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# CHARACTERIZATION OF SOME TOGO SURFACE WATERS

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**ABSTRACT.** The results of this study showed that surface waters in Togo are weakly mineralized. The values of the specific conductivity at 20°C varied from 20 to 240 µs/cm. The hardness of the waters is very low (lower than 100 mg/L $CaCO_3$). Bicarbonate ions are the major alkaline species contained in these waters. The maximum concentration of nitrogen is 0.6 mg/L $N\text{-}NH_4$ and 0.8 mg/L $N\text{-}NO_3$. In addition the results show that five different surface waters contain various concentrations of fulvic acids and humic acids. Chloroform and dichlorobromomethane have been detected in chlorinated solutions of fulvic acids.

## INTRODUCTION

Surface waters contain a large number of inorganic and organic compounds either dissolved or as suspended matters. These compounds set the physical and chemical parameters of the water (pH, salinity, alkalinity, hardness, turbidity, odour, colour, etc). Some of these compounds are toxic to the aquatic ecosystems while others constitute nutrients for the aquatic micro-organisms, and still others represent disturbing or unwanted elements for water treatment. For example it is a well known fact that the presence of organic matter and of nitrogenous and phosphorous minerals in a water can trigger off the eutrophication of the water [1-3].

Among the organic compounds found in surface waters, humic substances stand for the most important part. Indeed humic substances contain in average between 30 % and 50 % of dissolved organic carbon, and at times, up to 90 % in some very coloured waters [4]. Humic substances originate from biological and chemical degradation of animals as well as vegetables. Little is known about humic substances due to their complex structures. These compounds can be defined as macromolecules composed of simple aromatic nuclei or substituted by alkyl, carboxylic and hydroxyl groups. Humic substances contain also in their structure polycyclic groups, polysaccharides and amino acids [5,6].

Humic substances are responsible for the light yellow colour of surface waters. They contribute, through the formation of complexes, to the transportation of organic and mineral micropollutants (heavy metals, pesticide, etc) into the waters [7] and after chlorination lead to the release of many organochlorinated compounds some of which (trihalomethanes) are mutagens [8-11] in the water. Chloroform and dibromomethane have been detected in chlorinated solutions of humic substances extracted from Togo surface waters. The same compouds have been also detected in the raw water treated with chlorine [12,13]. Chloroform concentration in treated water ranged from 40 to 50 µg/L but it could reach 100 µg/L in parts of water distributing systems.

For some years, research work has been undertaken in our labolatory on surface waters characterization. Most of the inorganic compounds commonly encountered in surface waters have been analysed, the aquatic humic substances have been extracted and their characterization and reactivity with chlorine have been studied.

## EXPERIMENTAL

Our study focused on the characterization of some surface waters used in Togo. Table 1 shows the utilisation and the localization of these surface waters. In the case of surface waters utilised for the production of drinking water, the samples were collected right at the entry of the water processing factory. As for the others, the sampling has been performed at the level of the water resource not deeper than 50 cm. All the water samples were collected using polyethylene flasks. The samples were taken to the laboratory in cooling boxes and stored in a refrigerator and then analysed within 48 hours. Most of the analytical methods were taken from Stantard Methods of France Normalization Association (AFNOR) [14]. The extraction of humic substances was performed following the Thurman and Malcom method [15] with slight modification (Figure 1). The extraction comprises the concentration of humic substances on a XAD-8 resin previously purifed and the separation and purification of humic substances.

Table 1. Surface water locations and their uses.

| Water resource | Location (Town) | District | Region | Utilisation |
|---|---|---|---|---|
| Dam of Kozah (Kozah)* | Kara | Kozah | Kara | Drinking water |
| Dam of Notsé (Haho)* | Notsé | Haho | Plateaux | Drinking water |
| Dam of Glélou (Amou)* | Atakpamé | Ogou | Plateaux | Drinking water |
| Amouchi river | Amlamé | Amou | Plateaux | Drinking water |
| Dam of Aléhéridè (Bolé)* | Sokodé | Tchaoudjo | Centrale | Drinking water |
| Dam of Danyi (Tonon)* | Danyi | Danyi | Plateaux | Drinking water |
| Zio river | Tsévié | Zio | Maritime | Drinking water |
| Dam of Kpimé (Kpimé)* | Kpalimé | Kloto | Plateaux | Drinking water |
| Lac-Togo | Aného | Lacs | Maritime | Leisure |

* tributary.

