Removal of natural organic matter by conventional and enhanced coagulation in Nicaragua

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Abstract

Enhanced coagulation was applied to raw water from a drinking water plant in Nicaragua through bench scale jar test in order to reduce the presence of natural organic matter (NOM) and decrease the trihalomethanes (THMs) formation which has been linked to carcinogenic diseases. Due to the lack of information about the presence of chlorination by-products (CBPs) like trihalomethanes, a study of their formation by varying pH, contact time, temperature and chlorine dose was also performed; following conventional or enhanced coagulation treatment. The results show that enhanced coagulation decreases considerably the formation of THMs because it reduces strongly the presence of organic matter due to the fact that higher alum doses were used in comparison with conventional coagulation utilized at the facility. The removal of dissolved organic carbon (DOC) was improved from 44% at the facility to 67% with enhanced coagulation. Trihalomethanes concentration increases drastically when extreme conditions of the four parameters evaluated were applied exceeding the maximum contaminant levels of USEPA (80 μg/L) but not the Nicaraguan target value (460 μg/L) for both coagulation types.

Keywords: enhanced coagulation, fulvic acid, humic acid, natural organic matter, SUVA, trihalomethanes.

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1 Introduction

After the discover that chlorine can react with natural organic matter present in the aquatic environment to form chlorination by-products (CBPs) like trihalomethanes (THMs) and haloacetic acids (HAAs) (Rook [1]), many researches have been carried out to reduce the presence of NOM previous to the disinfection step. Chlorination by-products are correlated with cancer diseases and also considered of high mutagenicity (Cedergren *et al* [2]; Takanashi *et al* [3]). The levels of mutagenicity in tap waters have been found 19 times greater than in raw water (Takanashi *et al* [3]); and that mutagenicity increases dramatically as a result of chlorination during the water purification process.

The concern about the health risks for the population incentived the fact that many countries have established maximum contaminant levels (MCLs) for THMs and HAAs. In 1998, the United States Environmental Protection Agency (USEPA) published Stage 1 disinfection by-products (DBPs) rule that specified the maximum contaminant levels allowable in drinking water at 0.080, 0.060, 0.010 and 1 mg/L for THMs, $HAA_{5,}$ bromate, and chlorite respectively (USEPA [4]). It also recommended enhanced coagulation (EC) as one of the best ways of removing CBP precursor material; diminishing the formation of CBPs. In 2002, USEPA [5] issued the Stage 2 disinfectants and disinfection by-products rule (DBPR), which retains the same maximum concentrations as in Stage 1. The best available technologies suggested in the Stage 2 are granular activated carbon (GAC) and nanofiltration (NF) with the reservation regarding the formation of dioxin as a by-product of GAC regeneration, while nanofiltration alone cannot effectively remove THMs and HAA_s (USEPA [5]). In Nicaragua, four years after the publication of the DBP regulations (USEPA [4]), maximum contaminant levels of THMs (0.460 mg/L) and HAAs (0.25 mg/L) were included in the guideline for drinking water (CAPRE [6]) but the values are far from those defined by USEPA in 1998 (USEPA [4]).

Since technologies such as nanofiltration, ultrafiltration, granular or powder activated carbon, etc, which are suitable for the removal of NOM, are difficult to be afforded by a developing country like Nicaragua; the use of enhanced coagulation might be a good option to decrease the presence of NOM (Edzwald and Tobiason [7]). Crozes *et al* [8] indicated that enhanced coagulation is an uncostly method of controlling CBPs formation which does not require considerable capital investment.

Enhanced coagulation is defined as an optimized coagulation process for removing NOM which is precursor of CBPs. In general, the term enhanced coagulation is applied at higher coagulant dose and lower pH values. NOM consists of a great diversity of organic compounds including simple sugars, amino acids, proteins and many others; being humic substances the major components of aquatic NOM. The presence of NOM is measured through surrogate parameters as total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}), specific ultraviolet absorbance (SUVA), colour and turbidity.

