**KTH Chemical Science
and Engineering**

Removal of Natural Organic Matter to reduce the presence of Trihalomethanes in drinking water

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Doctoral Thesis

School of Chemical Science and Engineering

Royal Institute of Technology

Stockholm, Sweden 2011

Akademisk avhandling som med tillstånd av Kungliga Tekniska Högskolan framlägges till offentlig granskning för avläggande av Teknologie Doktorsexamen i Kemiteknik fredagen den 18 februari 2011, kl. 10.00 i Sal K2, Teknikringen 28, KTH, Stockholm. Avhandlingen försvaras på engelska.

I am the master of my fate.
I am the captain of my soul.
William Ernest Henley

Abstract

In countries located in tropical zones, a critical task in drinking water plants is the removal of the natural organic matter (NOM), particularly during the rainy season when a lot of organic matter is transported by run-off into the water bodies. It provokes overloaded in the plants and they have often needed to be shut down. In the dry season, the NOM removal is also difficult due to its low concentration, and greater coagulant dosages are needed to destabilize the negative charge of the NOM.

In order to increase the NOM removal, synthetic polymers based on acrylamide are sometimes used as coagulant aids. However, they have been associated with Alzheimer and are carcinogenic. Therefore, the present requirement is to find new treatments affordable for the conditions existing in tropical countries. The application of green compounds has become a responsibility to guarantee the health of the population.

The situation in Nicaragua is similar to that in many tropical countries. At present, there are ten drinking water plants which use conventional treatment. Nine of them use surface water supplied by rivers, and one uses water from a lake. Many of these plants have problems of continuity, quantity, water quality, and coverage, although the water cost is low.

The removal of natural organic matter by conventional or enhanced coagulation using aluminium sulphate or chitosan as coagulant while reducing the formation of trihalomethanes (THM) was the aim of this work. Chitosan is an environment-friendly compound that can act as coagulant, flocculant and adsorbent. Adsorption with activated carbon and chitosan has also been studied. The natural organic matter in the source waters was fractionated in order to determine which fractions are removed more easily by coagulation and which are recalcitrant.

The experimental works was carried out with a period of sampling between 2003 and 2010, taking into consideration the dry and rainy seasons. The results show that conventional coagulation with aluminium sulphate is not sufficient to reduce the presence of NOM sufficiently to avoid a high level of THM in the disinfection step. The NOM removal is greatly improved by treatment with enhanced coagulation, but a significant amount of NOM is not removed, with a high THM concentration as a consequence. High NOM removal can however be achieved by enhanced coagulation and subsequent adsorption with granular activated carbon.

Chitosan has good properties as a coagulant in water with a high NOM content and performs well as flocculant. It also has a high adsorption capacity for NOM. Therefore, chitosan could be a good option as a substitute for aluminium sulphate compounds. However, since chitosan does not work properly in the dry season, when the NOM content is low, the use of aluminium sulphate in combination with chitosan should be studied in more detail. A field with a large potential is the modification of the chitosan structure to increase its capacity for NOM removal and decrease the need for aluminium sulphate. Another advantage of using chitosan is the reduction of the negative impact of shrimp and squat lobster shells on the environment.

Keyword: Aluminium Sulphate, Chitosan, Coagulation, Natural Organic Matter, Trihalomethanes

List of Papers

This thesis is based on the following papers, which are referred in the text as Papers I to VII. The papers are appended at the end of the thesis.

I.   García, I and Moreno, L. (2006). Presence of trihalomethanes in drinking water plants in Nicaragua. Journal of Water Supply: Research and Technology-AQUA. **55**, 221-231.

II. García, I and Moreno, L. (2009). Use of GAC after enhanced coagulation for the removal of natural organic matter from water for purification. Journal of Water Science and Technology: Water Supply. **9(2)**, 173-180.

III. García, I., Benavente, M. and Moreno, L. (2010). Use of chitosan as coagulant in the removal of natural organic matter from four different raw waters. Submitted for publication.

IV. García, I and Moreno, L. (2010). Removal of humic acid by coagulation and flocculation with chitosan. Submitted for publication.

V.   García, I and Moreno, L. (2010). Removal of nitrogen and carbon organic matter by chitosan and aluminium sulphate. Submitted for publication.

VI. García, I and Moreno, L. (2010). Removal of natural organic matter from water in Nicaragua to reduce the total exposure cancer risk. Submitted for publication.

VII. García, I., Benavente, M. and Moreno, L. (2010). Sorption kinetics of fulvic and humic acid onto chitosan of different molecular weights. Submitted for publication.

Comment on my contribution to the publications

Papers III and VII, the first author designed and performed the experiments and wrote the manuscript. The second author participated in the analysis of the results.

Others papers which are not included in this thesis but which were presented in conferences and appear in Peer-Reviewed International Proceedings.

I.   García, I. and Moreno, L. (2008). Use of GAC after enhanced coagulation for the removal of natural organic matter from water for purification. In Proceedings of the 3rd IWA Specialist Conference on Natural Organic Matter: From Source to Tap (NOM 2008). Bath, UK. pp. 521-531.

II.   García, I. and Moreno, L. (2007). Removal of natural organic matter by conventional and enhanced coagulation in Nicaragua. Water Resources Management IV. Kos, Greece. Edited by C.A. Brebbia and A.G. Kungolos. ISBN 978-1-84564-074-3. pp. 399-409.

III.   García, I. and Moreno, L. (2006). Use of pH, contact time, chlorine dose and temperature on the formation of trihalomethanes and some predictive models. Water Pollution VIII: Modeling, Monitoring and Management. Bologna, Italy. Edited by C.A. Brebbia and J.S. Antunes do Carmo. ISBN 1-84564-042-X. pp. 411–422.

IV.   García, I. and Moreno, L. (2005). Use of two different coagulants for the removal of organic matter from a drinking water. In Proceedings of the 3rd IWA Leading-Edge Conference on Water and Wastewater Treatment and Technologies. Paper ID: P074. Sapporo, Japan.

V.   García, I. and Moreno, L. (2004). Influence of enhanced coagulation in the removal of natural organic matter to avoid formation of trihalomethanes in a drinking water plant in Nicaragua. In Proceedings of the 4th IWA World Water Congress and Exhibition. Paper ID: 23946. Marrakech, Morocco.

VI.   García, I. and Moreno, L. (2003). Drinking water treatment plants in Nicaragua: A short review. In Proceedings of the IWA Asia-Pacific Regional Conference (WATERQUAL'03). Paper ID: 1QHLO5. Bangkok, Thailand.

Contents

Chapter 1

Introduction

1.1   Background

The lack of safe drinking water and sanitation in many regions of the world leads to the spread of many water-borne diseases that affect the population health and increase the economic burden in poor countries. In addition, the scarcity of water causes other effects on the quality of life such as carrying water to the home, which means a gender discrimination because in many communities the women are those responsible for fetching water for the home. Other effects are the loss of recreational environment because many surface water resources are polluted and a loss of human life because of water-related diseases.

Although one of the eight goals of the millennium (MDGs) is to reduce by *half the population without sustainable access to safe drinking water and basic sanitation* (Prüs-Ütsün *et al.,* 2008)*,* this compromise is far from being achieved, due to the lack of commitment of the different governments. Many developing countries have no water shortage; on the contrary they have plenty water, but, this water is being contaminated due to industrial and agricultural activities, as a result of a lack of education of the population and poor enforcement of the regulations concerning water use and waste disposal.

According to the World Water Council (2010), 1 200 million peoples do not have access to safe drinking water and 2 600 million are living with inadequate sanitation. The drinking-water crisis could become the worst crisis of humankind due to the increment in the population, changes of lifestyle, and increasing industrial and agricultural needs; all of them demanding constantly more water. In addition, the aquatic ecosystem and its species are being affected by the pollution and reduction of their habitat.

Another effect of the high water demand is that drinking water plants are overloaded in many countries, and as a consequence, the quality of the water to the consumers does not meet the requirements of drinking water. Moreover, the plants do not cover all the population with a 24 hour supply. In some cases, this becomes a justification for the consumers not to pay the cost of the drinking water, so that, less economic resources are available to improve the service. In order to overcome these deficiencies, education campaigns, protection for the watershed, and an upgrading or construction of new plants should be carried out to improve the quality of the drinking water and sanitation for the population.

In developing countries, the approach for new water systems should focus on their own sustainability, the minimal requirements of skilled personnel, low maintenance and operating costs. Besides, the use of local materials to achieve an environment-friendly

operation can be a good option instead of synthetic materials, which increase the cost, have a secondary effect on the population health and lead to environmentally negative consequences.

Nicaragua does not escape the problems mentioned previously, even though the government makes significant efforts to improve the water supply and sanitation in the country. Nicaragua is ranked as having a poor level of hygiene, but is considered to be a country with no water stress (World Water Council, 2010), which means that there is still a balance between water needs and water resources. However, an imbalance in the distribution of the water sources leads to water scarcity in some regions. Most of the population (56%) is settled in the Pacific region into which only 10% of the watershed drains, and ground water is used as a raw water source. In the Caribbean region, however, 90% of the watersheds drain while only 13% of the population lives there. In the Central region, where the hydrogeology limits the use of ground water, surface water is the main source. All the drinking water plants in Nicaragua are settled in this region, using treatment of a conventional type.

The national drinking water coverage is 80.1%, of which 95.1% is in urban areas and only 46.0% in rural areas. The total sanitation coverage is slightly more than 84.9%, 96.0% in urban and 69.1% in rural areas (Carranza and Medina, 2008). In spite of this, 7.5% of the total annual deaths (25 700 inhabitants) are related to water, sanitation and hygiene problems (Prüs-Ütsün *et al.,* 2008). Most of these deaths occur in places with a small water system where the disinfection is deficient.

High chlorine dosages are used in some drinking water plants to overcome the deficiencies in the treatment to at least ensure a supply of microbiologically safe water to the population. This fact and the increment of natural organic matter (NOM) in the aquatic resources due to rainfall increases and anthropogenic activities are becoming a critical concern, due to the formation of chlorination by-products such as trihalomethanes, which are carcinogenic substances (USEPA, 1998). An upgrading of the Nicaraguan drinking water system using new treatments is essential to meet the quality guidelines. Among the necessary improvements in the water systems are an increase in the plant capacities, a change from the use of chemical compounds to substances with a low impact on the consumers and the environment, and a good disposal of the residues; all this to the benefit of the population.

Research into the drinking water plants in Nicaragua is scarce for economic limitations. The presence of chlorination by-products is still unknown, and this was the reason for this research in order to contribute to improving the treatment by introducing new technologies suitable for the economic and social situation of Nicaragua, to reduce the risk of cancer in the population.

1.2   Objective

The work described in this thesis has as its main objective the removal of natural organic matter using different coagulation and adsorption techniques to reduce the subsequent formation of trihalomethanes. Coagulation was studied using a conventional and enhanced type with aluminium sulphate or chitosan. Adsorption experiments were performed with activated carbon or chitosan.

All the research was carried out on a laboratory scale using raw water from four of the ten drinking water plants existing in Nicaragua. Some additional experiments were performed with synthetic water.

1.3   Thesis Outline

Chapter 2 covers the theory and practice of conventional treatment, with a special focus on coagulation and adsorption topics. This chapter also explains the factors and mechanisms that influence the formation of chlorination by-products. Chapter 3 gives details of the materials and methodology used in this study and Chapter 4 presents the results and the discussion. Finally, Chapter 5 presents the conclusions and recommendations for further work.

Chapter 2

Background

The focus of this chapter is the description of the natural organic matter (NOM), the surrogate parameters used to describe the presence of NOM, some treatments used to reduce NOM, and the mechanisms that participate in the formation of chlorination by-products, especially trihalomethane (THMs).

2.1   Natural Organic Matter (NOM)

The presence of natural organic matter in the aquatic resources is not harmful, but problems arise when the source water containing NOM is treated with chlorine in the disinfection step. The organic matter reacts with the chlorine and forms chlorination by-products (CBPs) in the drinking water, such as trihalomethane (THMs) and haloacetic acids (HAAs) which have been linked to cancerous diseases (Singer, 1999).

Natural organic matter in water is a heterogeneous mixture of humic compounds, hydrophilic acids, proteins, lipids, carbohydrates, carboxylic acids, amino acids and hydrocarbons. This NOM can be present in a particulate form (POM) or in a dissolved form (DOM), and the latter is more difficult to remove from the water.

NOM can be divided into two fractions (Thurman and Malcolm 1981): the hydrophobic and the hydrophilic fraction. The hydrophobic or humic fraction of high aromaticity is less soluble in water, it has a high molecular weight, is yellow to brown-black in colour and is poor in nitrogen. The hydrophilic or non-humic fraction, on the other hand, is considered to be less reactive and rich in nitrogen, and consists of carbohydrates, lipids, hydrophilic acids, and amino acids. However, some researchers such as Owen *et al*. (1995) and Imai *et al*. (2003) have reported that the non-humic fraction reacts with chlorine and produces THMs per unit of dissolved organic carbon (DOC) to a level similar to that of the humic fraction. Each of the NOM fractions can be subdivided into acidic, alkaline and neutral subgroups.

The humic fraction consists mainly of humic and fulvic acids. Humic acid is more reactive than fulvic acid and can be removed easily by coagulation due to its higher molecular weight, larger size, and lower solubility in water, so that low coagulant dosages are sufficient to form flocs. Humic acid is characterized by its dark brown to black colour due to its double bonds. Fulvic acid is less reactive, and higher coagulant dosages are required for its removal due to its low molecular weight, smaller size and greater solubility in water. Its colour varies from yellow to dark brown. Nevertheless, Krasner *et al*. (1996) and Lin *et al.* (2000) have shown that fulvic acid has a THM formation potential analogous to that of the humic acid.

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The humic fraction corresponds to 25% of the total organic carbon on the earth and represents 50-75% of the dissolved organic carbon (DOC) in the waters (Hertkorn *et al.,* 2002). DOC concentrations in natural fresh water are commonly between 2 and 15 mg C/L (Hepplewhite *et al.,* 2004). Figure 2.1 shows the classification of the organic matter.
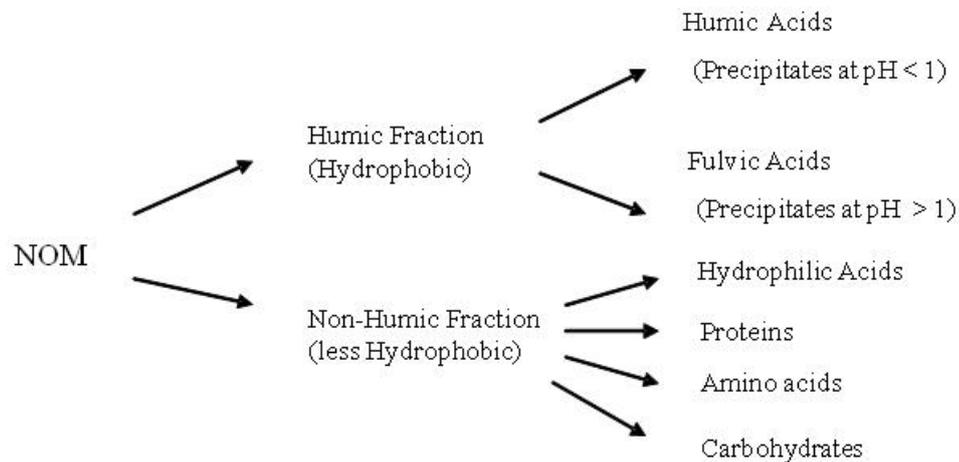

Figure 2.1 Classification of the natural organic matter.

According to Tan (2003), the type of soil and vegetation in the surrounding catchment area and seasonal variations influence the NOM in water bodies. The presence of NOM, measured as dissolved organic carbon (DOC) or dissolved organic matter (DOM), frequently tends to make the water bodies yellow or darker in colour. It has been found that there is a strong relationship between the intensity of precipitation and the NOM concentration, since the run-off leads to a higher NOM discharge from the upper part of the soil profile or percolation through the soil column. Therefore, a large amount of dark brown, organically rich water can be seen flowing from swamps and poorly drained areas into creek and rivers, especially after rainfalls. As a result, the drinking water plants in the rainy season frequently reduce their performance due to overload, and the quality standards are not achieved. Eikebrokk (2004) reported that during the last 10-20 years, the concentration of NOM has increased in the drinking water sources in Northern Europe and North America as a consequence of changing climatic conditions that intensively increase rain events.

Another classification of the aquatic humic matter is into autochthonous and allochthonous material, which is related to its formation. Autochthonous humic matter is formed in the aquatic environment from cellular constituents of indigenous aquatic organisms, whereas the allochthonous matter originates from the soil, from which it is leached by erosion into rivers, lakes and oceans (Tan, 2003). Tan (2003) also reported another type of organic matter, called anthropogenic organic matter, which is formed from agricultural, industrial and domestic waste and from other material in the watercourses. It is composed mainly of fulvic and humic acids.

Due to the heterogeneous and undefined character of the natural organic matter, it is measured through surrogate parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), specific ultraviolet absorbance at 254 nm (SUVA), colour and ultraviolet absorbance at 254 nm (UV_{254}).

Total and dissolved organic carbon are measured indirectly from the CO_2 produced by UV-oxidation or combustion of the organic matter in the water. UV and Colour are colligative properties measured as light absorbency in the UV and visible wavelength ranges, respectively. The UV absorption is linked to the amount of double bonds in aromatic rings of the organic matter. Colour is an indicator of the degree of conjugation of the complex molecules of NOM having multiple bonds with highly substituted aromatic groups and is associated with the NOM of higher molecular weight (Newcombe *et al.,* 1997). Another surrogate parameter is SUVA which is linked to the aromaticity and the hydrophobicity of the organic carbon (Eikebrokk *et al.,* 2006).

Dissolved organic nitrogen (DON) is another surrogate NOM indicator, but it is used less frequently. The importance of DON lies in the formation of nitrosamines, halonitromethanes, cyanogen-halides, haloacetroniles and other compounds which are nitrogen chlorination by-products formed when organic matter reacts with chlorine or chloramines. These nitrogen by-products (N-CBPs) had been linked with carcinogenic and mutagenic problems, even more strongly than other DBPs (Dotson *et al.,* 2009).

The presence of DON compounds in the water bodies also depends on soil erosion, catchment handle, vegetation cover, atmospheric deposition, agricultural and human activities, groundwater infiltration, and livestock wastes. For these reasons DON concentration varies significantly as organic matter of carbonaceous origin.

DON represents only 0.5-10% by weight of natural organic matter and 60-69% of the total dissolved nitrogen (TDN) in natural water (Ambonguilat *et al.,* 2006; Willet *et al*., 2004) with the exception in the deep ocean where it is about 10% (Ambonguilat *et al.,* 2006). Lee and Westerhoff (2006) found DON concentration of 0.37 mg/L of N in surface water and 0.24 and 0.18 mg/L of N in shallow and ground water respectively, and an average DON of 0.19 mg/L of N was found in the raw waters of 28 US water-treatment plants by Westerhoff and Mash (2002). Relatively higher concentrations of DON (1-2 mg N/L) can be found in surface waters around agriculture areas.

The ratio between DOC and DON determines the trend to form N-CBPs in the disinfection step (Dotson *et al.,* 2009). These authors reported that a high DOC/DON ratio has a much smaller tendency to form N-DBPs than a low DOC/DON ratio. A ratio of 18 mg C/mg N was found by Westerhoff and Mash (2002) for 28 raw waters in USA; with a range of 5-100 mg C/mg N. Lee and Westerhoff (2006) found a ratio of DOC/DON in the range of 10-30 mg C/mg N for drinking water. The DOC/DON ratio increases greatly in the hydrophobic fraction and tends to decrease in the hydrophilic fraction after treatment.

The concentration of dissolved inorganic nitrogen (DIN) can be higher; frequently between 5-10 mg N/L (Lee and Westerhoff, 2006) because nitrate is transported into the water bodies by runoff since it is repelled from the soils by anionic compounds (Martin *et al.,* 1999). In that case, DON corresponds to only 10% of the bulk TDN (Ambonguilat *et al.,* 2006).

2.2   Treatment for CBP Reduction

Eikebrokk *et al.* (2006) suggested that content of natural organic matter (NOM) has to be reduced before the disinfection step because it affects the organoleptic water properties, decreases the disinfectant power, and raises the disinfectant demand. The same authors report about other effects, which may increase coagulant demand, affect the stability and removal of inorganic particles, decrease adsorption capacity, increase the mobility of most chemical substances and produce complexes with them, form disinfection by-products (DBPs) of several kinds (when the organic matter reacts with chlorine the products are called chlorination by-products, CBPs), reduce the biostability and raise the biological re-growth in distribution systems.