Water was filtred successively through 10 μm and 1 μm membranes in order to eliminate insoluble particles. Concentration of humic substances on XAD-8 resin begins by the acidification (pH 2) of raw water followed by carbon dioxide elimination. Precipitation (pH 1) of sodium humic substances solutions allows to separate humic acids and fulvic acids which were washed, dissolved again in NaOH 0.1 N and filtered through a cationic ($H^+$) resin in order to eliminate sodium ions and liberate humic substances in acid form. Resins treatments before using are describe elsewhere [15].

The elemental analysis (C, O, H, N, and S) of the extracted humic substances were carried out in the central analysis laboratory of CNRS in Solèze (France). The analysis of the carboxylic functions was made using potentiometric titration proposed by Thurman [4]. The UV absorption was performed using a 601 Milton Roy spectrophotometer. Chlorine was prepared through the reaction of concentrated hydrochloric acid with potassium permanganate. The chlorine solutions was obtained by bubbling chlorine through 0.02 N of NaOH solution. Chlorine was determined using iodometry or by the DPD (diethyl-*p*-phenyldiamine) method [14].

Experiments for chlorine consumption were carried out in glass flasks. At time zero, a known amount of stock solution of chlorine adjusted to pH 7 was added with a microsyringe.

These flasks, containing chlorine and fulvic acid solution prepared in buffered double distilled water (phosphate buffer, ionic strength 0.02 mole/L, pH = 7), with caps closing smoothly, were wrapped in aluminium paper and then stored in an incubator set at 20 °C.

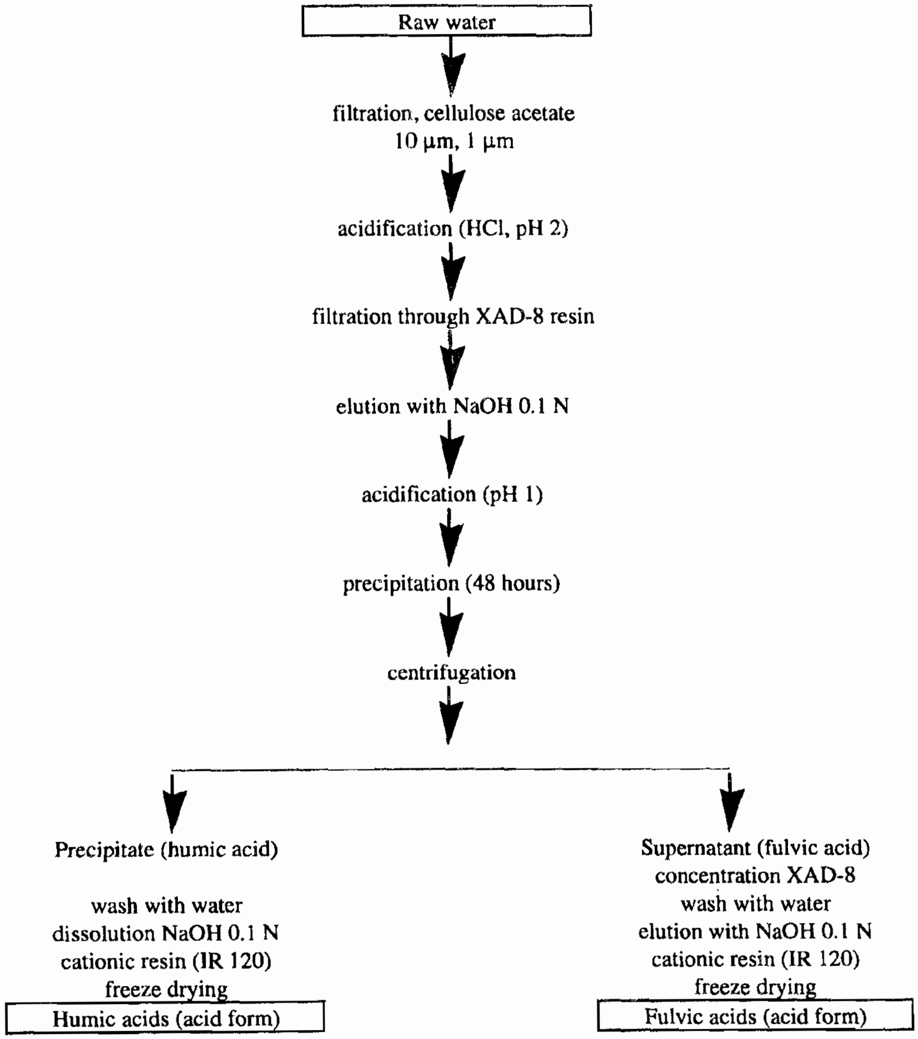

Figure 1. Extraction scheme of humic substances.