The aim of this paper was to study whether enhanced coagulation is or not appropriate for the removal of organic matter from raw water of Nicaragua drinking water plants in order to decrease the formation of trihalomethanes. In addition, a study of the impact of parameters such as pH, contact time, temperature and chlorines doses on the formation of THMs was also performed.

2 Methods

2.1 Sampling

Water samples were taken from the drinking water plant of Boaco. The conventional treatment used in the Boaco facility consists of mixing with aluminium sulphate, as coagulant, and calcium hydroxide to adjust the pH, followed by flocculation, settling, rapid sand filtration and disinfection with chlorine (Figure 1).

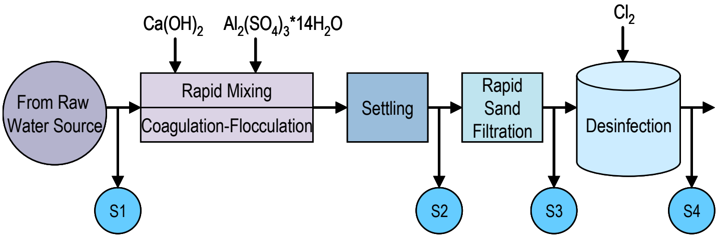

Figure 1: Diagram of the conventional treatment at the drinking water plant and the location of the sample points.

Sample 1 (S1) was used to determine the characteristics of the raw water used in the treatment plant. Water from this point was also used to analyze the NOM surrogate parameters as total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}) and specific ultraviolet absorbance (SUVA); and for enhanced coagulation tests at the laboratory using the procedures described by USEPA [4]. Samples 2 (S2) and 3 (S3) were taken to determine the removal of NOM and some other characteristics of the water after conventional coagulation was applied; and following rapid sand filtration step, respectively. Sample 4 (S4) was employed to establish the presence of THMs in the facility after disinfection with chlorine at their own working conditions. Twelve samples per point were collected over a period of 10 months during the rainy season (May-October) of 2004 and 2005. All the samples were preserved according to the analysis to be carried out by using the respective protocol of each test described in Standard Method (SM) [9] or HACH water analysis handbook [10].

2.2 Analytical procedures

Turbidity (turbidimeter HACH 2100P), colour (HACH Method 8025), water temperature (thermometer), pH (pHmeter HACH 2010), and residual chlorine

(SM 4500-Cl) were measured at the sample site. UV absorbance was determined using a UV/Vis spectrophotometer (Genesis II) at 254 nm in 1 cm quartz cells (SM 5910B) prior sample filtration with pre-washed 0.45 μm filter. Alkalinity was analyzed using SM 2320B procedure. The samples for TOC and DOC were taken using amber glass containers of 120 ml having a screw cap with Teflon septum. They were preserved with ice and were analyzed immediately after its arrival to the laboratory. The samples for DOC were filtered using pre-washed 0.45 μm fibre filter (Whatman). The Persulphate Oxidation Method (HACH 10129) was used for TOC and DOC analyzes. THMs were determined by HACH method 10132. The accuracy of both HACH methods was known by using the standard addition method. Besides, some samples were sent to Sweden to be compared with HACH methodology.

2.3 Jar test enhanced coagulation experiments

Water taken at the sampling point S1 was used to enhance coagulation experiments at the laboratory, following the procedure described by (USEPA [4]). The same coagulant type ($Al_2(SO_4)_3*14H_2O$) as that used at the drinking water plant was applied in these experiments. The common dose of coagulant at the facility is 20-30 mg/L of $Al_2(SO_4)_3*14H_2O$, depending on the turbidity of the raw water source. Enhanced coagulation experiments were performed using two Jar Test apparatuses (Phipps and Bird); initially the rapid mixing was 1 min to 100 rpm after adding the coagulants, following 20 minutes of slow mixing to 20 rpm, finally floc settling time of 30 minutes was used. The coagulant dose used in the enhanced coagulation tests depends on the TOC removal requirement; alum is applied in increment of 10 mg/L until the pH is lowered to the target pH value based on the water alkalinity (USEPA [4]). The ranges of doses used for the different raw waters were 20-70 mg/L.