Different types of treatment are used in the production of drinking water to remove the NOM from the raw water and to deliver safe drinking water to the population. These treatments also significantly affect, directly or indirectly, the formation, removal and speciation of CBPs in drinking water. The most common treatment used to reduce CBP formation consists of coagulation-flocculation-sedimentation, rapid sand filtration and disinfection. Other treatments are adsorption with activated carbon, ion exchange, electro-coagulation, bio-filtration, membrane filtration, sonochemical, and advanced oxidation; treatments that are almost impossible for developing countries to afford. After the treatment and before disinfection, the NOM still available in the water can indicate the amount of chlorination by-products to be formed in the disinfection step due to the aromaticity of the NOM fraction.

2.2.1   Coagulation

Coagulation is the process whereby a given suspension or solution is destabilized (Bratby, 2006). It occurs by neutralizing the negative charge of the particles with coagulant (Al, Fe) in order to aggregate the particles into flocs, which are removed by sedimentation, flotation and/or filtration.

According to Pertnisky and Edzwald (2006), the coagulation mechanisms depend mainly on whether turbidity or natural organic matter is to be removed. They established that for conventional turbidity removal, two mechanisms are involved. The first involves charge neutralization of the negatively charged colloidal particles by adsorption onto

positively charged coagulants species, and the second involves the enmeshment of colloids in precipitated Al(OH)$_3$ or Fe(OH)$_3$ solids.

However, Eikebrokk *et al.* (2006) pointed out that the presence of organic matter greatly affects the chemistry of coagulation. According with them, the destabilization of the colloids depends on the chemical nature and structure of the NOM. They also reported that NOM is removed by complexation reactions followed by a phase change when coagulant is added.

Gregor *et al.* (1997) established that coagulation could reduce the NOM level by four different pathways (Figure 2.2). First, NOM can combine with coagulants to form a complex and precipitate in regions of pH where aluminium hydroxide precipitation is minimal (pathway C). Cationic aluminium interacts electrotastically with anionic NOM to form insoluble charge-neutral products. NOM has a negative charge due to the presence of carboxylic (COOH), phenolic and alcoholic hydroxyl (OH) and methoxyl carbonyl groups (C=O). The carboxylic and phenolic groups have pKa values of 4-6 and from 9 to 11, respectively. Machenbach (2007) showed that humic substances have a negative charge in the range of pH pertinent to water treatment, because of the deprotonation of the functional groups available in the water.

Sweep coagulation (enmeshment, pathway A) or surface adsorption (pathway B) are the major mechanisms for NOM removal when higher coagulant dosages are applied to ensure rapid precipitation of Al(OH)$_3$. Colloidal NOM can act as nuclei for precipitate formation, or can become entrapped during floc aggregation.

These mechanisms apply mainly to the removal of colloidal NOM, typically the higher molecular weight humic acids. These acids generally have low charge densities and they therefore need lower coagulant dosages to induce destabilization. However, the more soluble fraction of NOM (fulvic acids) has a higher anionic charge density that facilitates their dissolution.

The enmeshment mechanism (pathway A), which operates most effectively on colloidal NOM, does not seem to be effective with these soluble fulvic acids. A mechanism such as charge neutralization (pathway C) reduces the presence of fulvic acids, but higher dosages of coagulants are necessary to neutralise the high anionic charge. Gregor *et al*. (1997) reported that a high coagulant dosage is necessary for the removal of soluble fulvic acids, causing a restabilisation of the humic acid colloids due to overdosing.

The fourth mechanism involves the chemical interaction of soluble NOM with soluble coagulant metal ions such as aluminium; it is called complexation/precipitation (pathway D). Gregor *et al.* (1997) explained that after the binding capacity of the NOM has been satisfied or the solubility of the metal-NOM complex is exceeded, the metal cation and the complexed NOM remain in solution. The complex does not need to be charge-neutral to precipitate.
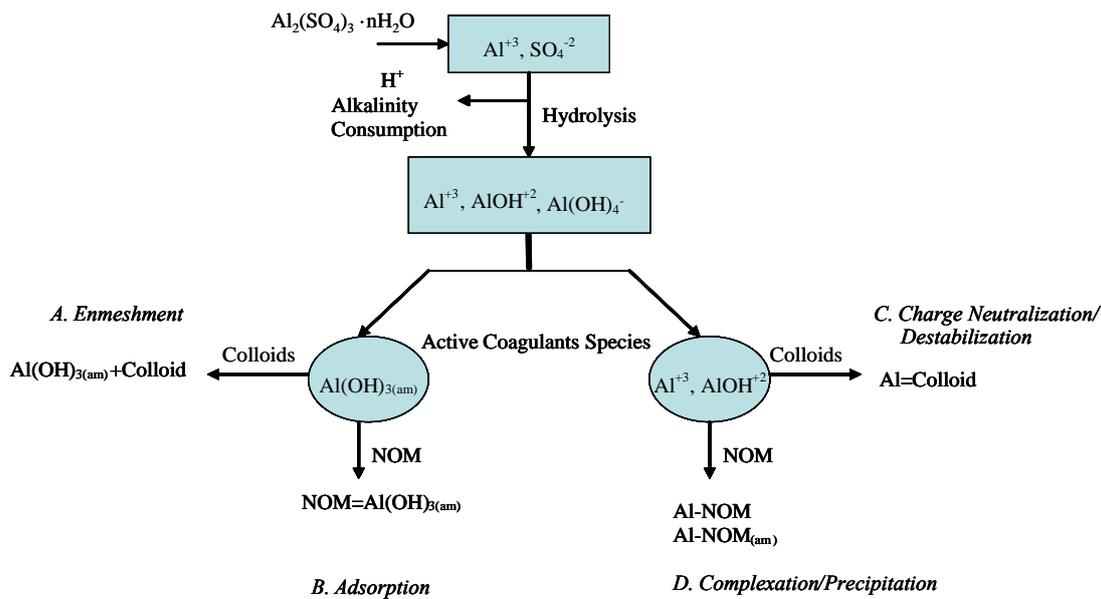
Figure 2.2 Pathways of coagulation reactions.
Source: Pernitsky, 2003.

A considerable amount of NOM can thus be removed by coagulation, sedimentation and filtration, especially at low pH (5.5 for alum) and/or higher coagulant dosages. Omelia *et al.* (1999) indicate that the dosages of coagulants required are determined by the content of NOM and to a certain extent by the turbidity. They reported that due to the negative charge carried by the NOM, there is a stoichiometric relationship between the required dose of coagulant and the NOM concentration in the water to be treated. According to Imai *et al.* (2002) the predominance of lower molecular weight materials increases considerably after coagulation.

Xie (2004) reported that the reduction in the amount of NOM after coagulation lowers the chlorine demand and chlorine dose. This can result in a significant reduction in chlorinated disinfection by-products (CBPs), but a dramatic increase in brominated CBPs may take place if bromides are present.

2.2.1.1 Enhanced Coagulation

In some cases, conventional coagulation is not sufficient to remove natural organic matter in the quantities necessary to stop the formation of DBPs. USEPA (1998), under the disinfectants and disinfection by-products (DBPR) rule, identified enhanced coagulation as one of the two best technologies to control DBPs.

The enhanced coagulation process is defined as an optimized coagulation process for removing DBP precursors or natural organic matter (NOM). In general, enhanced coagulation is practiced at higher coagulation dosages and lower pH values. Crozes *et al.* (1995) reported that enhanced coagulation is a valuable method of controlling DBP

formation, which does not require significant capital investment, a process that can be useful in developing countries where it is almost impossible to afford high technologies.

Liu *et al.* (2006) studied NOM removal by enhanced coagulation and polymer aid, and found that both processes achieved UV_{254} removal greater than 90% and that enhanced coagulation removed preferably the hydrophobic fraction whereas polymer aid removed the hydrophilic fraction.

Enhanced Coagulation Requirement

According to USEPA Stage 1 (1999), the implementation of enhanced coagulation or softening is necessary when the concentration of total organic carbon (TOC) is higher than 2 mg/L in the raw water. Waters with a TOC level less than 2 mg/L do not require enhanced coagulation or softening, since the NOM consists mainly of fulvic acids, which are less reactive with chlorine. Stage 1 is divided into two steps: Step 1 considers TOC removal as a percentage of the influent TOC to accomplish compliance based on the TOC and alkalinity of the source water. If the alkalinity is high, the pH has to be lowered to the level at which the TOC removal is optimal. USEPA has not developed Step 2 procedures for systems applying enhanced softening because it is expected that this can be accomplished in step 1.

Table 2.1 Required removal TOC percentages by enhanced coagulation.

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as $CaCO_3$)		
	0 – 60	60 – 120	> 120
2 -4	35%	25%	15%
4 -8	45%	35%	25%
> 8	50%	40%	30%

Source: USEPA, 1999.

Step 2 is applicable to systems where the treatment is difficult because the waters do not meet the requirements of Step 1 (Table 2.1). In Step 2, the systems are required to conduct jar or bench-scale testing using alternative combinations of coagulant, coagulant aid, filter aid, and acid addition. The jar test should be conducted by adding alum $(Al_2(SO_4)_3 \cdot 14H_2O)$ or an equivalent dose of ferric salts at 10 mg/L intervals until the pH is lowered to the target pH, as presented in Table 2.2.

Table 2.2 Target pH values under the step 2 requirement.

Alkalinity (mg/L)	0 - 60	60 - 120	120 – 240	> 240
Target pH	5.5	6.3	7.0	7.5

Source: USEPA, 1999.

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The TOC removal is then plotted versus coagulant dose. Enhanced coagulation should be carried out at the coagulant dosage coinciding with the point of diminishing return (PODR), defined as the dosage at which the addition of 10 mg/L alum, or the equivalent dose of some other coagulant, leads to a decrease in TOC of less than 0.3 mg/L and remains less than this value until the target pH is reached.

Enhanced coagulation has negative effects on the drinking water system such as corrosion, primary disinfection, inorganic constituent levels, and particle removal. It can also require process modifications for the handling, treatment, operation and disposal of the sludge generated. According to Carlson *et al.* (2000), none of these secondary effects are sufficient to make it impossible to use enhanced coagulation, but mitigating action may be required in some cases.

2.2.1.2 SUVA, Fractionation and Treatability

Analytical techniques to fractionate organic matter are very complex and expensive. This makes it impossible to routinely monitor parameters to control coagulation at the drinking water plants on a daily basis, and the concept of specific ultraviolet absorbance (SUVA) was therefore developed as an indicator of the nature of NOM and the effectiveness of coagulation in removing NOM, TOC, and CBP precursors (Edzwald and Van Benschoten, 1990; Edzwald and Tobiason, 1999).

Pertnisky (2003) suggested that SUVA is a parameter that is useful to characterize the NOM based on UV absorbance by a water sample with respect to DOC. SUVA is expressed as the absorbance in 1/m per mg/L of DOC.

$$SUVA = \frac{UV_{254}\,(cm^{-1})*100}{DOC\,(\frac{mg}{L})} \qquad (2.1)$$

Edzwald and Tobiason (1999) presented the guidelines for the interpretation of SUVA shown in Table 2.3. Water with a SUVA value of 2 L/mg-m or less is considered difficult to treat by coagulation and TOC will not control the coagulant dosages. In contrast, water with a higher SUVA value is considered to be easy to treat because the amount of NOM available in the water typically has a greater coagulant demand than the particles. Pertnisky (2003) found that for these types of waters the required coagulant dose increases with increasing TOC.

Table 2.3 SUVA guideline based on the nature of NOM and expected DOC removal.

SUVA (L/mg-m)	Composition	Coagulation	DOC Removals
< 2	Mostly Non-Humics Low Hydrophobicity Low molecular weight	NOM has little influence Poor DOC removals	< 25% for Alum Slighter greater for ferric
2 – 4	Mixture of Aquatic Humic and other NOM Mixture of Hydrophobic and Hydrophilic NOM Mixture of Molecular Weights	NOM influences DOC removal should be fair to good	25-50% for Alum Slightly greater for ferric
> 4	Mostly Aquatic Humics High Hydrophobicity High Molecular weight	NOM control Good DOC removals	50% for Alum Slightly greater for ferric

Source: Edzwald and Tobiason, 1999.

Archer and Singer (2006) proposed a SUVA guideline (TSUVA) based on total organic carbon (TOC) on raw water. TSUVA is obtained by dividing UV between TOC concentrations.

Table 2.4 TSUVA guideline for expected TOC removal.

SUVA	TOC Removal (%)
> 1-2	35
> 2-3	40
>3-4	40
> 4	55

Ødegaard *et al.* (2010) pointed out that the ratio between colour and dissolved organic carbon can be useful if the coagulation process is effective in the removal of NOM. They reported that ratios higher than 5-10 mg Pt/mg C could be considered excellent for coagulation effectiveness.

Fractionation

Although, the fractionation of natural organic matter is not a good way of monitoring the coagulation, it should be carried out in the different seasons in order to determine which fraction dominates in the NOM present in the raw water and therefore which fraction is more easily removed by coagulation and forms less trihalomethanes.

There are several methods for the fractionation of the organic matter; but due to their simplicity, rapid fractioning and adsorption/desorption methods are most frequently used. Both of them give good results and the organic matter is fractionated into four fractions; very hydrophobic acid (VHA), slightly hydrophobic acid (SHA), charged hydrophilic acid (CHA), and neutral hydrophilic (NEU).

Eikebrokk *et al.* (2006) indicate that the VHA and SHA fractions are mainly composed of high molecular weight humic acid and fulvic acids respectively, the CHA consists of proteins, amino acids and anionic polysaccharides, and the NEU fraction contains compounds that are not adsorbed on any resin. Fabris *et al.* (2008) reported that the NEU fraction consist of carbohydrates, aldehydes, ketones and alcohols.

Each fraction exhibits different properties in terms of treatability by coagulation; the high molecular weight hydrophobic NOM fractions (VHA+SHA) are less soluble in water and can be removed efficiently by coagulation while the low molecular weight hydrophilic fractions (CHA+NEU) are soluble and are poorly removed.

2.2.1.3 Types of Coagulants

The coagulants most widely used in drinking water treatments are hydrolysing metal salts based on aluminium or iron compounds, due to the high cationic charge that destabilizes the negatively charged NOM. These metal-based coagulants are known to preferentially remove hydrophobic rather than hydrophilic compounds, charged rather than neutral compounds, and high molecular weight (> 10 000 Da) rather than low molecular weight compounds (Carrol *et al.*, 2000). Even though these compounds are very effective, there are some complaints due to drawbacks such as: they increase the volume and metal content of the sludge, they change the water pH, they increase the soluble residues and they are not sufficiently efficient in the removal of organic nitrogen compounds. Another concern is that aluminium sulphate has been linked with some consequences to human health, such as Alzheimer's disease (Pontius, 2000).

Pernitsky (2003) points out that the best coagulation performance is achieved at pH values that are as close as possible to the pH of minimum solubility for aluminium-based coagulant, and a low pH (5.5) is often recommended to maximize TOC removal by aluminium sulphate. It controls the amount of dissolved Al residuals and maximizes the presence of floc particles for the adsorption of NOM.

According to Duan and Gregory (2003), other compounds that are applied in the coagulation process are pre-hydrolized forms of metal such as polyaluminium chloride (PACls) which are more effective, produce strong flocs and less sludge volume but are quite expensive compared with metal salts. Organic polyelectrolytes are also regularly used as primary coagulant; they can be synthetic or natural. In practice, more polyelectrolytes are synthetic but they have been linked with health implications due to the acrylamides (Bratby, 2006). As primary coagulants with no other additive, high

charge, low molecular weight, cationic polyelectrolytes are most often used. Their role is to neutralize the charge of the anionic impurities in the water. Another application of polymers is in conjunction with hydrolyzing metal coagulants, where the polymers are known as coagulant aids. Their function is to strengthen metal hydroxide flocs, which are otherwise weak. The polymers, depending on their charge, can be nonionic, cationic or anionic.

Chitosan

Due to concern for health implications, organic natural polymers such as chitosan have been used in drinking water. However, the application of chitosan in large drinking water plants has been scarcely studied. Regarding water-works for decentralized small populations, Hakonsen *et al.* (2008) described a ten-year experience of the use of chitosan as coagulant in Norway. Their results showed that a combination of coagulation with chitosan and filtration gave a high NOM removal measured as colour, but a low total organic carbon (TOC) reduction. Moreover, the amount of sludge and the bio-film formation in the distribution pipes were reduced significantly. Bratskaya *et al.* (2002) found that chitosan at neutral pH was able to reduce 95-100% of the humic acid. Similarly, Ganjidoust *et al.* (1997) reported a reduction of 70% in TOC and 90% in colour using chitosan and a reduction of only 40% in TOC and 80% in colour with aluminium sulphate.

Chitosan is obtained by the deacetylation in alkaline solution of chitin, which is a polysaccharide obtained mainly from crab, squat lobster and shrimp shells. Chitosan has been widely used in the food and pharmaceutical industries, in the agricultural, medical, and textile industries, and also for wastewater treatment. Chitosan is extensively used in these fields because it is an environment-friendly product, renewable, biodegradable, and non-toxic.

The benefits of using chitosan in water potabilization are less pollution due to the smaller amount of sludge for disposal, no consumption of alkalinity, lower dosages of coagulants, heavier flocs, and more rapid settling. A disadvantage is the higher cost in comparison with that of aluminium sulphate (Zeng *et al.,* 2008), although Crini (2005) says that chitosan can be considered to be a low cost polymer since it is a by-product.

Lower dosages of chitosan than of aluminium sulphate are necessary to destabilize NOM substances due to the high charge density of the amino groups in the chitosan. The presence of quaternary amino groups with a positive charge increases the electrostatic interaction with the negatively charged NOM, reducing the double layer repulsion and allowing its binding. In addition, more than one small particle can be adsorbed onto the polymeric chain of chitosan by an inter-particle bridging mechanism; strong aggregates of larger flocs are formed allowing more NOM removal (Roussy *et al.,* 2005; Renault *et*

al., 2009). The combined use of metal-based coagulants and polymers has been shown to give greater removal effects (Machenbach, 2007).

2.2.1.4 Factors Affecting Coagulation

There are a number of factors that can affect the performance of the coagulants; among them are:

- Alkalinity-pH: Pertnisky (2003) reported that the effectiveness of the coagulant in water with low alkalinity can be reduced because the pH is reduced under the optimal pH range for coagulation when all the available alkalinity is consumed, whereas, high coagulant dosages are required to decrease the pH to values favourable for coagulation in water with high alkalinity. NOM removal decreases at higher pH with all coagulants. Coagulants such as alum and ferric chloride salts are greater alkalinity consumers after the addition of either of the coagulants since these compounds are more acidic than polyaluminium chloride (PACls).
- NOM: The coagulation process is more effective in reducing NOM when enough coagulant is added to satisfy the charge demand of raw water (Pertnisky, 2003). In water where NOM, turbidity or other parameters are present, it is better to measure NOM than the other parameters. The selection of the coagulant depends more on the raw water alkalinity, and this is the key parameter to ensure a pH optimal for the coagulant performance rather than the amount or type of NOM available in the water.
- Temperature: The coagulation and flocculation processes are not so efficient at low temperature because the viscosity of the water is higher, shifting the coagulant solubility and reducing the kinetics of the hydrolysis reactions and particle flocculation. Another consequence is that the required coagulant dosages for NOM removal will also probably increase as the water temperature decreases (Pertnisky, 2003). Pertnisky (2003) found that polyaluminium coagulants are more effective in cold water than aluminium salts, as they are pre-hydrolyzed; and that the pH of minimum solubility of aluminium hydroxide species was higher at low temperatures.
- Turbidity: This parameter governs the coagulation process in raw waters with a low TOC and enough coagulant should therefore to be added to destabilize suspended colloids or to create a good settling floc. Pernisky (2003) indicates that SUVA guidelines are a good predictor for determining whether turbidity will influence or control the coagulant dosages. In addition, Pernisky (2003) points out that coagulant dosages increase when the raw water turbidity rises, but the relationship is not linear.

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- Several common anions can form complexes with aluminium and iron which affect the hydroxide precipitation. If the anion is a strong coordinator with aluminium and not readily replaced by hydroxyl ions, the pH of optimum destabilization will drop roughly with increasing anion concentration (*e.g.* phosphate). If the anion is a strong coordinator with aluminium but can easily be displaced by a hydroxide ion, the pH of optimum precipitation increases with a very basic anion, and decreases with a weakly basic anion. If the anion is a very weak coordinator with aluminium, it exerts only a slight effect on optimum precipitation; the trend is moving to lower pH (*e.g.* nitrates and perchlorates).

2.2.2   Flocculation

Flocculation is the process where destabilized particles are induced to come together, make contact, and thereby form larger agglomerates that tend to be larger and more open in structure (Bratby, 2006). The mechanisms responsible for the destabilization by polyelectrolytes are bridging, charge neutralization and electrostatic patches. These mechanisms can operate conjointly sometimes, whereas in other situations one can predominate over the others.

Bridging occurs when an individual chain can become attached to two or more particles, thus linking them together (Gregory, 2006). According to Bratby (2006), the requirement for this mechanism to take place is that there should be sufficient particle surface for attachment of polymer segments from chains attached to other particles and that the polymer chains should be of such an extent that they can bridge the distance over which interparticle repulsion operates. Gregory (2006) suggested that linear polymers of high molecular weight are most effective for bridging flocculation.