Chloroform and dichlorobromomethane were extracted by injecting 5 mL of pentane into closed penicillin flasks containing 60 mL of the reaction mixture. Chloroform and dichlorobromomethane measurement was performed by gas chromatography using a 3300 Varian gas chromatograph. A glass column (2 m, 6.35 mm) packed with 1.5 % OV 101 and 6 % OV 201 on chromosorb WHP 80-100 was utilised. The column temperature was 50 °C and the nitrogen carrier gas flow rate was 30 mL/min. The injector and the detector (ECD) temperature were 250 °C and 200 °C, respectively.

All the reagents used were of analytical grade and were used without any further purification.

## RESULTS AND DISCUSSION

In the present study the physical and chemical parameters of the waters were measured. In addition the concentration of some inorganic compounds were determined. The characteristics of the humic substances extracted from surface waters were studied .

*Physical and chemical parameters of surface waters.* The maximum and the minimum values of pH, electrical conductivity, turbidity and of the suspended matters are shown in Table 2 . The temperatures of waters are in the range 25-30 °C. The results show that the waters have pH values in the range 5.5-8.5. As for the mineral characteristic of these waters, one distinguishes two groups: the slightly mineralised waters (Aléhéridè, Glélou and Danyi) and the averagely mineralysed waters ( Kozah, Zio and Notsé). Moreover, these waters are hardly turbid during the dry season and heavier with suspended matters throughout the rainy season.

Table 2. Some physical and chemical parameters values of surface waters.

| Resource | pH | Electrical conductivity 20 °C (µs/cm) | Turbidity (NTU) | Suspended matters (mg/L) |
|---|---|---|---|---|
| Kozah - 0.2 m | 8.2 - 8.5 | 140 - 150 | 8 - 45 | - |
| Kozah - 11 m | 7.0 - 7.2 | 200 - 240 | 10 - 20 | - |
| Amouchi | 5.5 - 6.1 | - | 4 - 11 | - |
| Aléhéridè | 6.5 - 7.0 | 30 - 32 | 35 - 80 | - |
| Glélou | 6.9 - 8.3 | 45 - 54 | 7 - 17 | 3 - 8.8 |
| Danyi | 6.2 - 6.5 | 20 - 90 | - | 5 - 85 |
| Zio | 6.9 - 7.2 | 100 - 120 | - | 30 - 55 |
| Notsé | 7.9 - 8.5 | 130 - 160 | - | 15 - 32 |

The characteristics of the Kozah dam water vary with respect to the water depth. The pH decreases from the surface as the water depth increased whereas the mineralisation increases with increasing depth. As a matter of fact, this water, for some years now, has been showing signs of eutrophication characterized by an impressive production of green algae. The photosynthesis process (consumption of $CO_2$, dissolved salts, protons, etc.) results in the increment of pH of water on surface layer. Besides, the phenomena of the surface photosynthesis and the anaerobic fermentation (at a deeper level) entail a variation of the pH versus time for a given layer of water as indicated in Table 3. These pH variations of the raw water causes difficulties to adjust the processing conditions of the drinking water treatment.

The conductivity of the surface water (0.2 m) is relatively lower than the conductivity of the deeper water because of the assimilation of the inorganic salts required for the photosynthesis. The decomposition of the organic matters and the release of some inorganic compounds by sediments increase the dissolved salts concentration in deep waters. The surface waters contain calcium and magnesium less than 10 mg/L and the alkalinity of waters is essentially characterised by the presence of bicarbonates (Table 4).