2.4 THMs and the influences of pH, chlorine dose, contact time and temperature

The influences of pH, chlorine dose, contact time and temperature on the formation of trihalomethane were investigated for raw water treated with conventional and enhanced coagulation. According to the factorial design, 81 set of parameters were considered with three samples in each case. This yields a total de 243 experiments data. The description of the experiments is presented in Table 1.

For water treated with conventional treatment, the samples were taken in the facility in point S3 after conventional coagulation and rapid sand filtration. For water treated by enhanced coagulation at the laboratory, samples were taken after filtration with paper filter No. 1 (Whatman). Both water samples were treated in the laboratory using different chlorine doses, pH values, contact times, and temperatures. The ranges were chosen so that they included the values used at the facility (Table 1).

Reagent grade sodium hypochlorite was used as chlorine source. The pH was adjusted by addition of HCl or NaOH. A constant temperature was maintained using thermostats (LAUDA, M40). 300 ml of water was used for each test.

Table 1: Parameters to be evaluated.

Parameter	Level		
A: Chorine Doses (mg/l)	1	3	5
B: pH	5	7	10
C: Temperature (^oC)	20	25	35
D: Reaction Time (h)	24	50	100

3 Result and discussion

3.1 Natural organic matter (NOM) and other characteristics at the raw water

Natural organic matter is ever present in global aquatic systems, the mass concentration ranging from 0.5 to 100 mg/L of organic carbon (Frimmel [11]). They are classified according to their aqueous solubility, with fulvic acids being more soluble than humic acids. Because there is not a unique parameter that could characterize NOM, surrogate parameters such as TOC, DOC, UV_{254}, SUVA, Turbidity and Colour were measured to the raw water of the facility in order to determine the type of organic matter present.

TOC mean is 16.4±9.0 mg/L, value which is in the range of 1-40 mg/L for surface raw water (Croué *et al* [12]), but it is considered a high value and indicative of erosion problems at the watershed. It is reinforced with the high average value found for colour (97.7±90.4 mg/L Pt-Co). DOC value (7.6±5.1 mg/L) was within the typical range of surface waters (Croué *et al* [12]), DOC concentration is indicator of mass of organic material. The high SUVA (4.1±2.0 L/mg-m) value indicates that predominantly organic matter is hydrophobic DOC, mainly contains aquatic humic material of high molecular weight, and can be removed easily by enhanced coagulation (Edzwald and Tobiason [7]).UV_{254} on the other hand (0.27±0.16 cm^{-1}) was relatively low compared with water samples with similar DOC values (Croué *et al* [12]). UV absorbance at 254 nm specifies the humic or aromatic nature of NOM. A lower UV per mass of DOC would likely result in less CBP formation since UV and CBP are strongly correlated. The average value of turbidity was 35.9±43.5 NTU, alkalinity 101±28.4 mg/L, pH 8.05±0.39 and temperature 23.6±1.2^oC. According with the procedure of enhanced coagulation described in USEPA [4] when the raw water has an alkalinity ranging between 60-120 mg/L and TOC higher than 8 mg/L, the average TOC removal at the facility should be 40%, five of the twelve samples had TOC removal lower of the requirement of USEPA [4] and enhanced coagulation (Step 2) should be applied.