Other mechanisms that are possible in the flocculation process are charge neutralization and electrostatic patches (Gregory, 2006). Charge neutralization is the mechanism where polymers having a charge different from that of the adsorbate neutralize the charge of the latter and reduce the potential energy of repulsion between adjacent colloids. Cationic polyelectrolytes are more effective in being adsorbed strongly onto negatively charged NOM. Bolto and Gregory (2007) explain that an electrostatic patch occurs when highly charged cationic polyelectrolytes are adsorbed onto particles with a moderately low negative surface charge density, so that each surface charge cannot be individually neutralized by a cationic segment of the adsorbed chain. The average distance between charged surfaces sites may be significantly shorter than the spacing between cationic sites on the polymer chain. Therefore, overall charge neutralization may occur. At a suitable polymer dosage there will be a local heterogeneity of charges, giving an electrostatic patch arrangement.

Bratby (2006) describe two stages in the flocculation process: Perikinetic flocculation, which is due to thermal agitation (Brownian motion), and is a naturally

random process. In this case, flocculation starts immediately after destabilization and is complete within seconds; there is a limiting floc size beyond which Brownian motion has no or little effect. This stage is relatively unimportant in a system undergoing mixing except for very small particles. The second stage is Orthokinetic flocculation and it takes place from an induced gradient velocity in the water. The effect of velocity gradients in the water is to introduce relative velocities between particles, in this manner providing an opportunity for contact and aggregation. The rate and extent of particle aggregation and the rate and extent of breakup of these aggregates depend on the velocity gradient and on the time of flocculation.

In general, for effective flocculation to take place, polymers need to be added to the water bulk with intense mixing to achieve a rapid and uniform distribution of the polymers. The polymers then need to be adsorbed onto particles before flocculation can occur. After adsorption, polymer chains undergo rearrangement, and new aggregates or flocs are formed due to the collision of particles with adsorbed polymers. Finally, there is the possibility that the flocs may suffer breakage under certain conditions. Adsorption interactions can be of several types, including the following:

- Chemical Forces. Protonation can occur at the humic molecule surface and in the solution phase, i.e in the hydration shell of cations. It is important for the adsorption of anions and organic compounds that are basic in nature.
- Coordination Reaction and Complex Formation. The reaction involves coordinate covalent bonding, in which the ligand donates electron pairs to the metal ion. The compound formed is called a coordinate compound, complex compound or organo-metal complex.
- Electrostatic Bonding. It occurs between two molecules of opposite charge. A cationic polymer such as chitosan can be adsorbed onto the negative surface of NOM. This electrostatic attraction gives very strong adsorption. However, a high salt concentration can screen the electrical interaction reducing the adsorption.
- Hydrogen Bonding. It is a bond by which a hydrogen atom acts as the connecting linkage. Hydrogen bonding is a very important adsorption force for humic substances, because of the existence of functional groups containing hydrogen in their molecules, i.e., N-H, $-NH_2$, -OH, and COOH groups.
- Hydrophobic Bonding. It is associated with the adsorption of non-polar segments of polymer chain, which compete with water molecule adsorbed on the adsorption sites. In the process, the adsorbed water is expelled by or exchanged for the nonpolar molecule. Polysaccharides are adsorbed in this way.
- Ligand Exchange. It is the replacement of a ligand by an adsorbate molecule. The adsorbate can be an inorganic ion or an organic molecule, but in either case it must have a stronger chelation capacity than the ligand to be replaced.

- Physical Forces. They are related to van der Waals forces that are active at short distances among all types of molecules. They are additive in nature, therefore, the forces increase with increasing size of the compounds or an increase in molecular weight, such as humic acid. Tan (2003) indicated that this force is important for non-polar organic compounds and neutral organic substances.

2.2.3 Adsorption

According with Bansal and Goyal (2005), adsorption is a process occurring when a solid surface is brought into contact with a liquid. An interaction occurs between the fields of force on the surface and that of the liquid due to unsaturated or unbalanced forces that are present on every solid surface. The adsorption involves two types of force: physical forces such as dipole moment, polarization forces, dispersive forces or short-range repulsive interactions, and chemical forces that are valence forces arising from the distribution of electrons between the solid surface and the adsorbed atoms resulting in a chemical reaction. The chemical bond is stronger than in the physical sorption. The type of adsorption that takes places in an adsorbent-adsorbate system depends on the natures of the adsorbent and adsorbate, the reactivity of the surface, the surface area of the adsorbate, and the temperature and pressure.

Adsorption of a molecule or ion from solution onto the surface of a solid involves three steps: removal of the molecule from solution, removal of the solvent from the solid surface and attachment of the molecule to the surface of the solid (Tan, 2003). The adsorption of a molecule or ion from a solution is determined by the porosity and the chemical nature of the adsorbent, the nature of the components of the solution, its pH, and the mutual solubility of the components in the solution (Bansal and Goyal, 2005).

Many types of adsorbent are used in drinking water; carbon-based and polymer-based compounds (already explained before). Activated carbon is a versatile carbon due to its adsorptive properties such as a high surface area, a microporous structure and a high degree of surface reactivity. It is available in both powder and granular form. The pores in activated carbon are divided into micropores with a diameter less than 2 nm constituting approximately 95% of the total surface area of the activated carbon, mesopores with diameters between 2 and 50 nm, contributing 5% of the total surface area, and macropores with a diameter greater that 50 nm, that are considered unimportant since their contribution to the surface is less than $0.5 m^2/g$ (Bansal and Goyal, 2005). In addition, the same authors reported that the adsorption of natural organic matter present in surface and ground waters onto granular activated carbon depends on the pore size and on the chemical structure of the carbon surface. They explain that the pore size indicates the accessibility of a pore for adsorption and that the chemical structure determines the interaction between the carbon surface and the NOM molecules.

In order to determine the mechanism of adsorption and the kinetics that control the adsorption such as mass transport and chemical reaction processes, kinetics models such as the pseudo-first-order irreversible and the pseudo-second-order irreversible models are used.

The pseudo-first-order model or Lagergren equation is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.2}$$

where q_e and q_t are the sorption capacities (mg/g) at equilibrium and at time t, respectively; and k_1 is the pseudo-first-order rate constant (1/min). Equation 2.2 can be integrated with the initial condition $q_t = 0$ at t = 0, leading to:

$$q_t = q_e - \frac{q_e}{10^{\frac{k_1 t}{2.303}}} \tag{2.3}$$

The pseudo-second-order model is represented by the equation:

$$\frac{dq_t}{dt} = k_2(q_e - q)^2 \tag{2.4}$$

where k_2 is the pseudo-second-order constant rate (g/mg-min). Integration of this equation leads to:

$$q_t = \frac{t}{\frac{1}{q_e}\left(\frac{1}{k_2\,q_e} + t\right)} \tag{2.5}$$

The pseudo-second-order kinetics assumes chemisorption involving valence forces through the sharing or exchange of electrons between the positive groups of the adsorbent and the negative charge of the NOM (Septhum *et al.,* 2007).

2.3   Chlorination By-products

Rook (1974) observed that chlorine can react with organic matter such as humic and fulvic acid to form chlorination by-products (CBPs) like trihalomethanes (THMs) and haloacetic acids (HAAs), which are considered to be potentially carcinogenic. Villanueva *et al*. (2003) said that CBPs present diverse chemical and toxicological properties and that they may enter the human body by ingestion, inhalation or dermal absorption.

Information related to the mechanism of formation of THMs is still limited; attempts to develop kinetic or statistical models for the formation of chlorination by-products (CBP) have been impeded by the substantial costs and effort required to analyse the CBPs. These difficulties restrict the amount of data that can be obtained from chlorination reactions in laboratory or field studies, and they thus limit the information available to formulate or test models of a reaction sequence.

The distribution of the halogenated CBPs depends upon a number of factors: bromine and/or chlorine concentration, contact time, pH, temperature, and the natural organic matter (NOM). Trihalomethanes are the most common compounds among the CBPs found in drinking water (Singer, 1999; Wattanachira *et al.,* 2004).

2.3.1   CBP Formation Mechanism

The formation of chlorination by-products in drinking water is the result of a reaction between natural organic matter (NOM) and chlorine:

$$NOM + Chlorine\ Compound \rightarrow CBP \tag{2.6}$$

Reaction mechanisms between halogens and NOM include substitution within the NOM, which produces organic halides, and the oxidation of carbon bonds. Because of a lack of information on the chemical structures of humic and fulvic substances, the mechanism of CBP formation is not well understood. The site-specific behaviour and the heterogeneous nature of the natural organic matter make the situation more difficult.

Rook (1977) set the base for the study of the mechanism of formation of CBPs and proposed a pathway for this reaction type. He indicated that the haloform reaction occurs with the resorcinol type component of fulvic acids. The proposed pathway involves a fast chlorination of the carbon atom that is activated by the OH^- substituent or phenoxide ions in an alkaline environment. Hypochlorous acid (HOCl) is the typical source of the electrophilic halogenating species Cl^+. The reaction initially gives an intermediate carbanion (a carbon atom with a negative charge), which is rapidly halogenated to the product shown in Figure 2.3. After the aromatic structure has been halogenated and opened, a break at *a* will result in the formation of THM. Alternatively, an oxidative and

hydrolytic break at *b* will yield an HAA or chloral hydrate, whereas a break at *c* will yield a haloketone. If bromide is present, mixed bromochloro by-products will be formed.

Westerhoff *et al*. (2004) reported that this is due to electrophilic (aromatic) substitution by electron release to stabilize carbocation, which is more favourable for the bromine atom due to its higher electron density and lower bond strength than the chlorine atom, despite the fact that hypochlorous acid, HOCl (E^o_{red} = +1.630 V) has a higher redox potential than hypobromous acid, HOBr (E^o_{red} = +1.331 V). Chlorine may cleave aromatic rings producing both chlorinated and oxygenated by-products. Bromine may substitute into the ring structure without cleavage.
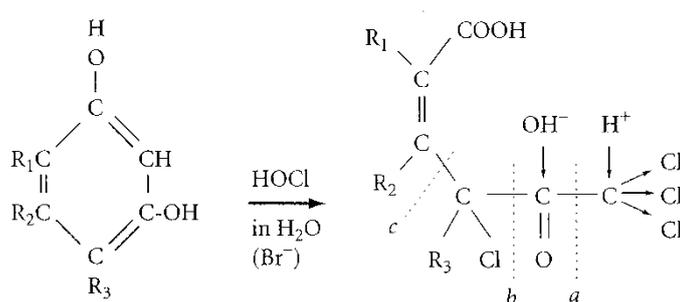

Figure 2.3 Haloform reactions with fulvic acid and resorcinol.
Source: Krasner, 1999.

Other authors such as Christman *et al*. (1978); Norwood *et al.* (1980); Reckhow and Singer (1985); Norwood *et al.* (1987); and Amy *et al.* (1998) have studied the reaction mechanisms of aromatic compounds with chlorine and have confirmed the hypothesis proposed by Rook (1977) that two mechanisms are present in the formation of CBPs: substitution and oxidation.

2.3.2 Factors Affecting CBP Formation

The concentration and speciation of the CBP depends on the water quality and on the operating conditions in the drinking water facility, including NOM concentration (hydrophobic and hydrophilic fractions), residual chlorine, reaction time, pH, and bromide concentration.

Effect of NOM

The formation of CBPs can be affected by the concentration and characteristics of the NOM in two ways. Firstly, an increase in NOM concentration raises the level of CBP precursors, and this increases CBP formation. Secondly, an increase in the NOM concentration increases the chlorine demand of the water. A high chlorine dosage will be necessary to maintain the appropriate chlorine residual in the distribution system; but it

promotes a greater formation of CBPs. Under the same chlorination conditions, each fraction of NOM results in a different CBP yield (Croué *et al.,* 1999). The sources of NOM can also affect the CBP formation.

There is limited information available related to the effects of NOM on CBP speciation. Xie (2004) has reported that in water containing bromide a low level of NOM generally leads to a higher percentage of brominated CBPs than a high level of NOM. According to Xie, this is because a higher NOM concentration requires a higher chlorine dosage, and this leads to a lower ratio of bromide to chlorine.

A high concentration of NOM increases the concentrations of THMs and HAAs. Therefore, NOM removal from the water is the key to controlling CBP formation in chlorinated waters.

Effects of Algae

The algae biomass and their extracellular products can easily react with chlorine to produce CBP precursors. Hoehn *et al.* (1990) observed that algal extra-cellular products, on reaction with chlorine, yielded a greater quantity of chloroform (trichloromethane) from the available TOC than did the algal biomass. They also observed that algae liberated high-yielding THM precursors in greater abundance during the late exponential phase of growth than at any other time during the algal life cycle.

Trehy and Bieber (1981) found that the chlorination of certain amino acids (from algae sources) and humic acid led to acetronile acids (HANs), which are also CBPs.

Effects of Bromide

Xie (2004) reported that the inorganic ion bromide does not react directly with NOM. Nevertheless, inorganic bromide can be oxidized by chlorine or ozone to hypobromous acid or hypobromite depending on the pH. As with hypochlorous acid and hypochlorite, both hypobromous acid and hypobromite react with NOM to form brominated CBPs. Bromine is more reactive with NOM than chlorine. In water containing bromide, brominated CBPs are formed upon chlorination and ozonation. Because of the higher reactivity of the bromine, the formation of chlorinated species is reduced.

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad (2.7)$$
$$HOCl + HOBr + NOM \rightarrow DBPs \qquad (2.8)$$

Xie (2004) also explained that the concentration of the bromoform will be twice that of the chloroform since the atomic weight of bromine is 80 g/mol and of the chlorine is 35.5 g/mol. Therefore, under given chlorination conditions, an increase in bromide could significantly increase the concentration of the THMs. Another consequence of the higher

bromide level is the formation of brominated HAAs and reduction in the formation of chlorinated HAAs (Xie, 2004).

Amy *et al.* (1991) found that HOCl acts as a more effective oxidant, whereas HOBr behaves as a more efficient halogen-substitution agent, and these authors established that, as the ratio of bromide to TOC increased, the percentage of brominated CBPs increased. This can occur when there is either an increase in bromide concentration or a decrease in TOC concentration.

Effect of Chlorine Dose

Chlorine is responsible for the formation of chlorinated by-products (CBPs). Some CBPs are intermediate products of chlorination reactions and others are end products. The intermediate products can be oxidized into end products according to the equations developed by Xie (2004):

$$NOM + HOCl \rightarrow Intermediate\ Products \qquad\qquad (2.9)$$

$$Intermediate\ Products + HOCl \rightarrow End\ Products \qquad\qquad (2.10)$$

A higher chlorine dosage usually increases the formation of chlorination end products in the treated water (Figure 2.4). Trihalomethanes and monohaloacetic acids and dihaloacetic acids are end products of chlorination reactions (Xie, 2004). Other compounds such as monohalogenated and dihalogenated CBPs are intermediate products, and chlorination of these intermediate by-products can result in the formation of dihalogenated, trihalogenated, and other CBPs. At a moderate level of residual chlorine, dihalogenated CBPs are formed. A higher chlorine dosage increases the formation of trihalogenated CBPs and leads to a reduction in dihalogenated CBPs.
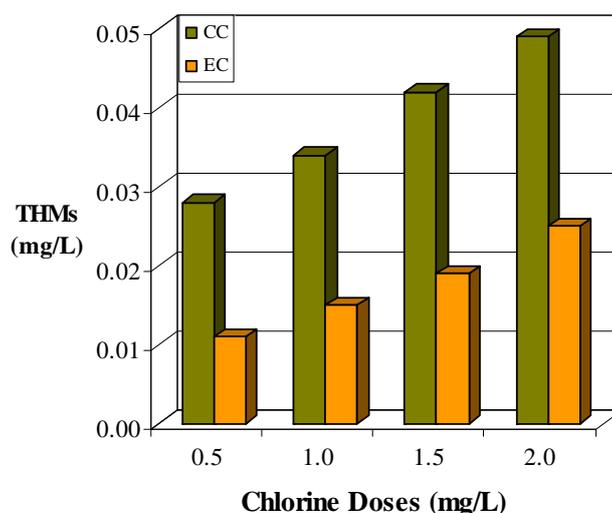

Figure 2.4 Influence of chlorine dose on THM formation.

CC: Conventional Coagulation; EC: Enhanced Coagulation

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Bank and Wilson (2002) and Xie (2004) reported that increasing the chlorine dose increases the formation of THMs, HAAs, and many other chlorinated disinfection by-products. However, Singer (1994) indicated that a high chlorine dose favoured HAA rather than THM formation; the formation of trihalogenated HAAs being higher than that of di-and mono-halogenated HAAs. A similar finding was reported earlier by Reckhow and Singer (1985).

Effect of Temperature

Krasner (1999) analyzed data from 35 utilities in United States and found that the mean THM formation was highest in summer and lowest in winter. Most of the other CBPs, except the haloketones, followed the same behaviour as the THMs. Stevens *et al.* (1976) and Singer (1999) found the same tendency. The lower temperature in the winter leads to less reactivity and a lower rate of production of final end products.

Williams *et al.* (1997) in a review of disinfection by-products in Canadian drinking water found that the total trihalomethane (TTHM) levels were higher in summer than in winter. They showed that TTHMs and HAAs were the major CBPs found in all the facilities evaluated. The HAA levels often equalled or exceeded the total THM concentrations.

Krasner (1999) demonstrated that seasonal variations would also affect the nature of the organic precursors, which may vary in composition with the season. He also observed that DOC and UV values were higher after rainfall. These increases can be attributed to the leaching of soil organic matter during high river discharges.

Effect of Contact Time

One of the most important factors in THM formation is the time during which a particular disinfectant remains in contact with the precursors. Koch *et al.* (1991) and Singer (1999) indicate that the concentration of THMs rises quickly during the first hours. Xie (2004) also showed that, if CBPs are end products, extending the reaction time would increase the formation of CBPs (THMs and HAAs). However, if CBPs are an intermediate product (dichloroacetonitrite, dichloropropanone), increasing the reaction time may decrease the formation of CBPs, especially at high chlorine dosages. Since THMs are typical hydrolysis products and chlorination end products, increasing the reaction time would augment the formation of THMs.

Effect of pH

A high pH results in a higher level of THMs but a lower level of HAAs and other halogenated CBPs including total organic halides (TOX). Several authors, such as Stevens *et al.* (1976), Morris and Baum (1978), Fleischacker and Randtke (1983), and

Reckhow and Singer (1985) have observed that the chlorination of most organic compounds led to larger amounts of chloroform at higher pH values.

Stevens *et al.* (1989) evaluated the effects of pH and reaction time on CBP formation. They observed that the formation of THM increased with time especially over the first 48 hours and that the THM formation was greater when the pH was increased. The HAA formation increased over time, but in the range from 5 to 9.4, the pH had no significant effect on dichloroacetic acid (DCCA) formation. Trichloroacetic acid (TCAA) formation was lower at a pH of 9.4 than at the lower pH levels.

Xie, (2004) establish that the chlorine species depend on the water pH; at low pH, HClO is the predominant species, whereas, ClO$^-$ is the main species at high pH. He also indicates that a low pH provokes the formation of HAAs, trihaloacetaldehydes, trihalopropanones, and cyanogen halides, but a high pH favours the formation of trihalomethanes. Krasner (1999) presented a summary of the effect of pH and reaction time on the formation of CBPs, which is reproduced in Table 2.5.

Table 2.5 Effect of pH and reaction time on CBPs formation.

CBP	pH 5	pH 7	pH 9.4
THMs	Lower Formation		Higher Formation
TCAA (Trichloroacetic acid)	Similar Formation		Lower Formation
DCAA (Dichloroacetic acid)	Similar Formation, perhaps slightly higher at pH 7		
$Cl_3CCH(OH)_2$ (Chloral Hydrate)	Similar Formation		Forms within 4 h; decays over time
DCAN (Dichloroacetronile)	Higher Formation	Forms within 4 h; decays over time	Lower Formation
1,1,1-TCA (Trichloroacetic)	Higher Formation	Lower Formation	Not Detected

Source: Krasner, 1999.

Chapter 3

Materials and Methods

As indicated in the objectives, the aim of the work described in this thesis is to improve the removal of natural organic matter by using different techniques to reduce the presence of trihalomethanes in drinking water. Therefore, in the experimental part of the thesis, several issues may be distinguished. One is the characterisation of the raw water; another is the determination of trihalometanes in the existing drinking water plants. Enhanced coagulation and adsorption were used as possible methods for removal of NOM, and the results were compared with conventional coagulation which is presently used. The chosen coagulants were aluminium sulphate and chitosan and adsorption onto activated carbon or chitosan was studied. Kinetics of adsorption were also studied.

The experiments were carried out on a laboratory scale using raw water from four of the ten drinking water plants existing in Nicaragua. Some additional experiments were performed with synthetic water. This chapter describes the location of the sampling sites, the analytical procedures, and the methodology applied in the experiments carried out.