Table 3. pH variation of Kozah river water versus time and deepness.

| Deepness (m) | 0.2 | 3.12 | 7.12 | 11.12 |
|---|---|---|---|---|
| Time (GMT) | pH | pH | pH | pH |
| 06 : 45 | 8.0 | 7.9 | 7.0 | 7.0 |
| 12 : 10 | 8.2 | 8.1 | 7.2 | 7.1 |
| 15 : 30 | 8.5 | 8.3 | 7.3 | 7.2 |

Table 4. Hardness and alkalinity concentrations.

| Resource | Hardness mg/L $CaCO_3$ | Calcium mg/L $CaCO_3$ | Alkalinity mg/L $CaCO_3$ |
|---|---|---|---|
| Kozah 0.2 m | 55 - 72 | - | 67 - 82 |
| Kozah 11 m | 85 - 100 | - | 92 - 125 |
| Aléhéridè | 15 - 22 | 5 - 10 | 10 - 12 |
| Glélou | 30 - 40 | 20 - 23 | 40 - 60 |
| Danyi | 10 - 40 | 3 - 20 | 12 - 25 |
| Zio | 32 - 45 | 19 - 23 | 50 - 60 |
| Notsé | 35 - 50 | 24 - 32 | 55 - 90 |

*Nitrogen-based mineral compounds.* Table 5 shows the concentrations of ammonium, nitrite and nitrate ions in the waters. The nitrite concentration is virtually non-existent in these waters except in Kozah dam water which contains very low concentration in deeper water layers. The nitrate concentrations in the surface waters are relatively lower (0.5 to 3.5 mg/L) than those in the ground water (20 mg/L) used for the production of drinking water in Lomé city [16]. However, Kozah dam water has exceptionally high nitrate concentration which is 45 mg/L. On the contrary the ammonium ions concentrations are higher in the surface waters (0.1 to 0.8 mg/L) than in the ground water in Lomé which contains not more than 0.1 mg/L of ammonium ions. In general, it can be noticed that the concentration of nitrogen-based inorganic compounds is very low in most of the studied waters.

Table 5. Nitrate, nitrite and ammonium concentrations.

| Resource | Ammonium mg/L | Nitrite mg/L | Nitrate mg/L |
|---|---|---|---|
| Kozah - 0.2 m | 0.65 - 0.80 | < 0.01 | 41 - 45 |
| Kozah - 11 m | 2.7 - 3.3 | 0.02 - 0.06 | 0.44 - 1.4 |
| Aléhéridè | 0.1 - 0.2 | - | - |
| Danyi | - | - | 1.2 - 1.8 |
| Zio | - | - | 1.6 - 3.5 |
| Notsé | 0.3 - 0.7 | - | 0.8 - 1.2 |

The nitrate ion concentration decreases from the surface down to deeper water layers. On the other hand, the concentration of nitrite ion and that of the ammonium increase in the deep water so as to reach 3.3 mg/L $NH_4$. Therefore, the results indicate an important assimilation of ammonium in the surface layer because of the photosynthesis activities and a remarkable reduction of nitrates to nitrites and then to ammonia. Akuna *et al.* [17] have reported that due to the abundance of facultative and obligate ammonium formers, the dissimilatory nitrate reduction to ammonium is the major nitrate reduction pathway in anaerobic conditions. The same authors have also reported that nitrate-ammonium reduction is favoured in carbon-rich environments. It is very likely that the nitrate-ammonium reduction conditions are achieved in deep water layer of an eutrophic reservoir.

*Chloride, sulphate, orthophosphate, iron and manganese.* The concentration of chloride, sulfate, orthophosphate, total iron and manganese (Table 6) confirm the weak mineralisation of these surface waters. The chloride ion concentrations vary from 2 to 10 mg/L, whereas the ground water in Lomé contains up to 250 mg/L of chlorides [16]. The total iron contents are relatively higher in the Zio and Danyi surface waters. Ferric iron and the suspended iron represent the most abundant forms in the surface water.

In the deep water layer of Kozah dam, phosphate concentration varies from 2 to 2.8 mg/L, iron and manganese contents reached up to 5.5 and 1.2 mg/L, respectively. Literature reports show that phosphorus may be released from sediments to oxygen poor water column [18-20]. This is also the case for iron and manganese. In the Kozah dam water, the occurrence of slime odours from 7 m downwards indicates that dissolved oxygen concentration is very low in the water layer deeper than 7 m. As a consequence, phosphate, iron and manganese concentrations are much higher in deep water layer than the ones in the surface layer.

