used or is expected to be used for the production of drinking water. Their recorded physical and chemical characteristics are similar to those reported for fulvic acids extracted from surface waters in Europe and North-America. The great production of THM from the chlorination of these fulvic acids could be attributed to the presence of numerous chlorine active sites. Reactivity with chlorine depends on the molecular weight of fulvic acids.

ACKNOWLEDGMENT

We would like to acknowledge all members of Laboratory of Water Chemistry at the University of Lome.

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