The details of the experimental part of each paper such as sampling period, raw water sources and methodology appear in each paper. The papers are annexed at the end of this thesis. Only a general overview of the experimental part is presented here.

3.1   Sampling Sites

Raw water was sampled in four different drinking water plants, which are located in the central region of Nicaragua (Figure 3.1). These plants are Boaco (P1), Camoapa (P2), Juigalpa (P3) and Santo Tomas (P4). These four plants were chosen for logistical reasons and because they are the major drinking water plants built in Nicaragua. Boaco, Camoapa and Santo Tomas use river surface water and the water to Juigalpa is taken from the Nicaragua Lake. In dry season, the Boaco facility uses a combination of river and ground water. All of them use conventional treatment that consists of intake, mixing with aluminium sulphate as coagulant and calcium hydroxide to adjust the pH in the coagulation step, followed by flocculation, sedimentation, rapid sand filtration and disinfection with chlorine.

Figure 3.1 Location of the four drinking water systems.

Sampling was done in several periods, starting in 2003 and finishing in July 2010, taking into consideration dry and rainy seasons. According to the types of experiments to be effectuated, raw water or waters flowing into the different treatment steps of the drinking water plants were sampled. All the samples were preserved with ice at a temperature of approximately 4°C and kept away from the light until extraction. Some samples were preserved with HCl.

After arrival at the laboratory, the sample temperature was adjusted to room temperature and the samples were analysed immediately. All the measurements were made in duplicate or in triplicate. The chemicals used for the analytical determinations were of reagent grade from Merck (Darmstadt, Germany) and Sigma Aldrich.

3.2   Analytical Procedures

Turbidity, colour, water temperature, conductivity, dissolved total solids, pH, and residual chlorine were measured at the sample site. The other parameters were measured in the laboratory using the procedures described in Standard Method (SM) (1998) and the HACH analysis handbook; the methods used are listed in Table 3.1. UV absorbance was measured using an UV/Vis spectrophotometer (Genesis II) at 254 nm in 1 cm quartz cells. The spectrophotometer was previously calibrated with potassium hydrogen phthalate (KHP) according to the procedure in the Standard Method (1998). The other equipment was calibrated according to the recommendations of the manufacturers.

Table 3.1 Evaluated parameters and methods.

Parameter	Method
Alkalinity	SM 2320B
Aluminium	SM 3500Al
Ammonia	HACH 8038
Bromide	SM 4500Br
Conductivity	Conductivimeter HACH 2010
Color	HACH 8025
Color Ratio ($Q_{4/6}$)	$\dfrac{\text{Log absorbance at 400 nm}}{\text{Log absorbance at 600 nm}}$
Dissolved Organic Carbon (DOC)	HACH 10129
Nitrate	HACH 10020
Nitrite	HACH 10207/HACH 8153
pH	pHmeter Orion 3 Star Plus
Residual Chlorine	SM 4500Cl-G/HACH 8021
Specific Ultraviolet Absobance (SUVA)	$((UV_{254})\cdot 100)/DOC$
Temperature	Thermometer
Total Dissolved Nitrogen (TDN)	HACH 10070
Total Dissolved Solids (TDS)	Conductivimeter HACH 2010
Total Iron	SM 3500Fe-B
Total Organic Carbon (TOC)	HACH 10129
Total Trihalomethanes (THMs)	HACH 10132
Turbidity	Turbidimeter HACH 2100P
Ultraviolet Absorbance (UV_{254})	SM 5910B/HACH 10054

The samples for TOC and DOC were taken using amber glass containers with a volume of 120 mL having a screw cap with a Teflon septum. They were preserved with ice and were analyzed immediately on arrival at the laboratory. The samples for DOC were filtered using a 0.45 μm filter (Whatman). THM samples were taken using 40 mL glass bottles sealed with Teflon-lined septa caps. The bottles were filled slowly to overflowing so that no air was included with the samples. The Persulphate Oxidation Method (HACH 10129) was used for TOC and DOC analyses. THMs were analysed by HACH method 10132. The accuracy of both HACH methods was determined using the standard addition method. All the samples were treated in accordance with the requirements for each analysis and the respective protocol for each test as described in the Standard Method (1998) and the HACH water analysis handbook.

Preparation of the glassware comprised washing with biodegradable detergent, rinsing with tap water, ultrapure water and acetone and drying in an oven at $150^{\circ}C$ for 2 h. All solutions were prepared with deionised water.

3.3 Preparation of Coagulants, Flocculant Aids and Synthetic Water

Aluminium Sulphate (AS) Stock Solution Preparation (Papers I-VII)

Aluminium sulphate $Al_2(SO_4)_3 \cdot 14H_2O$ (Papers I, II and VI) and $Al_2(SO_4)_3 \cdot 18H_2O$ (Papers III, IV, V and VII) were used in the experiments. Stock solutions were prepared using aluminium sulphate salt and deionized water. 1 mL of these solutions was equivalent to 10 mg of aluminium sulphate.

Chitosan Extraction (Paper III)

Shrimp shells were provided by CAMANICA (shrimp processing plant) and the method of processing to obtain chitin and then chitosan is explained in paper III.

The degree of deacetylation (*DD*) of the chitosan produced was determined by the procedure described by Qun and Ajun (2006). 0.5 g of dry chitosan (*G*) was dissolved in 100 mL (V_1) of HCl 0.1 M (C_1) and titrated with NaOH 0.1 M (C_2), and the degree of acetylation was calculated as:

$$\%NH_2 = \frac{(C_1V_1 - C_2V_2)}{G(100-W)}100$$

(3.1)

where V_2 is the volume (mL) of NaOH used in the titration and W is the percentage of moisture in the chitosan. 0.016 g of NH_2 are equivalent to 1 mL of HCl 0.1 M. The degree of deacetylation is then given by:

$$\%DD = \frac{\%NH_2}{9.94}100$$

(3.2)

where 9.94 is the theoretical NH_2 percentage in chitosan. A degree of deacetylation (DD) of approximately 84% was obtained.

Chitosan Solution for Coagulation/Flocculation Experiments (Papers III, IV, and V)

Using the chitosan obtained at the laboratory, a chitosan solution was prepared by adding 1 g of chitosan powder to 100 mL of 0.1 M HCl (Paper III). This solution was kept stirred overnight to ensure total dissolution of the chitosan powder. Deionised water was added to reach a volume of 1 L. 1 mL of this solution was equivalent to 1 mg of chitosan. A fresh solution was prepared daily.

A similar procedure was used to prepare the chitosan solution for the experiments reported in paper V, but chitosan bought from Sigma Aldrich with a deacetylation degree (DD) of 80% was used instead of the chitosan obtained at the laboratory.

For the flocculation experiment, the chitosan solution was prepared by adding 300 mg of chitosan to 50 mL of 0.1 M HCl. This solution was stirred overnight to ensure the total dissolution of the chitosan powder. Deionised water was then added to make the solution up to 1 L and to produce chitosan solution in which 1 mL of solution was equivalent to 0.3 mg of chitosan. The solution was prepared daily.

Disinfection Solution (Papers II, III, IV and V)

Chlorine dosing solution ampoules (HACH) were used for the disinfection step, which was performed on the water treated with conventional or enhanced coagulation on a laboratory scale. Dosages of 2 mg/L and contact times of 1 hour were applied in paper I; 2 hours in papers III and IV; and 5 hours in paper V. The concentration of trihalomethanes was determined in the disinfected water.

Synthetic Raw Water (Paper IV)

Humic acid solutions (Sigma Aldrich) with four different concentrations: 1, 3, 5 and 7 mg/L were prepared. To ensure an ionic strength of 0.05 M in the synthetic water, 2.925 mg/L of NaCl reagent grade was added. Humic acid was dissolved in deionised water and filtered through a Whatman filter of 0.45 μm. NaCl was then added and the synthetic water was then stirred for 1 h. Finally, the pH was adjusted to 6 with 0.1 M NaOH or 0.1 M H_2SO_4.

3.4   NOM Fractionation (Paper V)

Raw waters from the Boaco and Juigalpa sources were filtered through a 0.45 μm filter and acidified to pH 2. Then, following the procedure described by Chow *et al*. (2004), each raw water containing dissolved NOM was fractionated by rapid fractionation and adsorption/desorption methods. The four fractions are: very hydrophobic acid (VHA), slightly hydrophobic acid (SHA), charged hydrophilic acid (CHA), and neutral hydrophilic (NEU). Each fraction was coagulated with chitosan or aluminium sulphate using the same conditions described in 3.5. Figure 3.2 show a scheme of the procedure for fractioning the raw waters. Coagulation experiments were carried out using these four fractions.
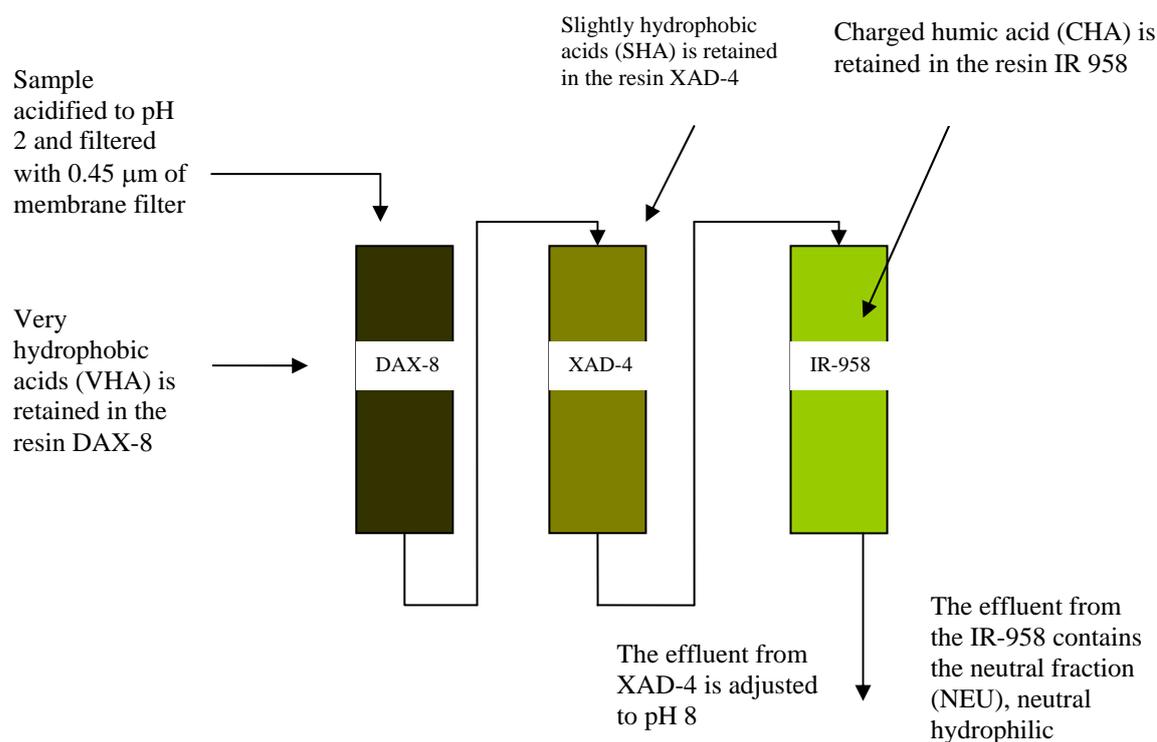
Figure 3.2 NOM fractionation procedure.

3.5 Conventional Coagulation Experiments (Papers III, IV and V)

Coagulation experiments (paper III) were performed using two jar test equipments (Phipps and Bird®) at room temperature (25°C) taking raw water from the four drinking water plants previously mentioned. The volume of raw water in each jar was 2 L. To compare the performances of aluminium sulphate and chitosan as coagulants, different dosages of aluminium sulphate (10, 20, 30, 40, 50, and 60 mg/L) and of chitosan (2, 4, 6, 8, 10 and 12 mg/L) were used. In preliminary experiments, it was found that a dose of aluminium sulphate greater that 60 mg/L did not significantly increase the NOM removal (Paper III).

In the coagulation experiments, a rapid mixing at 100 rpm for one minute was applied to disperse the coagulant, followed by flocculation with slow mixing at 30 rpm for 30 minutes, and settling for 1 h. Aliquots of the supernatant liquid were taken from each jar to measure the different parameters and to carry out disinfection after the filtration step. Filtration through Whatman No. 1 paper was performed to simulate sand filtration (Paper III, IV and V).

The same procedure was used for the experiments in paper IV, where synthetic water was used instead of natural water. It was prepared with humic acid to different concentrations and adjusted to pH 6. The coagulant dosages applied were from 15 to 90

31

mg/L. In the experiments of paper V, different dosages of aluminium sulphate (15 to 75 mg/L) and chitosan (2 to 10 mg/L) were applied.

3.6 Enhanced Coagulation Experiments (Papers I, II, and VI)

Water taken at the intake of the different drinking water plants was used for enhanced coagulation experiments at the laboratory, following the procedure described by USEPA (1999). The same coagulant type ($Al_2(SO_4)_3 \cdot 14H_2O$) as that used at that time in the four drinking water plants was applied in these experiments. The common dosage of coagulants at those facilities is 20-30 mg/L of aluminium sulphate, depending on the turbidity of the raw water sources.

Enhanced coagulation experiments were performed using two jar test equipments. The coagulant dose used in the enhanced coagulation tests depends on the TOC removal requirement according to the USEPA procedure (1999). The range of dosages used for the different raw waters was 10-70 mg/L (Paper I). Each jar equipment was placed in a Perspex box to keep the temperature at $25^{o}C \pm 0.1^{o}C$. The efficiency of the enhanced coagulation was evaluated in terms of the removal of precursors of THMs, and the decrease in THM level. Figure 3.3 presents a summary of the Enhanced Coagulation procedure, which is described in more detail in USEPA procedure (1999).
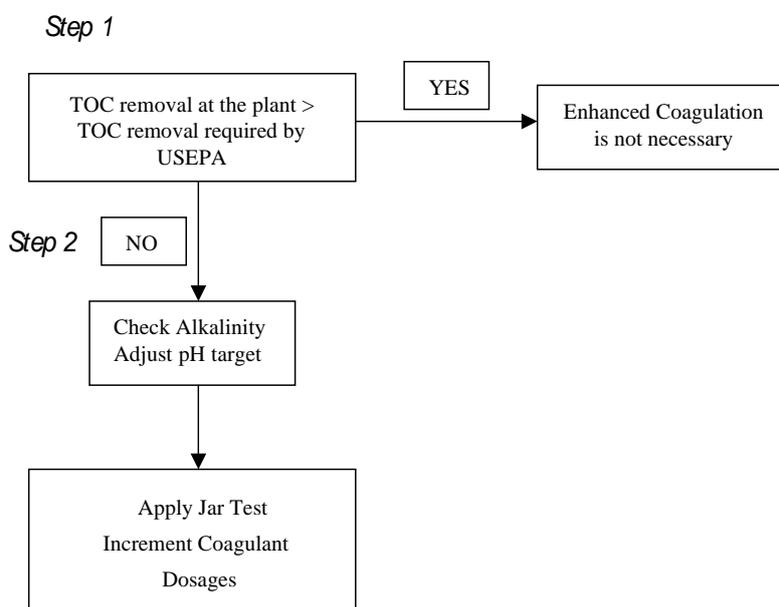

Figure 3.3 Enhanced coagulation procedures.

For the experiments with enhanced coagulation in paper II, coagulant dosages of 10 to 90 mg/L of aluminium sulphate were applied. For both experiments (Papers I and II) rapid mixing for 1 minute at 100 rpm, slow mixing at 30 rpm for 30 minutes and settling

for 60 minutes were used, these are the same conditions as in the conventional coagulation test.

A coagulant dosage of aluminium sulphate solution of 20 to 70 mg/L was applied for the experiments reported on paper VI. The operating conditions were changed to initial rapid mixing at 100 rpm for 1 minute, 20 minutes of slow mixing at 20 rpm and settling for 30 minutes.

3.7 Other Coagulation Techniques (Paper IV)

Conventional coagulation, preformed flocs and two-stage coagulation were the types of experiments carried out and presented in paper IV. Flocculation with chitosan was also carried out.

Preformed Flocs (PF)

300 mL of $Al_2(SO_4)_3 \cdot 18H_2O$ stock solution (10 000 mg/L) were added to 700 mL of a buffered solution prepared with deionised water at pH 7. The water was then mixed for 2 minutes at 150 rpm followed by slow mixing for 30 minutes at 30 rpm in the jar test equipment. Different volumes of the preformed flocs (PF) (7.5, 15, 22.5, 30, 37.5 and 45 mL) were transferred to each jar that contained 1.5 L of synthetic water using mixing condition to ensure a good dispersion of the preformed flocs. The same operating conditions as in conventional coagulation were then applied.

Two-stage Coagulation (SC)

Once conventional coagulation experiments were carried out, 1.5 L of the coagulated water was taken from each jar to perform the two-stage coagulation (SC) experiments. The pH was again adjusted to 6. The same coagulant solution, dosages and operation conditions as were applied in conventional coagulation were used in these second stage experiments.

Flocculation with Chitosan (Paper IV)

After the experiments with conventional, preformed flocs or two-stage coagulation with synthetic water had been carried out, they were repeated using chitosan as flocculant. Chitosan solution was added immediately after the aluminium sulphate into each jar to perform the flocculation process with chitosan. The same conditions of rapid and slow mixing and settling were used as in the experiment without chitosan as flocculant. A dose of 0.3 mg/L of chitosan was applied.

3.8 Filtration with Granular Activated Carbon (Paper II)

After enhanced coagulation had been applied to the raw water from Boaco, the water was filtered in a column packed with granular activated carbon (GAC) and sand. A column with an inner diameter of 0.035 m (3.5 cm) was partially filled with 0.45 m of GAC and 0.05 m of sand. The water was fed into the top of the column using a peristaltic pump, and the effluent was collected at the bottom. The flow was kept constant at 2.15 x 10^{-3} m^3/h (2.15 L/h) to ensure a residence time (empty bed contact time, EBCT) of 12 minutes. A low hydraulic loading rate of 2.3 m^3/m^2-h was applied in the experiments. The GAC used was Sigma-Aldrich type Darco® with a particular size of 10 A^o±1 A^o, a pore volume of 0.95 mL/g dry basis, and a surface area of 600 m^2/g. Dynamic adsorption capacities (A_d) of GAC were calculated to enable the adsorption of NOM on the total volume of activated carbon to be determined according to the following equation and the procedure explained by Okoniewska *et al.* (2007):

$$A_d = \frac{(C_i - C_e)Q\tau}{V}$$
(3.3)

where C_i and C_e represent the influent and effluent concentrations in mg/m^3, Q is the volumetric flow in m^3/min, τ is the residence time in minutes and V is the volume of activated carbon in the column, m^3.

The results obtained with the GAC filter on a laboratory scale were compared with the data for the three rapid filters on a plant-scale provided by the manager of the Boaco facility. The three filters have dual-media filter with 0.3 m of GAC and 0.45 m of sand in each.

3.9 Sorption Experiments to Different pH Levels (Paper VII)

Experiments were carried out in order to study the kinetics of the sorption onto chitosan. The amount of DOC in fulvic and humic acid solution or in natural waters adsorbed onto chitosan at time *t* was calculated using the equation:

$$q_{(t)} = \frac{(C_o - C_t)V}{w}$$
(3.4)

where $q_{(t)}$ (mg/g) is the adsorbent capacity at time *t*, C_o and C_t are respectively the initial DOC concentration and the concentration (mg/L) at time *t*. V is the volume of the solution (L) or of fresh water and *w* is the weight of chitosan (g).

The kinetic experiments were performed with humic and fulvic acid solutions and fresh natural water. The content of organic matter was measured as dissolved organic carbon (DOC).

For humic acid, the batch kinetic experiments were performed at humic acid concentrations of 10 and 20 mg/L. 0.2 g of chitosan (supplied by Sigma Aldrich) were added to 200 mL of humic acid solution. The mixture was stirred at 150 rpm to 25^oC. The experiments were performed using chitosan of low, medium and high molecular weights at a pH in the range from 4 to 8. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH. Samples were filtered through a 0.45 µm filter and the concentration of dissolved organic carbon (DOC) was determined. The experiments were done in duplicate.

For fulvic acid, the conditions used were similar but concentration of 3 and 30 mg/L were used. Fresh water from river and lake were used.

3.10 Trihalomethanes and The Influences of pH, Chlorine Dosages, Temperature, and Contact Time (Papers I and VI)

The influences of chlorine dosage (0.5-5 mg/L), contact time (15-120 minutes), pH (5-8) and temperature (15-30^oC) on the formation of trihalomethanes were investigated for waters treated with conventional and enhanced coagulation. Water samples taken after conventional coagulation and rapid sand filtration in the facilities were used. In the laboratory, the water previously treated by enhanced coagulation, which should fulfil the TOC requirements, was used after filtration through a paper filter (Whatman No. 1). Both waters were treated in the laboratory using different chlorine dosages, different contact times and different temperatures. The ranges were chosen so that they included the values used at the facilities (Paper I). Reagent grade sodium hypochlorite was used as chlorine source. A constant temperature was maintained using three thermostats (LAUDA, M40). 300 ml of water was used for each test.