Table 6. Chloride, orthophosphate, sulphate, total iron, and manganese concentrations.

| Resource | Chloride (mg/L) | Sulphate (mg/L) | Orthophosphate (mg/L) | Total iron (mg/L) | Manganese (mg/L) |
|---|---|---|---|---|---|
| Kozah - 0.2 m | - | - | 1.2 - 2.1 | 0.02 - 0.04 | < 0,05 |
| Kozah - 11 m | - | - | 2 - 2.8 | 5.0 - 5.5 | 0.5 - 1.2 |
| Amouchi | - | - | - | 0.1 - 0.23 | - |
| Glélou | 6 - 10 | - | - | 0.1 - 1.8 | - |
| Danyi | 2 - 7.5 | 0.5 - 1.1 | 0.15 - 1.6 | 0.5 - 2.7 | - |
| Zio | 2.5 - 3.8 | 9 - 12.8 | 0.25 - 0.75 | 2.8 - 3.8 | - |
| Notsé | 3 - 5 | 3.5 - 10 | 0.25 - 0.82 | 0.3 - 1.9 | - |

### *Extraction, characterization and reactivity of aquatic humic substances with chloride*

*Extraction and characterization.* The extraction and the characterization of aquatic humic substances were performed in the case of surface waters of Notsé, Zio, Kpalimé, Atakpamé and Lac Togo. As shown in Figure 1, the humic materials include both fulvic and humic acids. Table 7 shows the concentrations of these acids after the processing of the volumes of raw water comprised between 150 L and 200 L. These results indicate that, regardless of the origin of the water, the fulvic acids represent the most important portion with percentages often greatly superior to 50 %.

Table 7. Concentrations of fulvic acids and humic acids in some surface waters.

| Origin | Fulvic acid (mg/L) | Humic acid (mg/L) |
|---|---|---|
| Zio | 0.70 - 2.60 | 0.16 - 0.20 |
| Atakpamé | 0.40 - 1.40 | 0.35 |
| Notsé | 1.20 - 1.80 | 0.20 - 0.35 |
| Kpalimé | 0.20 - 0.60 | - |
| Lac Togo | 1.25 | 0.21 |

Considering their structure, the characterization of the humic substances is achieved by elemental analyses, UV absorption, measurement of carboxylic and phenolic functions and by the study of the reactivity of these compounds with the chemical oxidants commonly used in water treatment as chlorine or ozone.

The elemental analyses have been focused on the identification of the main elements included in structure of humic material (carbon, oxygen, hydrogen, nitrogen and sulfur). The results (Table 8), are in accordance with those of the literature [1,22,23], and clearly show the difference between the chemical composition of the fulvic acids and that of the humic acids. The carbon content is close to 50% in the fulvic acids and only 30 to 40% in the humic acids. The oxygen and hydrogen contents are higher in the fulvic acids than in the humic acids. These figures can partly account for the more polar characteristic of fulvic acids and thus why they are more soluble in water than humic acids. Besides, the residue content is higher in humic acids and varies a lot depending on the origin of the waters and period of sampling. Some authors have obtained 0.1 to 15% of residue in humic substances [22,23]. There is a probable relationship between the residue contents in humic acids and the contents of inorganic micropollutants in raw water which can precipitate during the separation of the humic substances (Figure 1).

Table 8. Elemental composition of fulvic acids and humic acids.

| Fulvic acid | C % | O % | H % | N % | S % | Residue % |
|---|---|---|---|---|---|---|
| Zio | 49.0-50.6 | 36.7-39.0 | 4.9-5.0 | 1.3-1.5 | < 0.1 | 2-11 |
| Atakpamé | 47.6 | 38.2 | 4.5 | 1.1 | 2.7 | 5.6 |
| Notsé | 48.0-50.3 | 36.4-38.2 | 5.1-5.2 | 1.4-1.5 | 0.5-2.7 | - |
| Kpalimé | 49.1-52.4 | 37.6-34.6 | 5.0-5.3 | 1.2-1.6 | 0.4 | 5.8 |
| Lac Togo | 47.6 | 36.2 | 5.0 | 1.6 | 2.3 | - |
| **Humic acid** | **C %** | **O %** | **H %** | **N %** | **S %** | **Residue %** |
| Zio | 31.0 | - | 3.6 | 1.9 | 5.7 | 33.4 |
| Atakpamé | 30.1 | 28.0 | 3.4 | 2.4 | 1.6 | 34.5 |
| Notsé | 34.5 | 29.6 | 3.9 | 2.2 | - | - |
| Kpalimé | 39.0 | 32.1 | 4.3 | 3.3 | - | - |