3.2 Natural organic matter after conventional (CC) and enhanced coagulation (EC)

Enhanced coagulation removes significantly more NOM that conventional coagulation (Table 2). It is explained by the fact that high coagulant doses (20-70 mg/L) were applied to remove natural organic matter and as result the reduction of the repulsive forces that keep the NOM particles separated; it is the opposite to conventional coagulation where doses ranging from 20 to 30 mg/L were used and thus lower NOM reduction was obtained. Increasing the coagulant doses resulting in higher amount of NOM is adsorbed due also to the high screening of electrostatic interactions between surface-adsorbed NOM molecules (Vermeer *et al* [13]). Other reasons are: raw water has an average pH of 8.05 causing that the humic compounds are more negatively charged; besides, raw water is rich in humic content (SUVA 4.1 L/mg-m), thus, more humic NOM was amenable to be removed when coagulation was applied, achieving higher removal with enhanced coagulation. Since the alum solubility is extremely low; as soon as the alum dose is augmented, the fraction of aluminium hydroxide precipitated as the hydrolyzed Al^{+3} species increases. Therefore, more humic acid can be adsorbed onto the aluminium hydroxide precipitates, causing higher removal of humic NOM.

The average reduction in DOC concentration using conventional coagulation was 44%, whereas a DOC removal with enhanced coagulation was 67%. A removal of 50% of DOC has been reported by Amy [14]; nevertheless, higher NOM removals of over 80% has been found by Parsons *et al* [15] which is quite high in comparison to the average removal obtained in this study. The degree of DOC removal by coagulation depends on the chemical characteristic of the organic matter, also of the physicochemical properties of the raw water, and type of coagulant employed.

Table 2: NOM parameters after coagulation processes.

Techniques	TOC (mg/l)	DOC (mg/l)	UV (cm^{-1})	SUVA (l/mg-m)	*Colour (mg/l Pt-Co)*
CC	8.6 ± 3.8	4.8 ± 3.5	0.06 ± 0.03	2.8 ± 1.9	*11.0 ± 10.5*
EC	*2.7 ± 1.0*	*1.2 ± 0.5*	*0.04 ± 0.02*	*1.4 ± 0.6*	*1.9 ± 1.3*

On Table 2, it can also notice that organic carbon removal was accompanied with a higher reduction in UV absorbance at 254 nm after coagulation process was applied, when compared to DOC removal, the average percentage of UV reduction was higher for both coagulation type (58% CC, 74% EC) indicating that coagulation was more effective in removing UV absorbing materials than DOC. Also, SUVA decreases considerably after coagulation to values is much lower than 3 L/mg-m, indicating that the DOC remaining is possibly of hydrophilic character, low in molecular weight, low in charge density and therefore, less reactive with chlorine because the aromatic carbon has been preferentially removed. However, because some NOM remained in the treated water after both coagulation processes, THMs can still be formed at the disinfection step.

3.3 Presence of trihalomethanes after conventional and enhanced coagulation

Comparison of the results of both coagulation procedures with the guideline of USEPA [4] and CAPRE [6] showed that the mean values of THMs found are much less that the MCLs values in both guidelines (Table 3). Nevertheless, with conventional coagulation, the MCLs of USEPA [4] is exceeding in some opportunities, which never occurred with enhanced coagulation. It is explained by the fact that in conventional coagulation SUVA average value was 2.8 L/mg-m which indicates that the remaining organic matter still present in the disinfection step is a mixture of hydrophobic and hydrophilic NOM of intermediate molecular weight, therefore, it is still quite reactive with chlorine. On the contrary, average SUVA for enhanced coagulation was 1.4 L/mg-m being the organic matter mainly non-humic, of low hydrophobicity and low molecular weight; as a consequence with lowest aromatic carbon, less reactive with chlorine, forming much lesser trihalomethanes. A mean THM level of 80 μg/L was reported by European survey of surface waters (Villanueva *et al* [16]), being lower than the average THMs concentration (57.5 μg/L) found for this facility.

Table 3: Trihalomethanes.