A more exhaustive study of the formation of trihalomethanes after conventional and enhanced coagulation was carried out in order to determine the influences of the four parameters previously mentioned using raw and filtered water from Boaco (Paper VI). According to a factorial design, 81 sets of parameters were considered with three samples in each case, giving a total of 243 experiments. The experimental design is presented in Table 3.3.

Table 3.3 Experimental design.

Parameters	Levels		
A: Chlorine Dosages (mg/	1	3	5
B: pH	5	7	10
C: Temperature (^{o}C)	20	25	35
D: Reaction Time (h)	24	50	100

3.11 Total Exposure Cancer Risk (Paper VI)

The total exposure cancer risk was calculated using the methodology described by Lee *et al*. (2006) but adequate to the social conditions specific for Boaco population. The total risk takes into account the risk by ingestion, inhalation and dermal intake. These risks are additive and the total is determined by the following equation:

$$Total\ exposure\ cancer\ risk\ (R_T) = Risk_{ingestion} + Risk_{inhalation} + Risk_{dermal\ intake} \qquad (3.5)$$

Each individual risk is estimated by the application of the equations below:

$$Risk_{ingestion} = CDI_{ingestion}\ x\ SP \qquad (3.6)$$

$$Risk_{inhalation} = CDI_{inhalation}\ x\ SP \qquad (3.7)$$

$$Risk_{dermal\ intake} = CDI_{dermal\ intake}\ x\ SP \qquad (3.8)$$

where *CDI* is the chronic daily intake in mg/kg-day and *SP* is the trihalomethane slope factors for chloroform in kg-day/mg. The *SP* values are 6.10 x 10^{-3}, 3.05 x 10^{-2} and 8.05 x 10^{-2} kg-day/mg for ingestion, inhalation and dermal intake respectively (Wang *et al.,* 2007). *CDIs* are calculated according to each risk:

$$CDI_{ingestion} = \frac{(CW\ x\ 0.8\ x\ IR\ x\ EF\ x\ ED}{(AT\ x\ BW)} \qquad (3.9)$$

where *CW* is the concentration of trihalomethanes in water (mg/L), *IR* is the ingestion rate (2 L/day assumed for Boaco), *EF* is the exposure frequency (365 day/year), *ED* is the exposition duration (68 years is the mean life for the Boaco population), *AT* is the average exposure time (68 year x 365 day/year), *BW* is the body weight 65 kg for male and 60 kg for female for the Boaco population according to MINSA (2003).

CDI for inhalation takes into consideration the time a person spends in the shower which is taken to be an exposure time (*ET*) of 10 min/day for Boaco conditions, and also the THM concentration in the air in the bathroom (*C*$_{air}$) in mg/L. In addition, *VR* is the ventilation rate (14 L/min for male and 11 L/min female) (USEPA, 1997).

$$CDI_{inhalation} = \frac{\left(C_{air} \, x \, VR \, x \, EF \, x \, ET \, x \, ED \right)}{\left(AT \, x \, BW \right)} \qquad (3.10)$$

C$_{air}$ was calculated using the equation given by Wang *et al.* (2007):

$$C_{air} = \frac{(Y_s(t) + Y_{si})}{2} \qquad (3.11)$$

where *Y*$_{si}$ is the initial THM concentration as chloroform in the shower room (0 mg/L) and *Y*$_s$*(t)* is the THM concentration as chloroform in the shower room at time t (10 minutes was assumed to represent the social conditions of the Boaco population). To calculate *Y*$_s$*(t)*, it is necessary to know the Henry constant and overall mass coefficient for chloroform, the bathroom volume, and the water and air flow rates. The equations for the calculation of *Y*$_s$*(t)* are presented below:

$$Y_s(t) = [1 - exp(-bt)](\frac{a}{b}) \qquad (3.12)$$

$$a = \frac{\{Q_L \, CW \, [1 - exp(-N)]\}}{V_s} \qquad (3.13)$$

$$b = \frac{\{(\frac{Q_L}{H})[1 - exp(-N)] + Q_G\}}{V_s} \qquad (3.14)$$

where *Q*$_L$ is the water flow rate (2 L/min assumed for Boaco), *Q*$_G$ is the airflow rate (50 L/min) (Little, 1992), *V*$_s$ is the bathroom volume (2 m^3 assumed for Boaco), *H* is the Henry constant (0.12 for chloroform) (RAIS, 2005), and *N* is a dimensionless coefficient calculated according to:

$$N = \frac{(K_{OL} \, A)}{Q_L} \qquad (3.15)$$

where *K*$_{OL}$ *A* is the overall mass coefficient for chloroform (7.4 L/min) (Little, 1992).

The chronic daily dermal intake is calculated (Lee *et al.* 2006) as:

$$CDI_{dermal\ int\ ake} = \frac{(CW\ x\ PC\ x\ SA\ x\ EF\ x\ ET\ xED)}{(AT\ x\ BW)} \qquad (3.16)$$

where *PC* is the dermal intake permeability coefficient (1.48 x 10^{-6} m/min for chloroform) (RAIS, 2005) and *SA* is the skin surface area (m^2) calculated according to the equation developed by USEPA (1997):

$$SA = \frac{(4BW + 7)}{(BW + 90)} \qquad (3.17)$$

The total exposure cancer risk for Boaco water was calculated with respect to the maximum, mean and minimum trihalomethane concentrations measured as chloroform in the waters treated by conventional or enhanced coagulation. In addition, this risk was determined for both the male and the female population.

Chapter 4

Results and Discussion

This chapter focuses on the results obtained in the different experiments performed to accomplish the objective achieving a greater NOM removal using treatments affordable to the Nicaragua social and economic conditions. First, a description of the raw waters tested is presented. Then, the fractionation of the organic matter of the sources is described. In addition, the results of the experiments using conventional coagulation and enhanced coagulation are presented, and sorption kinetic experiments are also reported. The trihalomethane formation and the study of the influence of operation conditions on the formation of trihalomethanes are also presented.

4.1 Raw Water Characteristics

Table 4.1 presents the ranges of the values of the parameters measured during the sampling period. The input of contaminants from urban, agricultural and geological sources to the catchment areas mean that these rivers and lakes present a wide variation in quality, as is shown in this table.

Table 4.1 Raw water characteristics.

Parameters	River Water			Lake Water
	Boaco	**Camoapa**	**Santo Tomas**	**Juigalpa**
pH	7.0-8.05	7.3-8.1	7.0-7.2	7.1-7.8
Temperature (^{o}C)	21.9-24.2	22.1-23.2	21.7-26.0	22.3-26.5
Turbidity (NTU)	22.6-43.5	16.7-52.2	27.4-66.0	15.5-29.1
Colour (mg/L Pt-Co)	35.1-240.0	101.2-132.3	114.0-269.3	44.8-60.8
Conductivity (μS/cm)	191.0-231.0	121.5-143.6	181.6-187.4	201.9-202.0
Total dissolved solids (mg/L)	94.3-107.6	63.9-70.6	89.7-90.5	99.8-101.2
Alkalinity (mg/L CaCO$_3$)	101.0-114.0	70.0-97.3	90.4-109.6	101.1-134.5
UV$_{254}$ (1/cm)	0.140-0.289	0.150-0.302	0.355-0.407	0.070-0.126
DOC (mg/L)	4.9-9.6	5.3-21.0	11.5-23.9	2.7-4.5
SUVA (L/mg-m)	1.5-4.1	1.4-3.0	1.7-3.1	2.0-2.8

As can be seen on Table 4.1, the raw waters have a pH that is almost neutral and is within the range for fresh water (6.5-9.0). The alkalinity is moderately high with sufficient capacity to neutralize the pH changes. The total dissolved solids and conductivity were in the normal interval for lowland rivers (125-2200 μS/cm), but for the lake, the conductivity exceeded the range reported by Chamberlain (2010) of 20-30 μS/cm.

NOM was determined indirectly by surrogate parameters such as colour, DOC, UV_{254}, and SUVA. These parameters characterize the complex mixture of organic matter present in the waters. The highest NOM values were found in the Santo Tomas and the lowest in the Juigalpa water sources.

The high colour values in all these plants indicated the presence of an elevated content of organic matter. This parameter is an indicator of a high degree of conjugation in the complex molecules of NOM having multiple bonds with highly substituted aromatic groups. It is linked to the higher molecular weight NOM (Newcombe *et al*., 1997).

Like the colour, the DOC values are quite high in the Camoapa and Santo Tomas sources, and lower values were found in Boaco and Juigalpa. However, these DOC values are within the commonly found range from 2.0 to 15.0 mg/L reported by Hepplewhite *et al*. (2004) and they indicated that the organic matter present in the raw water sources is of the humic type.

The same tendency was found with UV_{254} that measure the aromatic content in the waters. A low UV_{254} implies less formation of chlorination by-products due to low aromaticity.

SUVA is a parameter that is used as an indicator of the organic matter content in relation to the coagulation process and its reactivity with chlorine. SUVA values lower than 2 L/mg-m indicate the presence of organic matter of low molecular weight, hydrophilic and less reactive with chlorine. SUVA values between 2 and 4 L/mg-m indicate a mixture of aquatic humic and other NOM, and a combination of hydrophobic and hydrophilic substances of low and high molecular weight more reactive with chlorine. SUVA values higher than 4 L/mg-m show the presence of hydrophobic organic matter of high molecular weight. The diversity in the SUVA values obtained for these four sources confirms the great variation of organic matter in the raw water.

The higher values of DOC, UV_{254} and SUVA were found in the rainy seasons and are related to land-use practices, since soils rich in humic matter are transported into the water by run-off. Lower values were found in the dry season.

Other parameters that influence the presence of organic matter in the rainy season are temperature, where high values increase the degradation of organic matter in the soil producing more mobile NOM, which may be removed with the precipitate.

Raw Water Fractioning

In order to determine whether the hydrophobic or the hydrophilic fraction predominates in these sources, fractionation with an adsorption/desorption method was carried out in one of the river sources (Boaco) and the lake source (Juigalpa). Four fractions were obtained: very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic acid (CHA) and neutral hydrophilic (NEU). In addition, the presence of

nitrogenous organic matter was shown. Tables 4.2 and 4.3 shows the results obtained. Juigalpa water presents lower values of NOM (DOC, UV_{254}, Colour, SUVA), dissolved organic carbon (DON) and dissolved inorganic carbon (DIN) than the Boaco water, but both waters are more hydrophobic than hydrophilic. The DOC values in the fraction that characterizes the hydrophobicity of the NOM (VHA+SHA) (solid circle on tables) in the water were 71.7% and 64.6% for Boaco and Juigalpa respectively. The hydrophilic fractions (CHA+NEU) (dashes circle in the tables) were 28.3% and 35.4% respectively. These higher proportions of the hydrophobic fractions in both sources are indicative of more aromatic or conjugated compounds, which are more reactive with chlorine.

Table 4.2 Boaco water characterisation.

Sample	UV_{254} (1/cm)	DOC (mg/L)	DON (mg/L)	Colour (mg/L)	DIN (mg/L)	DIN/TDN (mg/mg)	DOC/DON (mg C/mg N)	SUVA (L/mg-m)	Specific Colour
Whole NOM	0.163	4.9	0.283	35.1	0.755	0.73	17.3	3.3	7.2
VHA	0.096	2.5	0.035	21.6	0.120	0.77	71.4	3.8	8.6
SHA	0.042	1.3	0.044	9.7	0.185	0.81	29.5	3.2	7.5
CHA	0.018	0.6	0.143	4.3	0.236	0.62	4.2	3.0	7.2
NEU	0.010	0.9	0.068	1.2	0.219	0.76	13.2	1.1	1.3
Total Fractions	**0.166**	**5.3**	**0.290**	**36.8**	**0.760**	**0.72**	**18.3**	**3.1**	**6.9**

Table 4.3 Juigalpa water characterisation.

Sample	UV_{254} (1/cm)	DOC (mg/L)	DON (mg/L)	Colour (mg/L)	DIN (mg/L)	DIN/TDN (mg/mg)	DOC/DON (mg C/mg N)	SUVA (L/mg-m)	Specific Colour
Whole NOM	0.126	4.5	0.214	29.2	0.141	0.40	21.0	2.8	6.5
VHA	0.072	2.0	0.027	17.9	0.016	0.37	74.1	3.6	9.0
SHA	0.036	1.1	0.032	9.4	0.025	0.44	34.4	3.3	8.5
CHA	0.017	0.7	0.104	3.1	0.070	0.40	6.7	2.4	4.4
NEU	0.012	1.0	0.054	1.3	0.038	0.41	18.5	1.2	1.3
Total Fractions	**0.137**	**4.8**	**0.217**	**31.7**	**0.149**	**0.41**	**22.1**	**2.9**	**6.6**

In both tables, it can be seen that the fractions have the same trend VHA>SHA>CHA>NEU for DOC, UV_{254} and colour, but for DON and DIN the trend is CHA>NEU>SHA>VHA which means that the hydrophilic fraction which is more polar has a higher nitrogen content than the hydrophobic fraction.

The DOC/DON ratio determines the trend not to form nitrogen disinfection by-products (N-DBPs) in the disinfection step (Dotson *et al*., 2009). That means that Juigalpa source with the higher DOC/DON value has a much lower tendency to form N-DBPs than the Boaco source which has a lower DOC/DON ratio. In contrast, the DIN/TDN ratio is quite high for Boaco raw water in comparison with the Juigalpa water.

The inorganic dissolved nitrogen (DIN) content is 72.7%, which is higher than the 27.3% of organic dissolved nitrogen (DON) in Boaco. The high DIN content is probably due to the fact that the water source for Boaco is the Fonseca River that receives untreated domestic and wastewater effluents, since the sewage system does not cover the whole city. Some of the sewage is dumped into the soil. In addition, these are inputs of agricultural runoff into the river, which carry fertilizers and pesticides. In Boaco, nitrate and ammonia constituted 45.8% and 24.1% of the total dissolved nitrogen (TDN) respectively. The concentrations for $N-NH_4^+$, $N-NO_2^-$, and $N-NO_3^-$ were 0.250, 0.030, and 0.475 mg/L N respectively; these values exceed the guidelines of 0.015 mg/L $N-NH_4^+$, 0.0015 $N-NO_2^-$ and 0.10 mg/L $N-NO_3^-$ for unpolluted rivers (Meybeck, 1982). These concentrations agree with the fact that there is more DIN than DON in this source. In the case of the Juigalpa raw water, the ammonia or nitrite concentrations were below the detection limit of the equipment, nitrate being the dominant form of the inorganic nitrogen compounds. The dissolved inorganic nitrogen (DIN) was 39.7% and the dissolved organic nitrogen (DON) the remainder of the total dissolved nitrogen (TDN) in Juigalpa. The presence of DIN in the Nicaragua Lake could be due mainly to agricultural runoff and not to domestic or industrial effluent.

The SUVA values were higher for the hydrophobic fraction, which has a lower organic nitrogen content than the hydrophilic fraction. The hydrophilic fraction had a lower SUVA value but was richer in organic nitrogen. Specific colour showed the same tendency as SUVA, being higher for the hydrophobic than for the hydrophilic fraction. Specific colour values found in both sources indicated the presence of an intermediate degree of conjugation or aromatic group substitution.

4.2　NOM Removal by Coagulation with Aluminium Sulphate or Chitosan

Table 4.4 shows the removal of the NOM surrogates after treatment with aluminium sulphate (AS) or chitosan (Ch) as coagulant for the four raw waters without fractionation. It is evident that chitosan gave slightly higher removal values for the parameters measured in the plants that use river water as sources. On the other hand, Juigalpa that uses lake water, showed better removal results with aluminium sulphate than with chitosan.

The turbidity removal with chitosan ranged from 76.1 to 93.1%, and these removals were less than the values reported by Roussy *et al.* (2005) of 95% with chitosan at pH 7. Similarly, the removal by aluminium sulphate was 72.9-89.8%, which is also less than the turbidity reduction reported by Rizzo *et al.* (2008) of 85% at pH 7.

Table 4.4 NOM removal, in percentages.

Parameters (% Removal)	Boaco		Camoapa	
	AS	Chitosan	AS	Chitosan
Turbidity	88.5	90.7	79.0	84.4
Colour	88.1	92.0	86.3	88.5
UV_{254}	82.9	86.8	77.8	79.7
DOC	77.6	82.4	60.4	66.0
SUVA	23.3	23.3	43.3	40.0

	Santo Tomas		Juigalpa	
	AS	Chitosan	AS	Chitosan
Turbidity	89.8	93.1	72.9	76.1
Colour	91.4	92.8	69.2	63.4
UV_{254}	85.1	87.0	71.1	68.4
DOC	78.3	82.6	63.0	55.6
SUVA	32.3	25.8	21.4	28.6

AS: Aluminium Sulphate

However, the colour removal for the river waters was greater than the range reported by Hakonsen *et al.* (2008) of 50-80% with chitosan and very close to the value of 90% using aluminium sulphate mentioned by Bratby (2006). Nevertheless, the remaining colour exceeded the target value of 15 mg/L Pt-Co set by USEPA (2009).

A greater reduction of UV_{254} with chitosan was also observed in the rivers waters, because chitosan acts as both coagulant and flocculant, so that the interaction with dissolved and particulate compounds in the water is very efficient. Aluminium sulphate acts only as a coagulant. UV_{254} removal in the Juigalpa water was higher with aluminium sulphate although this removal was lesser than that from the river waters (Figure 4.1). In general, UV_{254} removal achieved with aluminium sulphate was in the range of 80-90%, as reported by Edzwald (1993).

The UV_{254} reduction using chitosan exceeded the range of 30-60% obtained by Rizzo *et al.* (2008) with this coagulant. The greatest UV_{254} reduction was observed in the Santo Tomas water, where 85.1% and 87.0 % UV_{254} removal were found with aluminium sulphate (50 mg/L) and chitosan (12 mg/L) respectively. Lower dosages of chitosan than of aluminium sulphate are sufficient to destabilize NOM substances due to the high charge density of the amino groups in the chitosan. The presence of quaternary amino groups with a positive charge increases the electrostatic interaction with the negatively charged NOM, reducing the double layer repulsion to bind them. In addition, more than one small particle can be adsorbed onto the polymeric chain of chitosan by an inter-particle bridging mechanism, forming strong aggregates of large flocs and allowing more NOM removal (Roussy *et al.,* 2005; Renault *et al.,* 2009).
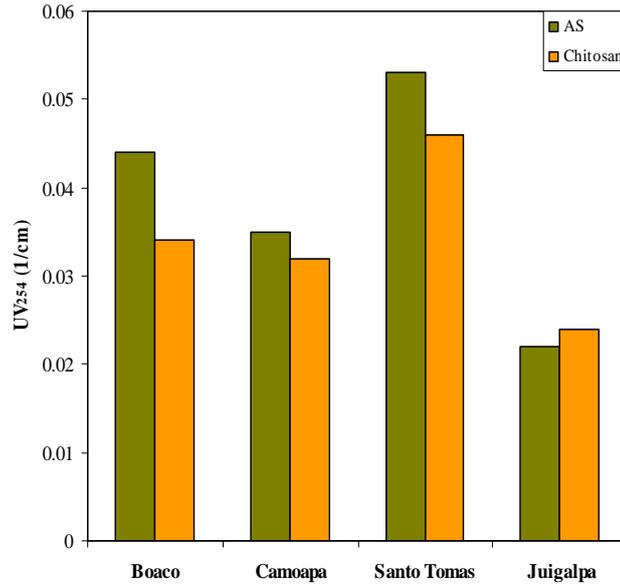
Figure 4.1 UV_{254} remaining after aluminium sulphate or chitosan treatment.

The removal of dissolved organic carbon (DOC) was lower than the removal of turbidity, colour, and UV_{254}. However, these values exceeded those given by Edzwald and Tobiason (1999) of about 25-50% when SUVA is between 2 and 4 and aluminium sulphate is used as coagulant. Nevertheless, Sharp *et al.* (2006) reported DOC removal in the range of 10-90% when aluminium sulphate is used as coagulant. The removal of DOC was slightly higher with chitosan than with aluminium sulphate for the river waters and the opposite was true for lake water. Machenbach (2007) indicates that chitosan is a poor coagulant for water with organic matter of low molecular weight like the Juigalpa water. The highest DOC removals were found in the river waters that had a high DOC concentration. The richer the water is in humic compounds, the greater is their removal due to their high molecular weight, low solubility and large size.

SUVA decreased after the coagulation treatment with aluminium sulphate or chitosan to values of about 2 L/mg-m in most of the treated waters. These values indicate that the treated water may be less reactive with chlorine because the NOM of humic type had been largely removed in the coagulation process. The formation of chlorination by-products such as trihalomethanes will therefore be less, since most of the organic matter still present is non-humic having a low molecular weight. The lowest SUVA values were observed in the Camoapa water ($\cong$ 1.7-1.8 L/mg-m), whereas high SUVA values were found in the Boaco river water (2.3 L/mg-m) regardless of the coagulant applied.