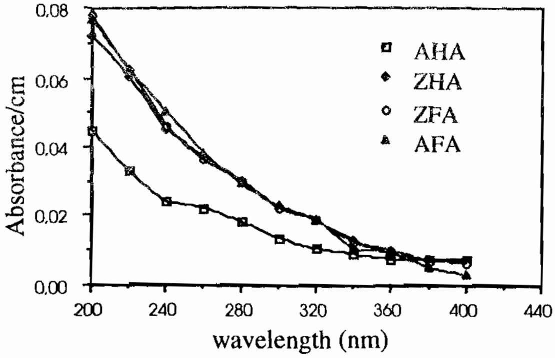

Figure 2. Absorbance *versus* wavelength. (AHA- Atakpamé humic acid, ZHA-Zio humic acid, ZFA-Zio fulvic acid, AFA-Atakpamé fulvic acid).

Figure 2 shows the UV absorption spectra for four humic substances. In the range of 200-400 nm, absorbance decreases regularly as the wavelength increases. No specific absorption band was observed. The results are in accordance with literature reports [23,24]. The absorbances showed by Zio fulvic acid (ZFA), Zio humic acid (ZHA) and Atakpamé fulvic acid (AFA) are nearly identical, Atakpamé humic acid shows the lowest absorbance values. At 254 nm, the absorbance per centimeter and per mgC/L was 0.020-0.025 for Atakpamé humic acid and 0.040-0.050 for the three other humic substances. Literature reports that, on the whole, absorbance range was 0.030-0.040 for fulvic acids and 0.050-0.070 per centimeter and per mgC/L for humic acid [25].

Table 9 shows the concentration of the carboxylic functions contained in fulvic acids and humic acids. For the fulvic acids 6 to 13 meq/gC were obtained. We note that in each water resource, the carboxylic functions content is higher in fulvic acids than in humic acids.

Table 9. Mean values of concentration of carboxylic groups contained in fulvic acids and in humic acids.

| Origin | Fulvic Acid meq -COOH /g FA | Humic Acid meq -COOH /g HA |
|---|---|---|
| Zio | 3.2 - 6.5 | 3.1 |
| Atakpamé | 5.7 | 3.1 |
| Notsé | 3.0 - 6.0 | 4.7 |
| Kpalimé | 5.7 | 4.2 |
| Lac Togo | 5.6 | - |

*Reactivity with chlorine.* For the initial concentrations of 10 mg/L of fulvic acid and 20 mg/L of chlorine (2 mg $Cl_2$/mg fulvic acid), Figure 3 shows the evaluation of the chlorine consumption. These results indicate a fast consumption of chlorine in the first minutes of the reaction, for example in the case of Kpalimé fulvic acid, about 40% of the chlorine consumed over a contact time of 120 min are consumed within 10 min. The fast chlorine consumption during the first minutes period of time is due to the activated aromatic rings such as resorcinol found in fulvic acid structure.

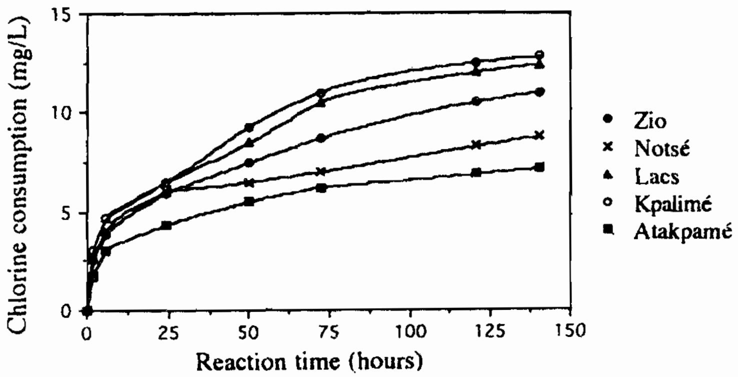

Figure 3. Chlorine consumption by some solutions of aquatic fulvic acids.

These results indicate that the kinetic of chlorine consumption depends on the origin of the fulvic acid. Indeed, after a 120 min reaction time, 60% of the applied chlorine dose are consumed in the case of Kpalimé fulvic acid as against about 30% in the case of Atapkamé fulvic acid.