THMs (μg/l)	Maximum Value	Minimum Value	Mean Value	EPA MCL Guideline	*CAPRE MCL Guideline*
CC	130.0	15.0	57.5 ± 39.8	80	*460*
EC	*35.3*	*2.4*	*12.2 ± 13.4*	*80*	*460*

3.4 Trihalomethanes formation: Impact of the operating parameters

The influence of pH, chlorine dose, contact time and temperature on the formation of trihalomethane was investigated with filtered water treated with conventional or enhanced coagulation (Table 1). The database was generated using coagulant doses of 20-30 mg/L and 20-70 mg/L; DOC concentration of 1.19-2.02 and 0.76-1.23 mg/L; and UV_{254} values of 0.05-0.09 and 0.04-0.09 cm^{-1} for conventional and enhanced coagulation respectively. One example of the results is depicted in Figures 2. The lines in the figures correspond to the average values of three samples taken at different times in 2004. The red solid, blue dashed and green dash-dotted lines show the experimental results for pH 5, 7 and 10 respectively. In the figure, the effect of enhanced coagulation (EC, right side) for reducing the formation of trihalomethanes in comparison with conventional coagulation (CC, left side figure) can be observed.

Nevertheless, higher chlorine doses, pH, temperature and time increases the formation of THMs as can see in Figures 2 and 3. At Figure 2 with a chlorine dose of 1 mg/L, it can notice that at pH 10, time of 100 h; trihalomethanes lightly exceed the MCL of 80 µg/L of USEPA [4] when conventional coagulation is applied. However, with enhanced coagulation a value of 72 µg/L of THMs was found using the same conditions. On the other hand, in Figure 3 with a chlorine dose of 5 mg/L, the concentration of THMs was 158 µg/L with CC at pH 10 and time of 100 h, whereas 112 µg/L was obtained by EC under the same circumstances. Therefore, the formation of THMs was much lower with enhanced coagulation than conventional coagulation. When the chlorine dose was increased from 1 to 5 mg/L, the THMs concentration for both coagulation types exceeded the MCL of 80 µg/L of USEPA [4] in some cases. However, in any case MCL THMs (460 µg/L) used in Nicaragua was overpassed (CAPRE [6]). The higher THMs found in this study were 176 and 145 µg/L for CC and EC respectively to the extreme conditions of pH 10, chlorine dose 5 mg/L, temperature 35°C and 100 h of time (Figure 3).

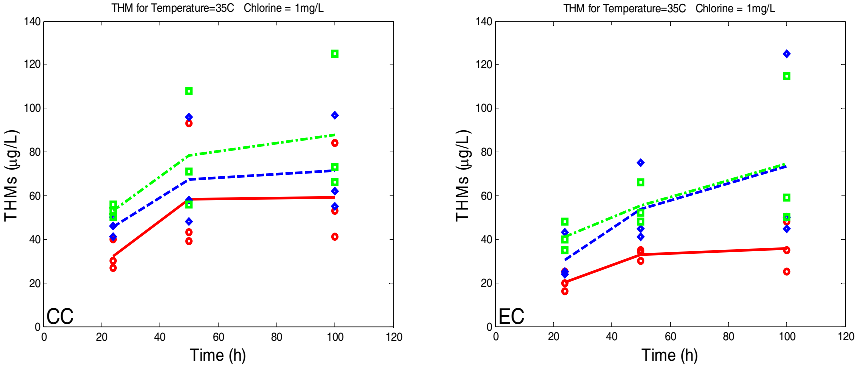

Figure 2: Influence of temperature, pH and time on THMs for chlorine doses 1 mg/L.

The tendency to increase the concentration of THMs when high values of pH, temperature, contact time and chlorine dose are used have been reported by others researchers (Xie [17]; Rodriguez and Serodes [18]; Amy *et al* [19]). It is because the high pH creates an alkaline environment which causes a fast chlorination, the high chlorine dose provokes more halogenations and opening of the aromatic structures of the still available NOM after conventional and enhanced coagulation. As a consequence of fast substitution and oxidation of the organic matter structures by chlorine, more THMs are formed. On the contrary, when pH value of 6 or lower is used, the environment is acid and the reaction is too slow to form end products as THMs, only intermediate products can be formed (Xie [17]). Also, the temperature has influenced in the formation of THMs (Figure 4(a)); high values of temperature increase the reactivity between chlorine and NOM. This reaction leads to a fast rupture of aromatic bonds, allowing halogenations and more formation of THMs as final end products. With low temperature, the formation of THMs is much lower.