Coagulation of the Fractionated Water

The fraction that showed the highest $UV_{254,}$ DOC and colour removal with aluminium sulphate or chitosan for both sources was the hydrophobic acid (VHA) fraction, followed by the hydrophilic acid (SHA) fraction, the charged hydrophilic acid (CHA) fraction, and

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the lowest removal was the neutral hydrophilic (NEU) fraction, as is shown in Figure 4.2. This behaviour is because the hydrophobic fraction (VHA+SHA) is less soluble in water and is more easily to coagulate than the hydrophilic fraction which is soluble (CHA+NEU). The CHA and NEU fractions are recalcitrant and therefore difficult to remove by coagulation with either of the coagulants.
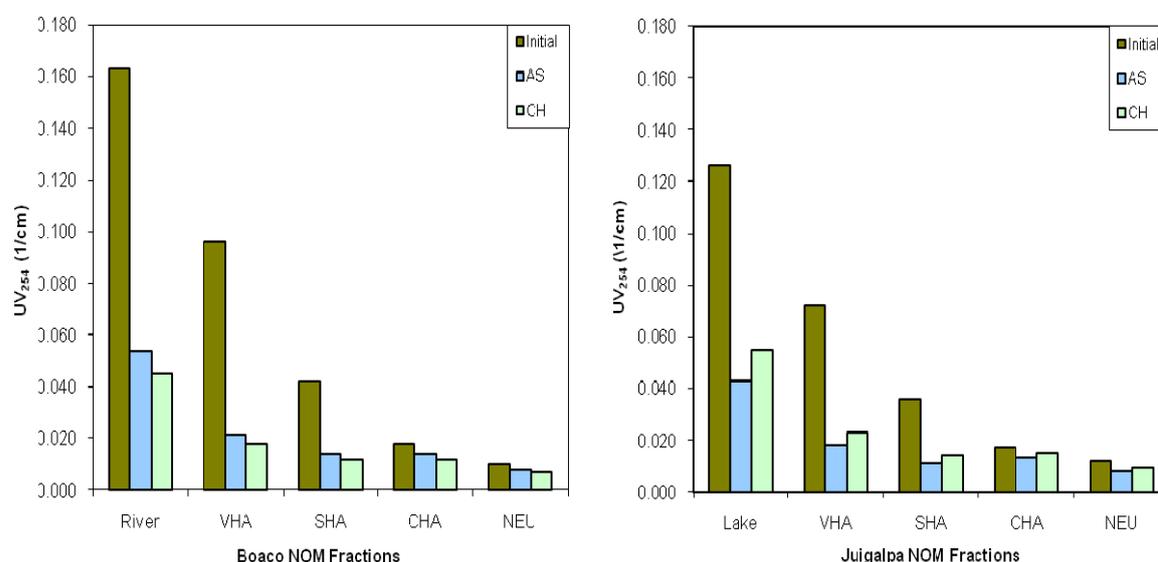

Figure 4.2 UV_{254} remaining after (AS) or (Ch) coagulation.

Specific colour and SUVA show the same trend in the different fractions, decreasing slightly more in the hydrophobic than in the hydrophilic fraction (Tables 4.5 and 4.6), indicating that organic compounds are removed more from the hydrophobic than from the hydrophilic fractions.

The DOC/DON ratio decreased with aluminium sulphate or chitosan in the whole water. The values of these ratios for the treated water are in the range of 10-30 mg C/mg N for drinking water (Lee and Westerhoff, 2006).

Table 4.5 Characteristics of the coagulated whole and fractionated water in Boaco.

Water Treated with Aluminium Sulphate								
Sample	UV_{254} (1/cm)	DOC (mg/L)	DON (mg/L)	Colour (mg/L)	DIN (mg/L)	DIN/TDN (mg/mg)	DOC/DON (mg C/mg N)	SUVA (L/mg-m)	Specific Colour
Whole NOM	0.054	2.3	0.176	7.3	0.426	0.71	13.1	2.3	3.2
Hydrophobic	0.035	1.6	0.026	5.1	0.099	0.79	61.5	2.2	3.2
Hydrophilic	0.022	0.9	0.157	3.4	0.334	0.68	5.7	2.4	3.8
Water Treated with Chitosan								
Whole NOM	0.045	2.0	0.188	5.7	0.460	0.71	10.6	2.3	2.9
Hydrophobic	0.030	1.4	0.041	3.8	0.125	0.75	34.1	2.1	2.7
Hydrophilic	0.019	0.9	0.156	3.0	0.343	0.69	5.8	2.1	3.3

Table 4.6 Characteristics of the coagulated whole and fractionated water in Juigalpa.

Sample	UV$_{254}$ (1/cm)	DOC (mg/L)	DON (mg/L)	Colour (mg/L)	DIN (mg/L)	DIN/TDN (mg/mg)	DOC/DON (mg C/mg N)	SUVA (L/mg-m)	Specific Colour
Water Treated with Aluminium Sulphate									
Whole NOM	0.043	2.4	0.147	6.3	0.092	0.38	16.3	1.8	2.6
Hydrophobic	0.029	1.8	0.022	4.4	0.022	0.50	81.8	1.6	2.4
Hydrophilic	0.021	0.9	0.129	2.8	0.077	0.37	7.0	2.3	3.1
Water Treated with Chitosan									
Whole NOM	0.055	2.8	0.158	7.2	0.103	0.39	17.7	2.0	2.6
Hydrophobic	0.037	2.0	0.023	5.4	0.027	0.54	87.0	1.9	2.7
Hydrophilic	0.024	1.1	0.139	3.0	0.086	0.38	7.9	2.2	2.7

The DOC/DON ratio increased greatly in the hydrophobic fraction and decreased in the hydrophilic fraction, which means that hydrophobic fraction with a higher DOC/DON value had much less tendency to form N-DBPs than the hydrophilic fractions that had a lower DOC/DON ratio.

Figure 4.3 shows the remaining concentrations for DON and DIN for the whole and fractionated treated waters. DON and DIN in Boaco and Juigalpa decreased in the whole water and in each fraction after treatment with aluminium sulphate, and this gave a greater reduction than with chitosan.
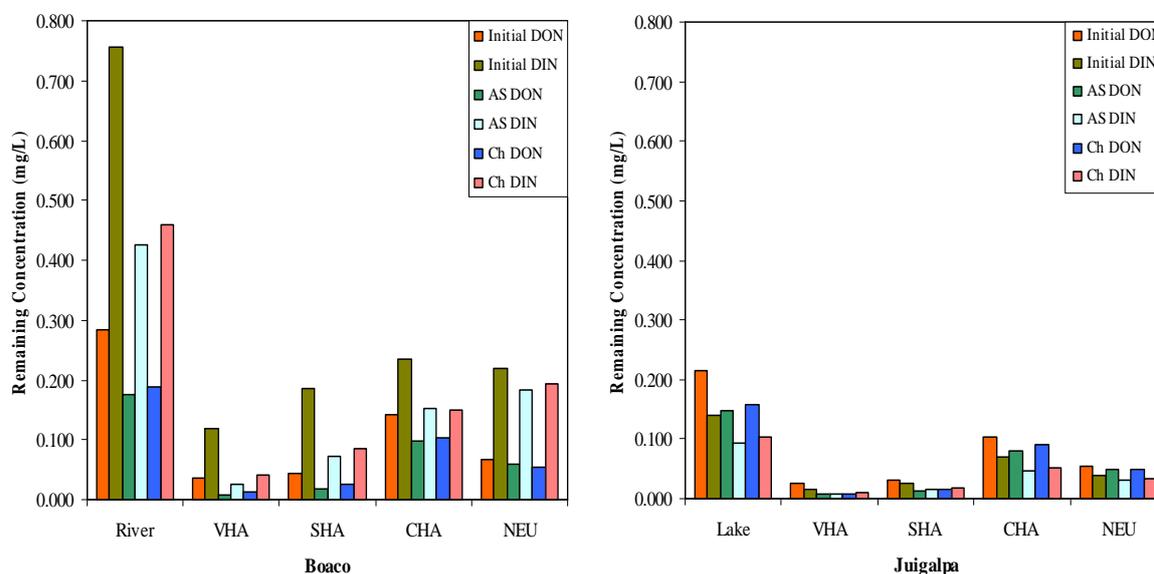
Figure 4.3 DON and DIN remaining after (AS) or (Ch) coagulation.

In the same figure, it can be observed that the remaining DON and DIN concentration of the hydrophilic fractions (CHA+NEU) of Boaco and Juigalpa were higher than the hydrophobic fraction (VHA+SHA), indicating that these compounds are difficult to remove in that fraction regardless of the coagulant used. According to these results, the

nitrogenous organic matter in the hydrophobic fraction can more easily be removed by coagulation and DON and DIN are therefore in a lower proportion in this fraction than in the hydrophilic fraction, where due to its great solubility they are difficult to remove. Pietsch *et al.* (2001) found that the elimination of nitrogenous compounds is difficult to achieve with coagulation and that they are better removed by ozonation and microbial degradation.

Furthermore, Vilge-Ritter *et al.* (1999) reported that nitrogenous compounds correspond to a small fraction of the DOC in the raw waters and that their removal is so much lower that they considered that aluminium or ferric salts do not coagulate these compounds. Both coagulants do have high a selectivity for aromatic compounds, which are significantly reduced in the coagulation process.

Cost-Benefit Analysis

Chitosan seems to be an excellent alternative to reduce the NOM, particularly in river waters. Some of the advantages of chitosan over aluminium sulphate are: lower dosages are needed, it is environment-friendly, improved floc settling may reduce settling time, a smaller sludge volume, and the sludge effluent can be dumped directly to the landfill because chitosan is non-toxic, can be further degraded by micro-organisms, or can be used for feed animal supplement or soil improver (Rinaudo, 2006). However, the toxicity should always be tested.

In addition, pollution due to shrimp and squat lobster waste shell dumping can be diminished in the Nicaragua water sources, but a possible drawback could be the cost of chitosan.

According to Sekine *et al.* (2006), chitosan and aluminium sulphate cost about $ 21.8/kg and $ 3.5/kg respectively. The coagulant dosages needed to achieve the required NOM removal in the raw waters evaluated in this research were approximately 10 mg/L for chitosan and 50 mg/L for aluminium sulphate; and the amounts of these coagulants required per cubic meter of water produced are 0.01 kg/m^3 and 0.05 kg/m^3 respectively. Therefore, the costs are $ 0.218/m^3 and $ 0.175/m^3 for chitosan and aluminium sulphate, which means that the chitosan cost exceeds the aluminium sulphate cost.

However, the production of chitosan is increasing worldwide and the price has dropped. For example, China offers chitosan at $ 13/kg (Chi and Cheng, 2006), which is lower than the price reported by Sekine *et al.* (2006).

Using an average of these two prices ($ 17.5/kg), the cost of the coagulant is similar for chitosan and aluminium sulphate: $ 0.175/m^3 of water produced. The advantages of chitosan and its lower price can make it feasible to use chitosan as coagulant instead of aluminium sulphate, and to reduce the pollution in the Nicaragua water bodies.

4.3   NOM and Enhanced Coagulation

The efficiency of enhanced coagulation was studied also in terms of the removal of NOM surrogate parameters. The reduction of total organic carbon (TOC) for the four plants can be observed in Figure 4.4. With high coagulant dosages above 40 mg/L, the total organic carbon dropped to below 2 mg/L for Boaco (P1) and Camoapa (P2). The raw water from Juigalpa (P3) showed the poorest removal of TOC as can be seen in the figure. Water with less organic matter is more difficult to coagulate. The TOC in Santo Tomas (P4) was removed to 95% at a dosage of 60 mg/L. The high concentrations of coagulant used neutralised the negative charge of the humic compounds.
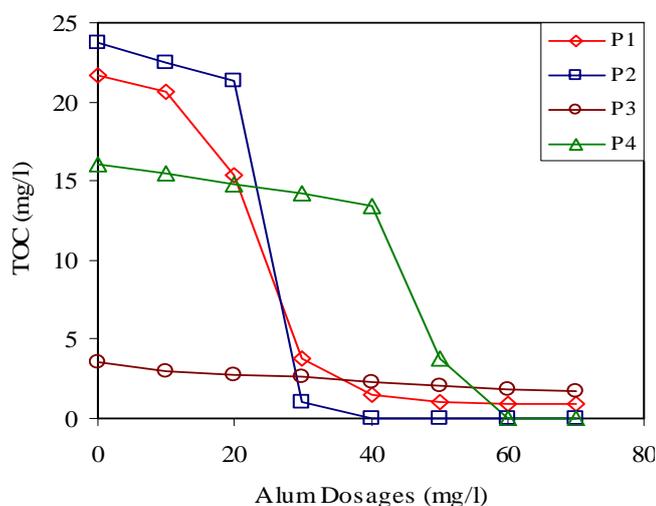
Figure 4.4 Enhanced coagulation at the different drinking water plants.

Figure 4.5 shows the behaviour of TOC and DOC during 2006 at the Boaco plant. Both parameters presented higher values in the rainy than in the dry season. In December, the concentrations of TOC and DOC in the raw water were slightly high because the rainy season had recently finished. Afterwards, the NOM concentration decreased greatly because of the dry season. Later, in May, it increased considerably because the start of the rainy season run-off brought soil rich in humic matter into the source (Fonseca river). Besides, it is noticed that TOC and DOC were significantly reduced by the enhanced coagulation treatment.
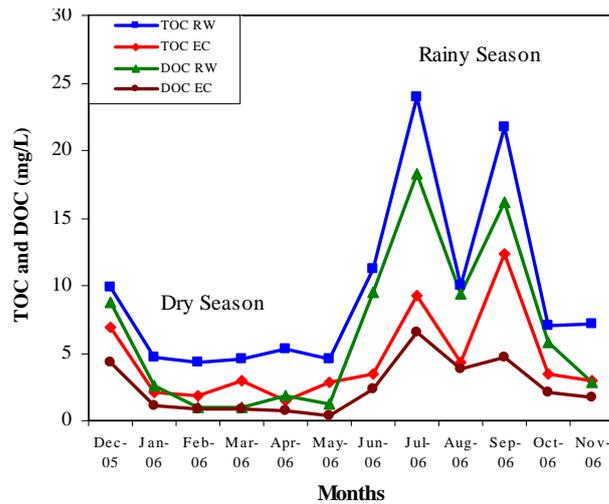
Figure 4.5 TOC and DOC in dry and rainy seasons.

NOM Removal by Enhanced Coagulation (EC) and Granular Activated Carbon (GAC)

It is known that granular activated carbon (GAC) is one of the best treatments for reducing the presence of CBPs precursors (USEPA, 2002). Experiments using GAC after enhanced coagulation were performed in order to determine the capacity of activated carbon for the adsorption of low molecular weight organic matter. Figure 4.6 shows the removal of some parameters after both treatments using raw water from the Boaco drinking water plant.

Figure 4.6a shows that the removal of TOC was 50% by EC, and that a total removal of 84.8% was obtained when the enhanced coagulated water was treated with GAC. DOC was reduced by 53.1% when the raw water was treated with EC. A total reduction of 85.9% for DOC was obtained by the whole process (EC+GAC). The higher capacity of EC+GAC for NOM removal compared with EC alone is attributed to the pore size of the carbon (100 A^o ±10 A^o), which allows preferential adsorption of low molecular weight compounds and to the lower load of NOM compounds after enhanced coagulation treatment.
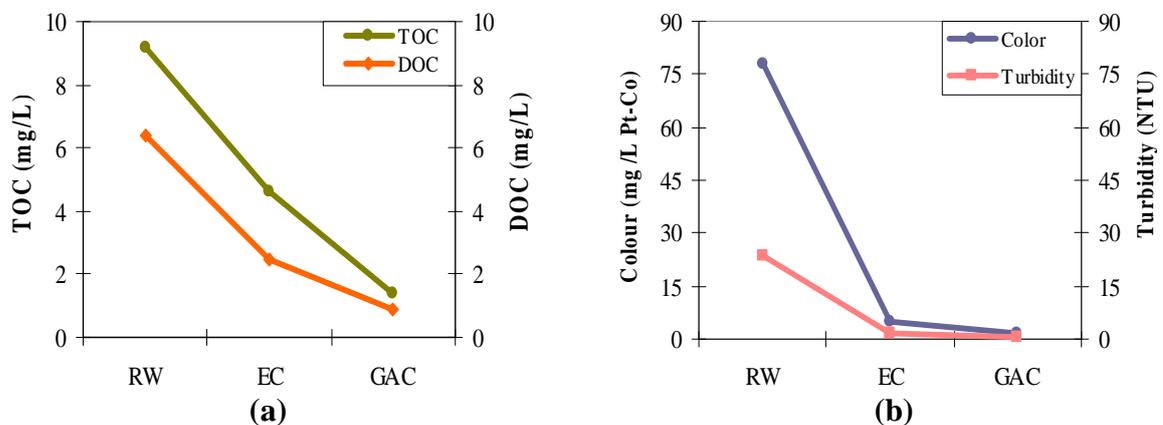
Figure 4.6 Removal of TOC, DOC, colour and turbidity after EC and GAC treatment.

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Colour and turbidity decreased by 93.3 and 94% respectively during EC (Figure 4.6b). An additional reduction of both parameters in the enhanced coagulated water was obtained by GAC. A total reduction of 97.9% and 98.3% was obtained for these two parameters after both EC and GAC treatment were applied to the raw water.

Figure 4.7 presents dynamic adsorption capacities; A_d (adsorption under flow conditions) for TOC and DOC in the GAC column after the NOM had been reduced by EC. It can be seen that A_d decreased when the water had a low concentrations of TOC and DOC during the dry season, probably due to the characteristics of the NOM which is less adsorbable by the GAC because of the NOM humic content. In contrast, after May, A_d increased considerably because the NOM concentration was higher and, after enhanced coagulation, the remaining organic matter was of low molecular weight which has greater access to the adsorbent surfaces in the activated carbon (Karanfill and Kilduff, 1999).
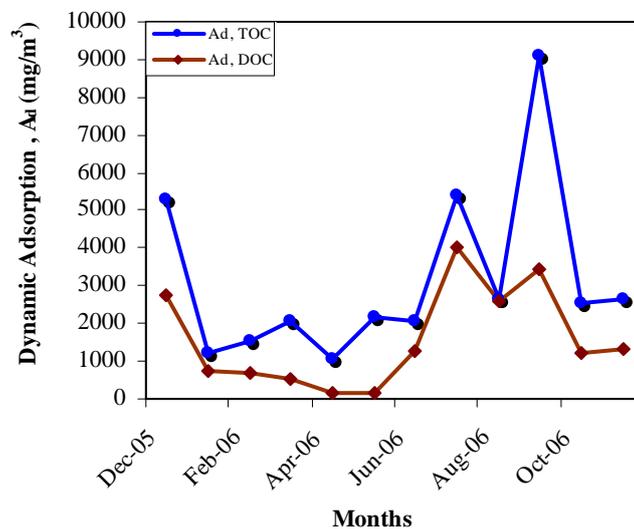
Figure 4.7 Dynamic adsorption (*Ad*) of TOC and DOC in GAC column.

4.4 Other Coagulation Techniques and Flocculation with Chitosan

Experiments were performed using synthetic raw water (SRW) prepared with a low concentration of humic acid (HA) to mimic the range of DOC found in the fresh water in the dry season. Since the NOM is more difficult to be removed by coagulation in that condition, other coagulation strategies such as preformed flocs (PF) and two-stage coagulation (SC) were studied. Aluminium sulphate (AS) was used as coagulant with and without chitosan (Ch) as flocculant; the results were compared with those from the conventional coagulation process (CC).

Regardless of the type of coagulation used, the removal of DOC and UV_{254} increased as the humic acid concentration increased from 1 to 7 mg/L as is shown on Figure 4.8. This is due to the higher charge density that is available at higher humic acid

concentrations making it easy to neutralize the negative charge of humic acid with the positive charge of the coagulant. The figure shows the removal of DOC and UV_{254} by the different coagulation strategies. A greater reduction of both parameters was obtained with two-stage coagulation and chitosan (SC+Ch) with humic acid concentrations of 7 mg/L. The DOC removal after the two-stage coagulation ranged from 48.3% to 70.4% without chitosan and from 55.0% to 79.7% with chitosan at the concentrations of humic acid tested. DOC values below 1 mg/L were obtained in this case, which ensures less trihalomethanes formation during the disinfection step.