Besides, we have scrutinized the evolution of chloroform formation (chloroform is the major trihalomethane formed) during the chlorination of the fulvic acid obtained from Notsé surface water. Figure 4 shows the curves for the formation of chloroform for 5 or 10 mg/L of fulvic acid, for 2 hours or 72 hours reaction time with chlorine at pH = 7. The results show that for a given concentration of fulvic acid and for a given dose of applied chlorine, the quantity of chloroform generated increases as the contact time increases. The maximum concentration of chloroform tends to be obtained as soon as the lower doses of chlorine are applied. For example, for an initial concentration of 10 mg/L of fulvic acid, the chloroform concentration obtained is 80 µg/L for 5 mg/L of applied chlorine against 125 µg/L for a dose of 20 mg/L of chlorine. It means that chloroform is obtained by the oxidation of the most oxidizable fulvic acid chemical functions which are responsible for chlorine consumption at the beginning of the reaction.

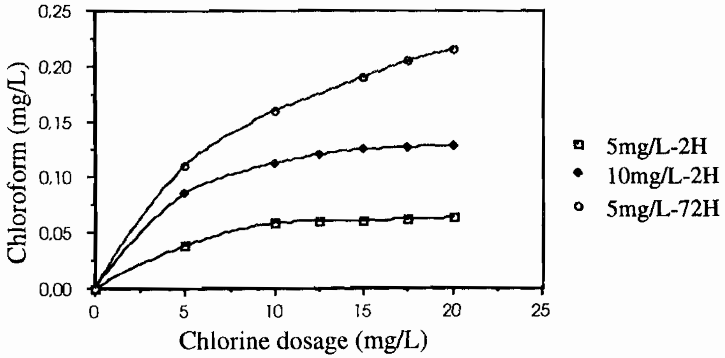

Figure 4. Chloroform production during chlorination of solutions of fulvic acid extracted from Notsé river.

Table 10 shows that 15 to 45 µg/mgC of chloroform are obtained in chlorinated solutions of fulvic acids (pH = 7; 72 hours reaction time; 20 mg/L of chlorine; 10 mg/L of fulvic acid, 20 °C). Under our experimental conditions (without any addition of bromide ions) we have highlighted the formation of dichlorobromomethane.

Table 10. Chloroform and dichlorobromomethane production during chlorination of various solutions of fulvic acids.

| Fulvic acid | Zio | Atakpamé | Lac Togo | Kpalimé |
|---|---|---|---|---|
| THM* (µg/mg FA) | | | | |
| $CHCl_3$ | 35 | 25 | 15 | 42 |
| $CHCl_2Br$ | < 0.1 | 1.4 | 1.3 | 1.8 |

*Mixture of trihalomethane.

Dichlorobromomethane, chlorodibromomethane and bromoform are sometimes detected together with chloroform in chlorinated solutions of humic substances. The concentrations of these compounds depend on that of bromide ions. In chlorinated solution of fulvic acid containing 9 mg/L of bromide, some authors [26] have measured 350 µg/L, 200 µg/L, and 40 µg/L of bromoform, chlorodibromomethane and dichlorobromomethane, respectively. In this study, neither chlorodibromomethane nor bromoform were detected. In addition dichlorobromomethane concentration was only just 2 µg/L. These observations were consistent with the idea that the bromide ions concentration in our chlorinated solutions was low.

Besides, our results did not show any relationship between chlorine consumption (Figure 4) and the quantity of THM formed. Atakpamé fulvic acid which presents a relatively slower chlorine consumption, produces a quantity of chloroform that is more important than the quantity produced by Lac Togo fulvic acid. It means that some of the fulvic acid chemical functions which are reactive with chlorine do not lead to THM formation.

## CONCLUSION

Comparison of the salinity of the studied surface waters with that of Lomé whose electrical conductivity at 20 °C range is 850 to 1000 µs/cm, led us to distinguish two types of surface waters. The slightly mineralised waters and the moderately mineralised waters. These results are confirmed by the low values of the concentration of chloride, sulphate, magnesium and calcium ions. The nitrogen-based inorganic compounds are represented by ammonium and nitrates. The humic substances extracted from surface waters are essentially carbonated with more important impurities in the humic acids fraction. The Kpalimé and Lac Togo fulvic acids present a chlorine consumption higher than the others. THM quantity formed during chlorination is not a function of chlorine consumption kinetic.

Studied surface waters exhibit the general characteristics of surface waters to be made drinkable. Considering the presence of THM precursors in these waters, it is crucial to efficiently clarify them so as to avoid the presence of important THM contents after chlorination and to also avoid the draining of micropollutants in the treated water.

## ACKNOWLEDGEMENT

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