THMs are typically hydrolysis products and chlorination end products (Xie [17]). Therefore, increasing the reaction time will lead to an increase in the formation of THMs. As shown in Figure 4(b), THMs increase with time, especially within the first 50 h. A similar behaviour has been observed by Krasner [20]. The reason is that a higher chlorine activity, the THMs formation rate is faster at the beginning; and decreases when the chlorine concentration decreases. THMs are continuously formed after 1-2 days but at a slower rate.

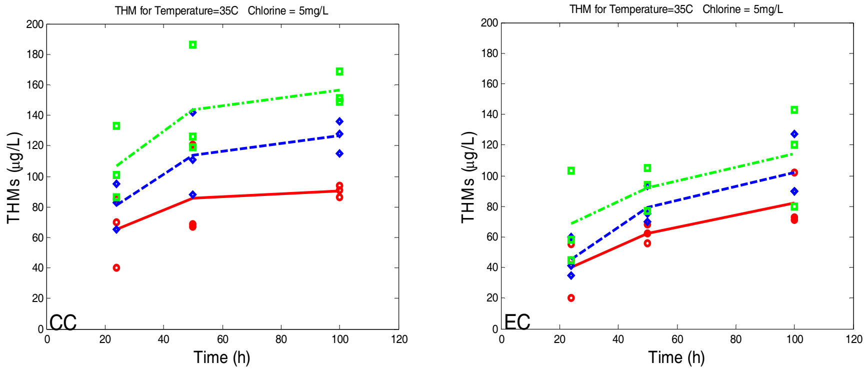

Figure 3: Influence of temperature, pH and time on THMs for chlorine doses 5 mg/L.

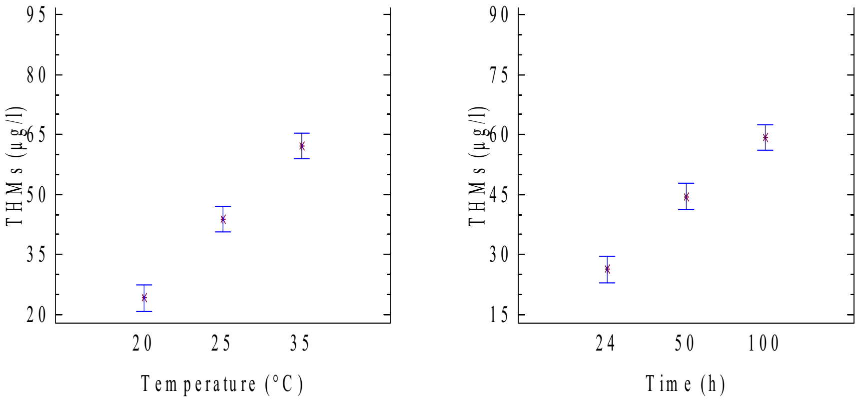

Figure 4: Influence of temperature (a) and time (b) on the formation of THMs after enhanced coagulation treatment.

4 Conclusions

Organic matter was removed easily by enhanced coagulation due mostly to humic types rich in aromatic carbon; therefore, to high coagulant doses, higher amounts of NOM are adsorbed due to the screening of electrostatic interactions between surface-adsorbed NOM molecules.

Comparison between water treated by conventional or enhanced coagulation shows that enhanced coagulation dropped considerably the THM concentration and never exceeds the existing guidelines to the ongoing working conditions of evaluated drinking water plant because the organic matter still present after the filtration step was mainly non-humic, of low molecular weight and low hydrophobicity (SUVA 1.4 L/mg-m) and consequently less reactive with chlorine.

The study of the trihalomethane formation by the variation of pH, time, temperature, and chlorine dose, using water treated by conventional or enhanced coagulation demonstrates that higher values of those parameters increase greatly the formation of THMs because to an alkaline environment result in fast chlorination provoking more halogenations and opening of the remaining NOM where THMs are formed easily as final end product.

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