The same behaviour as for DOC was observed for UV_{254}. The greatest removal occurred with SC and varied from 60.9% to 78.5% without chitosan and from 71.7% to 89.6% with SC+Ch. The remaining UV_{254} is therefore lowest with this type of treatment (Figure 4.8b). In the same figure can be seen that the UV_{254} remaining in the treated waters with aluminium sulphate and chitosan than with the coagulant alone.
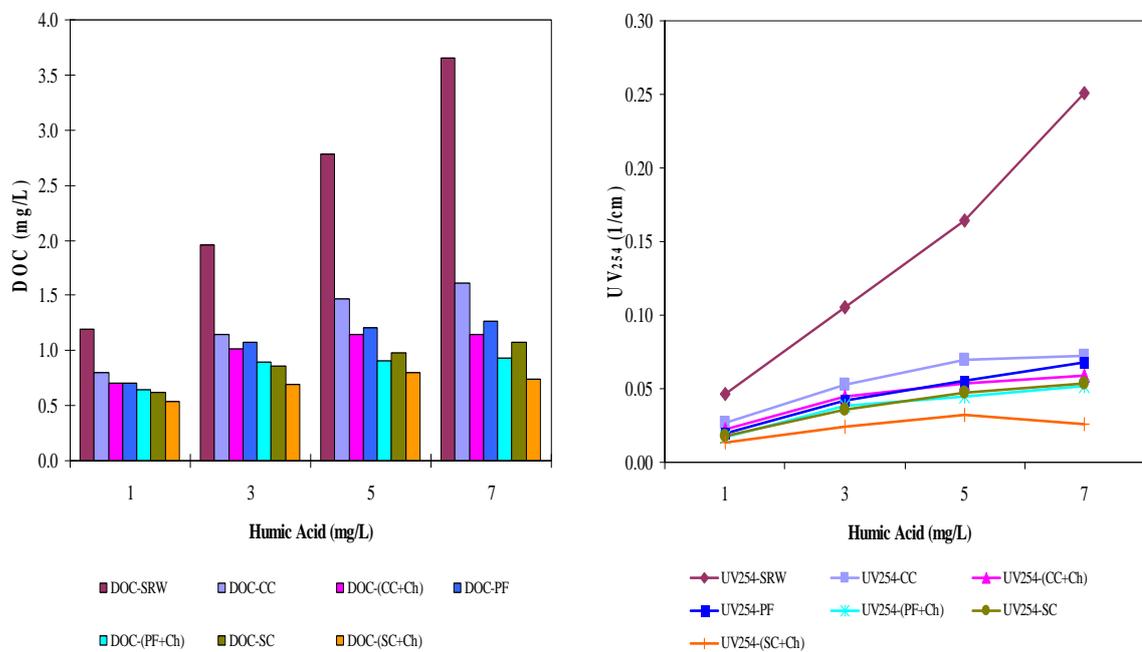
Figure 4.8 DOC (a) and UV_{254} (b) removal after treatment.

Other parameters analyzed were colour and turbidity. Colour shows the highest removal in all the experiments, followed by UV_{254} and DOC. The lowest removal was obtained for turbidity. Figure 4.9 shows that the remaining colour and turbidity showed the same trend as DOC and UV_{254}, having the lowest values after two-stage coagulation and chitosan.

Nevertheless, Figure 4.9a shows that colour exceeded the guidelines of 15 mg/L Pt-Co of USEPA (2009) in the waters with HA concentrations higher than 3 mg/L for CC, CC+Ch and PF. Colour concentration dropped very significantly with SC+Ch, to values below 10 mg/L.

Turbidity removal was lower than the removal of others NOM surrogate parameters, the higher removal percentages were 58.3%-68.9% and 67.4%-79.4% for SC and SC+Ch respectively. This may be explained since NOM controls the coagulation process instead of turbidity. The guideline of 1 NTU of turbidity was exceeded in the treated waters (Figure 4.9b) in several cases; however, synthetic waters treated with two-stage coagulation with and without chitosan always achieved this criterion (USEPA, 2009).
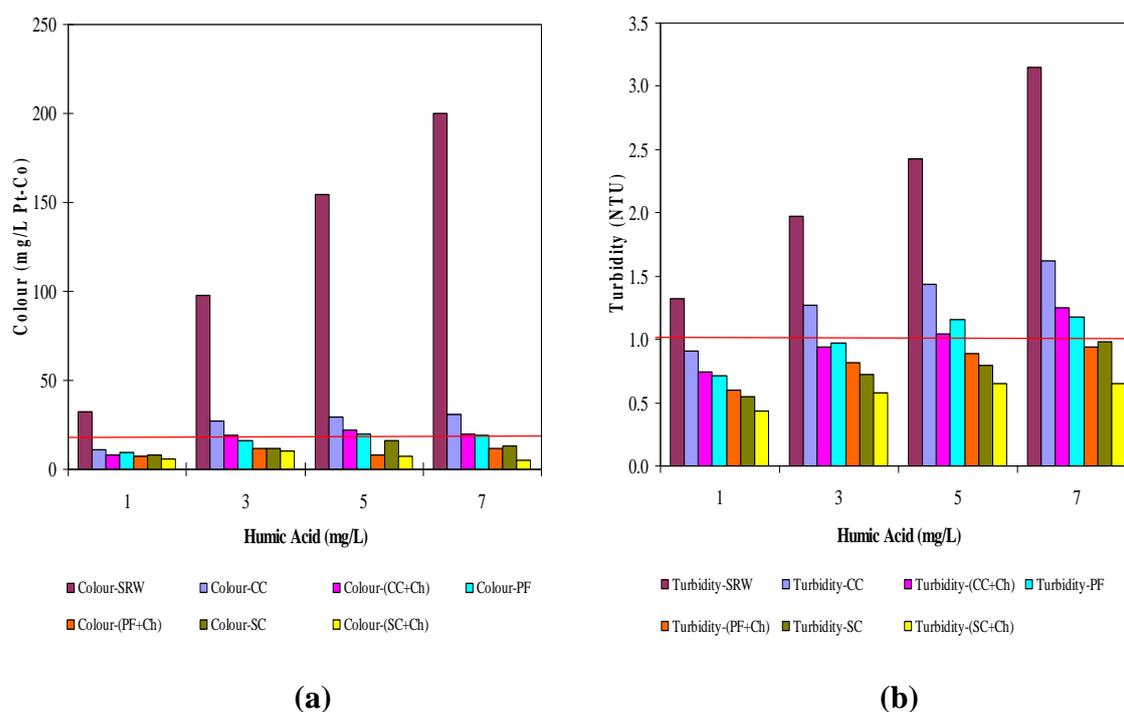

(a)   **(b)**

Figure 4.9 Removal of (a) colour and (b) turbidity after treatment.

Regarding the results, the experiments with two-stage coagulation showed greater NOM removal than was obtained by conventional coagulation and preformed flocs regardless of the humic acid concentration in the synthetic water. Bratby (2006) indicated that two-stage coagulation improved the NOM removal since the aluminium hydroxide colloids are produced almost immediately, while the sorption reactions of NOM compounds with aluminium hydroxide colloids are slower. As a consequence, in conventional coagulation, agglomeration of the small flocs not occurs due to the stabilization of the aluminium hydroxide colloids. However, in two-stage coagulation, the second dosage applied carries out the agglomeration of the initially formed particles, improving the sweep floc regime which gets better settling and filtration characteristics (Bratby, 2006).

It can also be seen in Figures 4.8 and 4.9 that greater NOM removal was achieved when chitosan was applied as flocculant in a complementary treatment step than with coagulation with aluminium sulphate alone. This may be explained since, in the flocculation step, the large flocs grow due to the polymer bridging NOM-Al(OH)$_3$-

Chitosan forms heavier flocs that settle quickly, and the NOM removal is therefore increased, whereas in the coagulation process, the flocs are formed during the destabilization of humic acid molecules with negative charges and the flocs are then smaller (NOM-Al(OH)$_3$).

However, in spite of the greater NOM removal with two-stage coagulation, the use of twice the amount of aluminium sulphate means that the use of this technique cannot be recommended for environmental and health reasons. More sludge containing aluminium sulphate dumped to the water bodies will be a threat to humans and the biota. Therefore, preformed flocs and chitosan seems to be the best option for the removal of NOM. The results demonstrate that the remaining aromatic NOM such as colour and UV$_{254}$ are quite similar and preformed flocs can therefore give good results in the removal of the trihalomethanes precursors.

4.5 Sorption Experiments

Effect of the pH, Chitosan Molecular Weight and Ionic Strength in Fulvic and Humic Acid Adsorption

Figure 4.10 shows the effect of pH and NOM concentration on the adsorption capacity (q). The adsorption capacity on chitosan increases as the pH decreases, since at acidic pH the electrostatic attraction between humic substances and chitosan amino groups is increased. However this effect is more significant at high concentrations of fulvic or humic acids. At low concentration of NOM, *q* is almost constant over the range of pH studied (4 to 8).

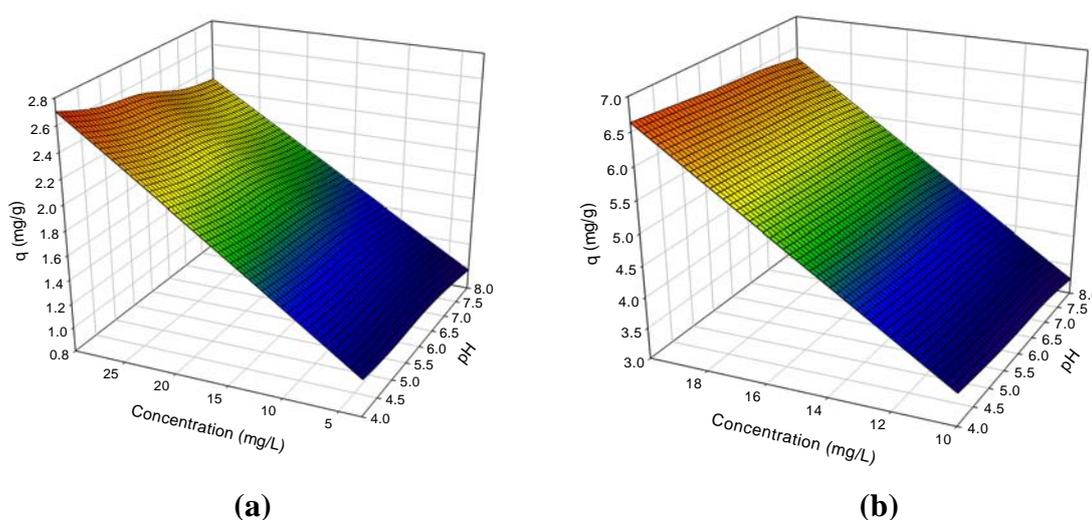**(a)**   **(b)**

Figure 4.10 Adsorption capacities of (a) fulvic acid and (b) humic acid onto chitosan HMW as a function of pH at the tested concentrations.

The influence of chitosan molecular weight is presented on Figure 4.11 where it can be seen that the sorption capacity *q* was higher when chitosan of high molecular weight was used and at higher concentrations of fulvic or humic acid. The sorption capacity decreased slightly when the pH increased, particularly in the range of 6-8.
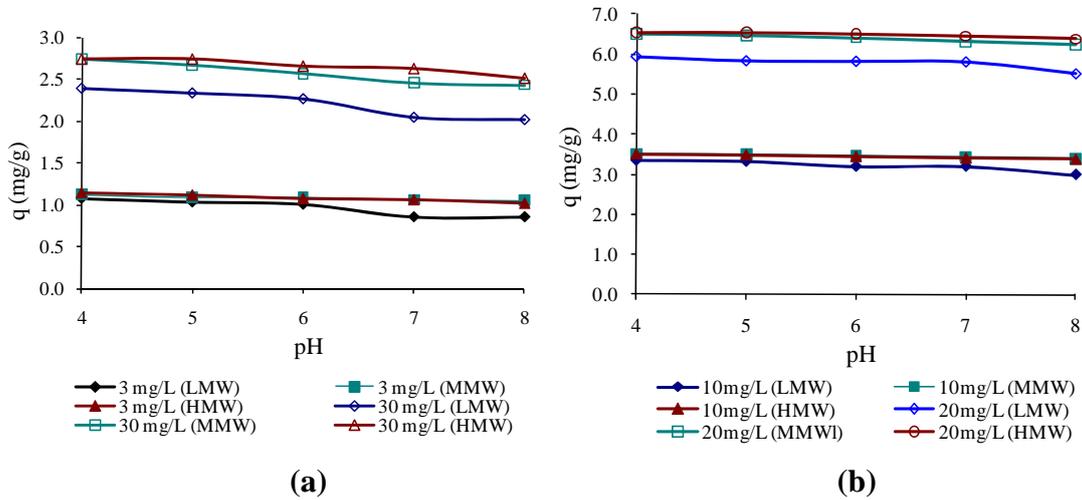

(a)   **(b)**

Figure 4.11 Adsorption capacities of (a) fulvic and (b) humic acid onto chitosan as a function of pH and chitosan molecular weight.

The effect of ionic strength and chitosan molecular weight on the adsorption capacity (*q*) of the humic acid is presented on Figure 4.12. It can be seen that *q* is at its lowest value when chitosan of low molecular weight and zero ionic strength was tested. The highest sorption capacity was observed at an ionic strength of 0.05 M and intermediate molecular weight.
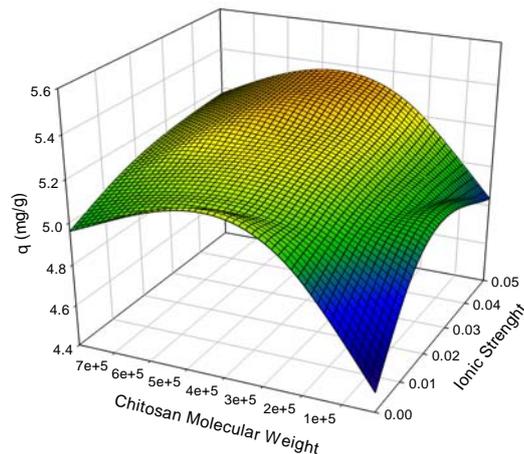
Figure 4.12 Adsorption capacity of humic acid onto chitosan as a function of ionic strength and chitosan molecular weight.

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Adsorption Kinetics of Fulvic and Humic Acid

Figures 4.13 and 4.14 show the adsorption of fulvic and humic acid onto chitosan of high molecular weight as a function of time. The adsorption of humic substances onto chitosan is mainly due to electrostatic interactions, which depend on the solution pH. At pH 4, the adsorption is favoured because the amino groups of the chitosan take the protons available in aqueous solutions, allowing an electrostatic attraction between positive amino groups of the adsorption sites and the negative charge of the fulvic or humic acid. At pH 8, deprotonation of the amino group occurs and the electrostatic interactions are lows, so that, the adsorption decreases.

Figure 4.13 also shows that the adsorption at a low concentration of fulvic acid did not reach equilibrium in spite of the long adsorption time. The fulvic acid is difficult to remove because of its low molecular weight, smaller molecule size and high solubility in water and its low concentration. The low concentration means that the charges of the fulvic species can be scarce, taking more time for binding with the available adsorption sites on the chitosan.
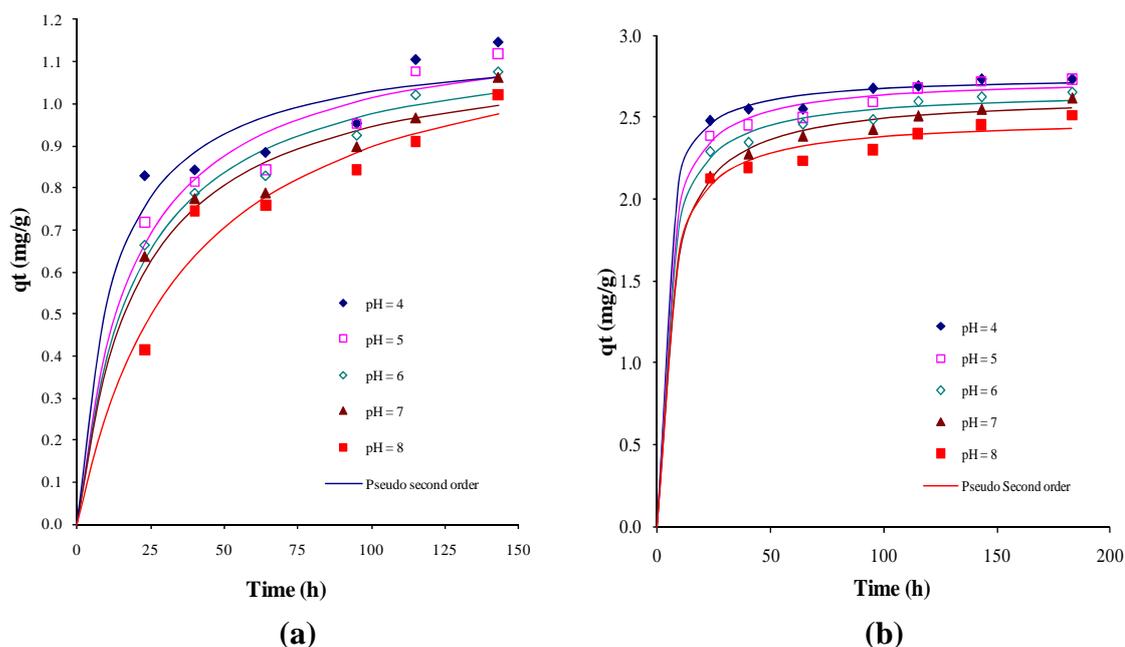

Figure 4.13 Comparison between experimental data and model results using the pseudo-second-order model at different pH and fulvic acid concentration of (a) 3 mg/L (b) and 30 mg/L.

Figures 4.13b and Figure 4.14 illustrate that for fulvic acid of 30 mg/L and the two concentrations of humic acid tested, the adsorption rate was faster in the initial stages, but decreased rapidly with time when the sorption sites had been occupied. Figures 4.13 and 4.14 also shown that increasing the concentration of the fulvic or humic acids leads to an increment of the adsorption capacity onto chitosan due to the higher concentration

gradient (Septhum *et al.,* 2007). Comparing Figures 4.14a and 4.14b, it can be seen that at a higher concentration of humic acid, the time to reach equilibrium is increased.
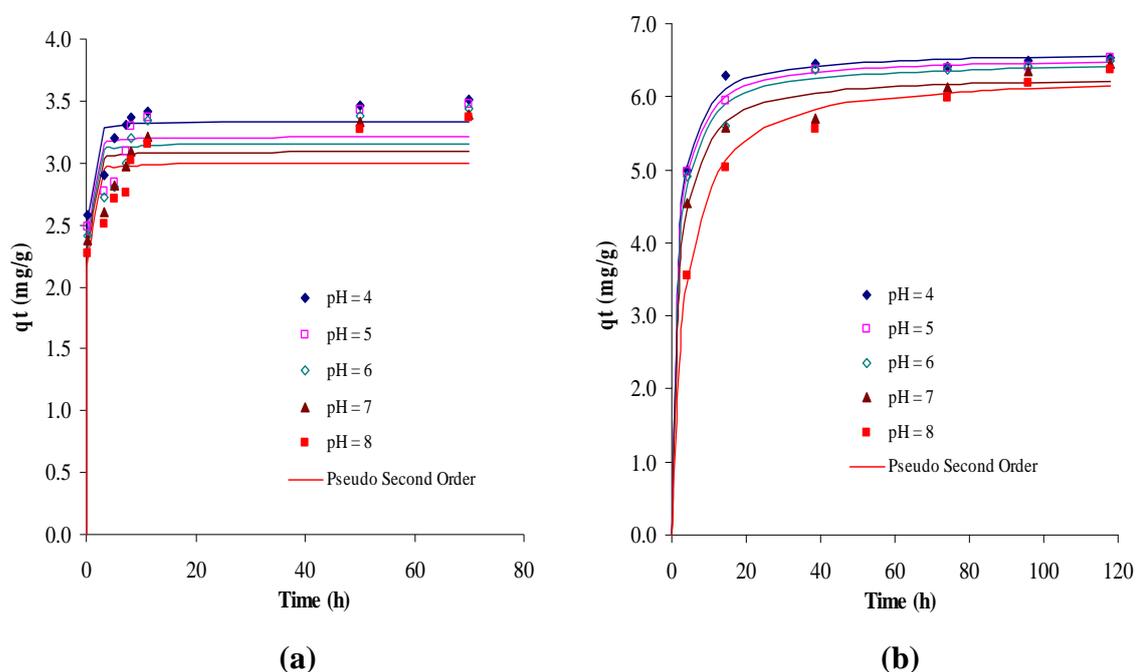

(a)   **(b)**

Figure 4.14 Comparison between experimental data and model results using the pseudo-second-order model at different pH and humic acid concentration of (a) 10 mg/L and (b) 20 mg/L.

From the fitting between the experimental data and the models presented in Section 2.2.3, it was found that the adsorption of fulvic and humic acid follows a pseudo-second-order reaction kinetics model. The pseudo-second-order kinetic assumes that chemisorption, involving valence forces by the sharing or exchange of electrons between the positive amino groups of the chitosan and the negative charge of the fulvic and humic compounds, is the rate-determining step (Septhum *et al.,* 2007). The overall rate of removal of the fulvic and humic acid is thus controlled by adsorption reactions and not by mass transport.

It was also found that humic acid was adsorbed much faster than fulvic acid because the adsorption capacity (*q*) for humic acid was much greater than for fulvic acid. The adsorption was somewhat greater onto chitosan of high molecular weight since it has a structure that is more rigid and does not change appreciably, increasing the binding compared to the flexible structure of the low molecular weight where the constitution often varies (Davydova *et al.,* 2000).

Figure 4.15 compares the adsorption of chitosan using raw water from a river (Boaco) and from a lake (Juigalpa) at pH 4 and 7 for different chitosan molecular weights. As expected, the adsorption capacity (*q*) was higher at low pH than at high pH. It was also noticed that the lowest adsorption capacity was obtained with chitosan of low molecular

weight; nevertheless, the adsorption capacity was quite similar with chitosan of medium and high molecular weights.
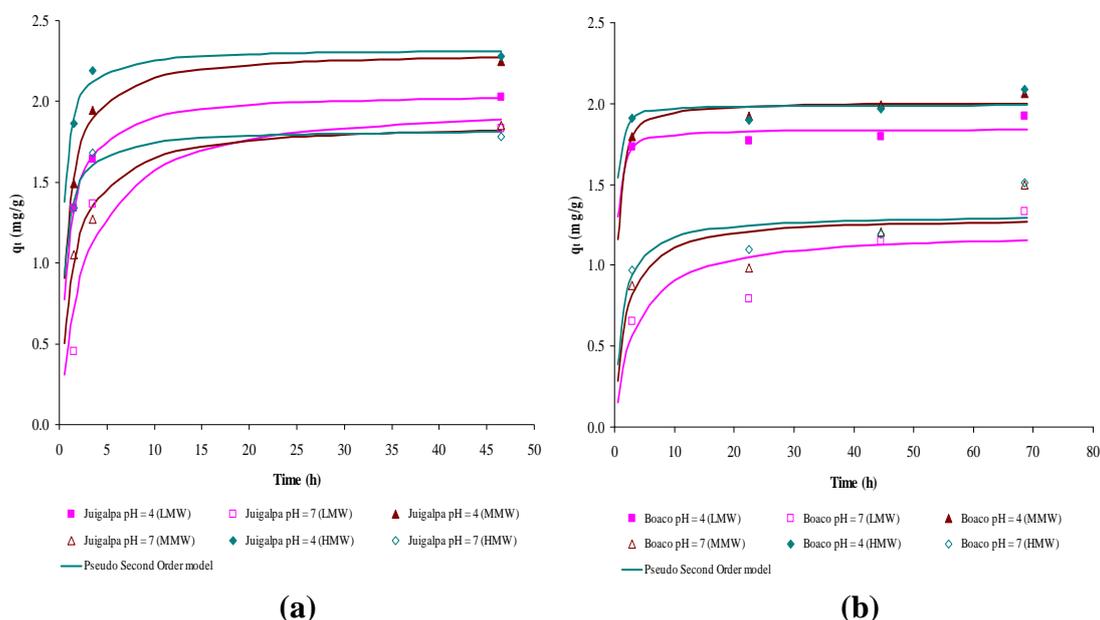

(a)   **(b)**

Figure 4.15 Comparison between experimental and model results for the pseudo-second-order model using different pH for (a) Boaco and (b) Juigalpa raw water.

Figure 4.16 shows the influence of ionic strength on the adsorption of humic acid onto chitosan. The results show that the adsorption capacity is greatest at the highest ionic strength because the salt screening reduces the mutual repulsion between the humic acid molecules, and thus improves the adsorption. This trend was more marked at high humic acid concentrations. According to Machenbach (2007), the molecule of humic acid has a smaller overall size at higher ionic strength due to the screening of the charged sites, which causes charge depression. The molecules change from a linear to a spherical form and the structure becomes more coiled. Therefore, a reduction in size allows more sorption.
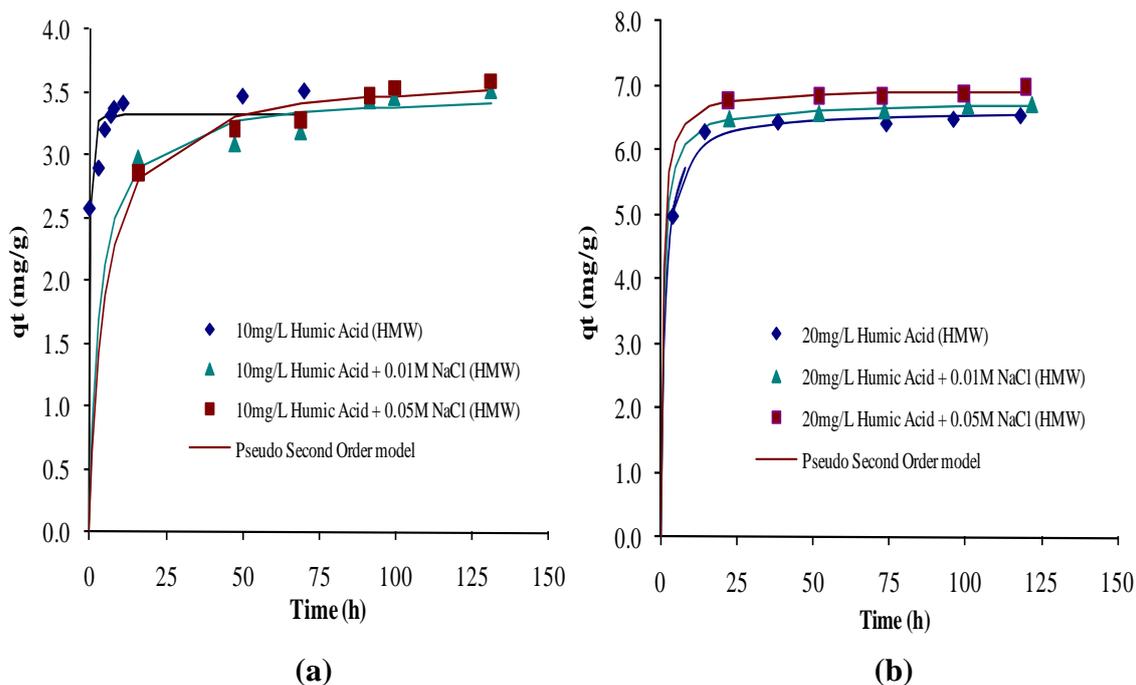
Figure 4.16 Comparison between experimental data and model results for the pseudo-second-order model at pH 4, at different ionic strengths, and at humic acid concentrations of (a) 10 mg/L and (b) 20 mg/L.

4.6   Trihalomethane Formation

The concentration of trihalomethanes after the disinfection step was dependent on the concentration of NOM in the water entering this step. Therefore, the high reduction of NOM surrogates parameters achieved by chitosan in the river waters meant that the concentration of trihalomethanes was lower in those waters treated with chitosan than in waters treated with aluminium sulphate, as shown in Figure 4.17.

The Santo Tomas water had the highest residual UV_{254} and DOC values, which may explain the high trihalomethane concentrations obtained after disinfection; 65.3 µg/L (using AS) and 47.1 µg/L (with chitosan).

The lowest trihalomethane concentration was found in the treated Juigalpa water (7.5 µg/L with AS and or 16.0 µg/L with Ch), which had the lowest UV_{254} values. However, none of the average THM values exceeded the maximum contaminant levels of 80 and 460 µg/L set respectively by USEPA (2009) and the Nicaraguan guidelines (2000).
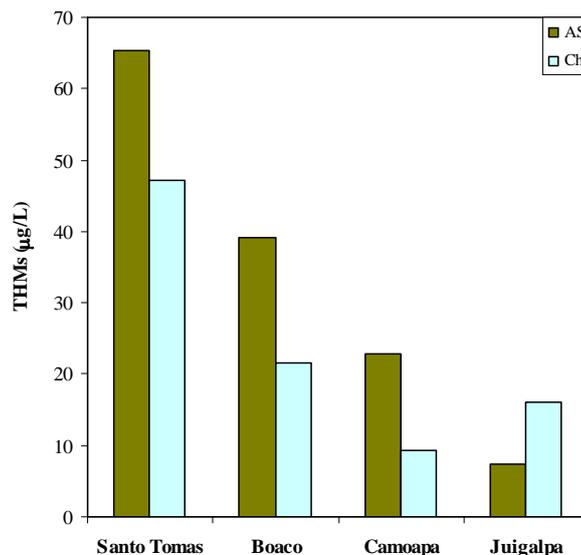
Figure 4.17 THMs after aluminium sulphate (AS) or chitosan (Ch) treatment.

Figure 4.18 shows the trihalomethane concentration in: a) the drinking water from Boaco plant that was treated with conventional coagulation and dual rapid sand filtration, b) the same water treated by enhanced coagulation (EC) and c) the water treated by enhanced coagulation and granular activated carbon (GAC).
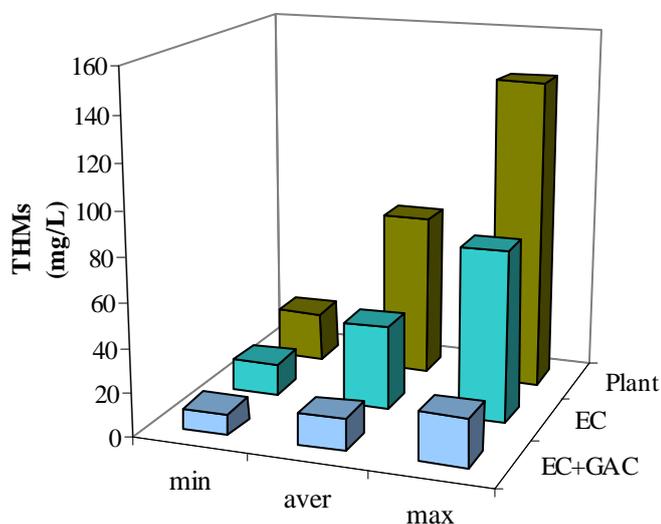

Figure 4.18 Trihalomethane concentrations after different treatments.

The average concentration of trihalomethanes was 73.8 ± 41.2 µg/L and the maximum value was 141 µg/L at the Boaco drinking water plant. The high concentration of THMs is the result of the conventional coagulation applied in this plant, which does not significantly reduce organic matter, so that the adsorptive capacity of the GAC in the sand filter is rapidly reduced as a consequence of the still high load of NOM.

In contrast, a lower concentration of NOM in the water after treatment by EC+GAC led to a lower formation of THM (average 14.5±5 µg/L). The NOM was mostly non-humic before disinfection because most of the NOM had previously been removed by EC and adsorbed by GAC.

When the water was treated only with enhanced coagulation and then disinfected after sedimentation, the average THM concentration was higher (average 38±23 µg/L) and a maximum THM of 78 µg/L was found, which is close to the maximum permissible contaminant level (MCL) of 80 µg/L for THMs (USEPA, 2009) but lower than the Nicaraguan guideline of 460 µg/L (CAPRE, 2000). Although enhanced coagulation removed 50% of the NOM, this process alone is in some cases unable to reduce the formation of THM, mainly because the type of organic matter remaining (a mixture of humic and non-humic fractions) is most probably of moderate molecular weight and quite reactive with chlorine.

The concentration of trihalomethanes after applying sodium hypochlorite to the different fractions of organic matter is depicted in Figure 4.19. It shows that the fraction that contributes most to THM formation for the Boaco and Juigalpa waters was SHA followed by VHA, CHA and NEU. The SHA fraction shows this behaviour because it has a lower removal of NOM than VHA. The CHA and NEU fractions that were poorly removed in the coagulation process can contribute significantly to the formation of THMs.
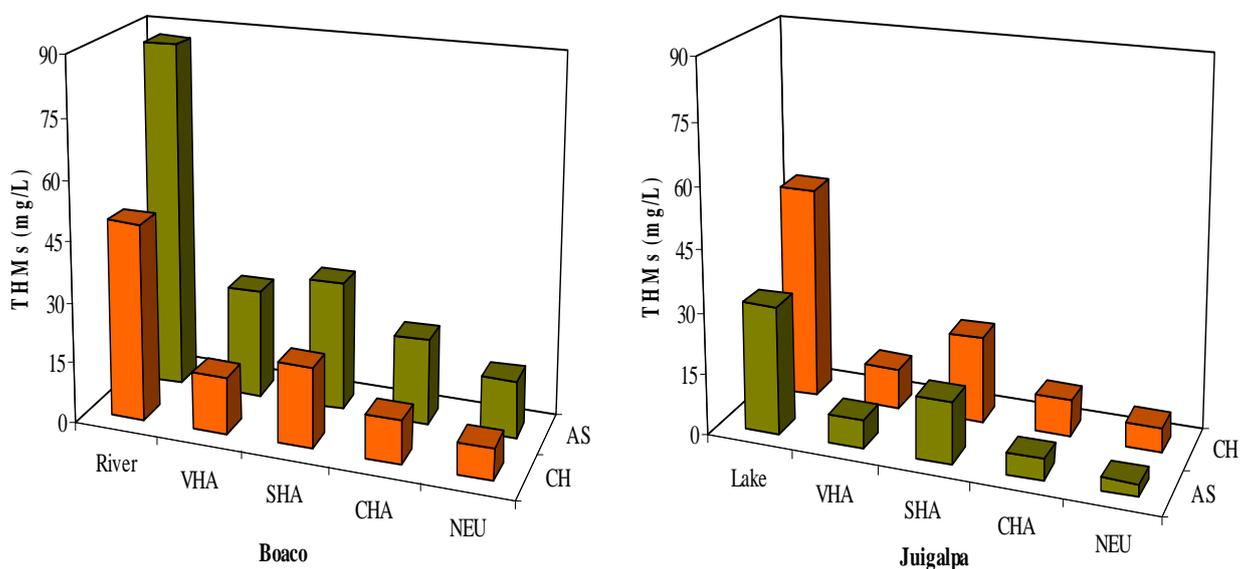

Figure 4.19 THMs for whole and fractionated water.

The contributions of the hydrophobic and hydrophilic fractions to the formation of THMs were 64.2% and 35.8% with chitosan; and, 62.8% and 37.2% with aluminium sulphate respectively for Boaco. The same trend was found for Juigalpa, where the

contributions of the hydrophobic and hydrophilic fractions were respectively 73.3% and 26.7% with AS and 67.4% and 32.6% with chitosan. The hydrophobic fraction is the main contributor to the formation of THMs compared with the hydrophilic fraction which is non-humic. This hydrophobic fraction is more abundant, in spite of the high removal achieved in the coagulation process, so that this fraction is available to react with chlorine.

Trihalomethanes and the Influence of pH, Contact Time, Temperature and Chlorine Dosages

The CBP formation depends on the nature and concentrations of precursors and on other parameters such as dosage of disinfectant, contact time, pH, and temperature. Figure 4.20 presents the impact of temperature, time, and chlorine dosage on the formation of trihalomethanes (THMs) for the four facilities after the raw waters had been treated by conventional (CC) or enhanced (EC) coagulation.

Figure 4.20 also shows that enhanced coagulation reduces the formation of trihalomethanes below the maximum contaminated levels of 0.08 mg/L (horizontal red line) set by USEPA (2009). However, when these waters were treated by conventional coagulation, the concentration of trihalomethanes exceeded that guideline in several cases, since the soluble organic matter was not properly removed and reacted with the chorine to form chlorination by-products (CBPs). In the figure, it is also seen that the concentration of trihalomethanes increases at high chlorine dosages, with long times and at high temperatures. At high chorine dosages, the break-up of the aromatic bonds increased allowing more halogenation and the formation of trihalomethanes. This break-up is faster when the temperature is higher because the reactivity between chlorine and NOM is enhanced accelerating the formation rate of trihalomethanes. In addition, a longer time increases the concentration of trihalomethanes because this type of chlorination by-product is a final end product, and a longer time is necessary to complete the hydrolysis reaction. The formation rate of THMs is faster at the beginning and decreases because of the loss of residual chlorine. These results are in agreement with the findings of Stevens *et al.,* (1976) and of Singer (1999).
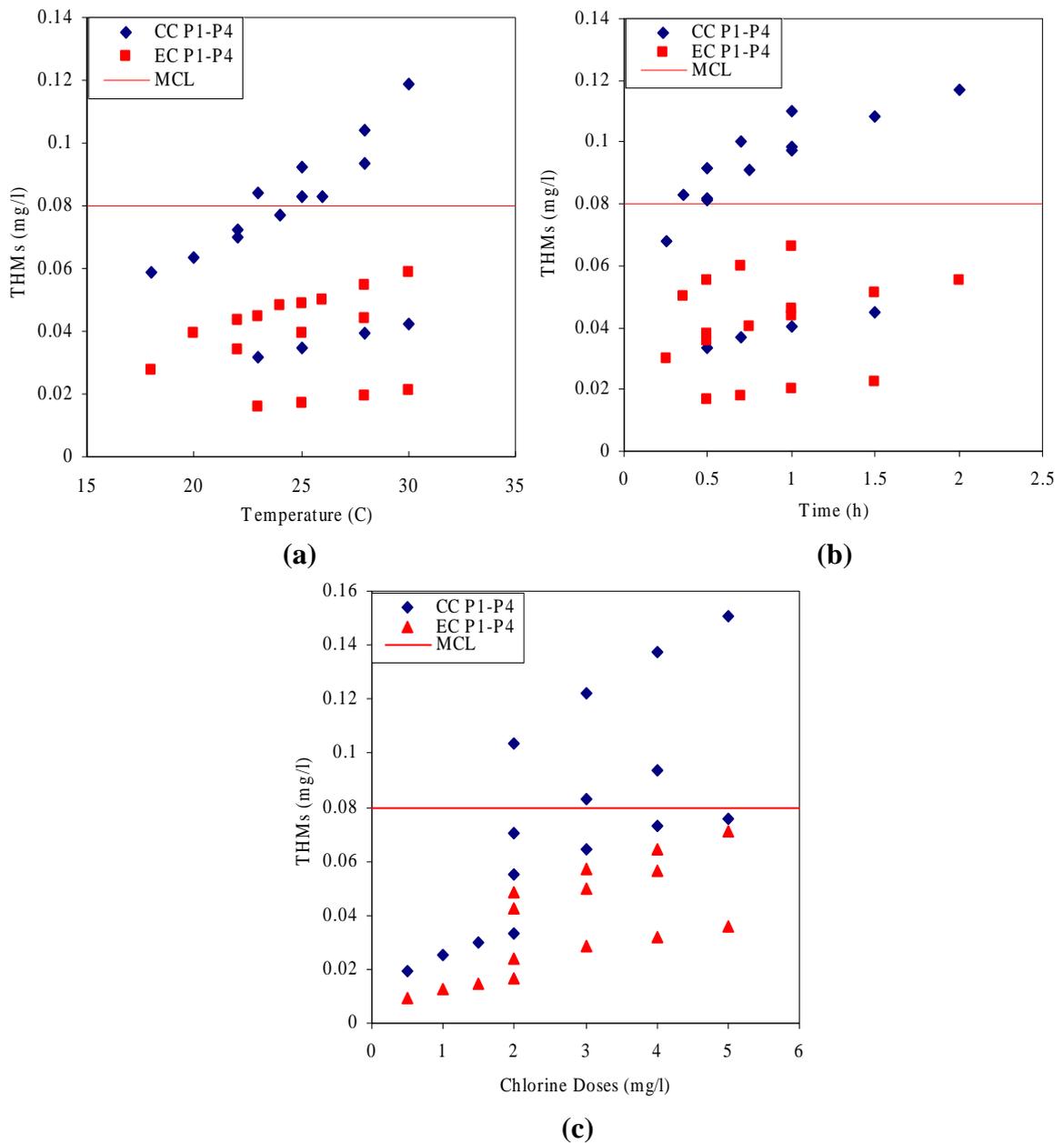
(a)

(b)

(c)

Figure 4.20 Influence of temperature, time, and chlorine dosages on THM formation.

Figure 4.21 presents the influence on THM formation of pH, temperature and time with a chlorine dosage of 5 mg/L using treated water by conventional (CC, left-hand side) and enhanced coagulation (EC, right-hand side) from Boaco source.

The fact that THM concentration increases at high pHs, high temperatures, long contact times, and high chlorine doses has been reported by other researchers (e.g., Xie, 2004). The high pH creates an alkaline environment which leads to a fast chlorination; and a high chlorine dose provokes more halogenation and opening of the aromatic structures of the NOM still remaining after coagulation. More THMs are formed due to the rapid substitution and oxidation of organic structures by chlorine. In contrast, at a pH of 6 or lower, the reaction is too slow to form end products such as THMs; only intermediate products can be formed (Xie, 2004). In the same figure, it can be seen that

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almost all the THM values after conventional coagulation experiments are greater than the THM guideline of USEPA (2009) of 80 µg/L compared with the THM values after enhanced coagulation. The formation of THMs was much lower after enhanced coagulation than after conventional coagulation. The highest THMs found in this study were 189.4 and 145.3 µg/L after CC and EC respectively.
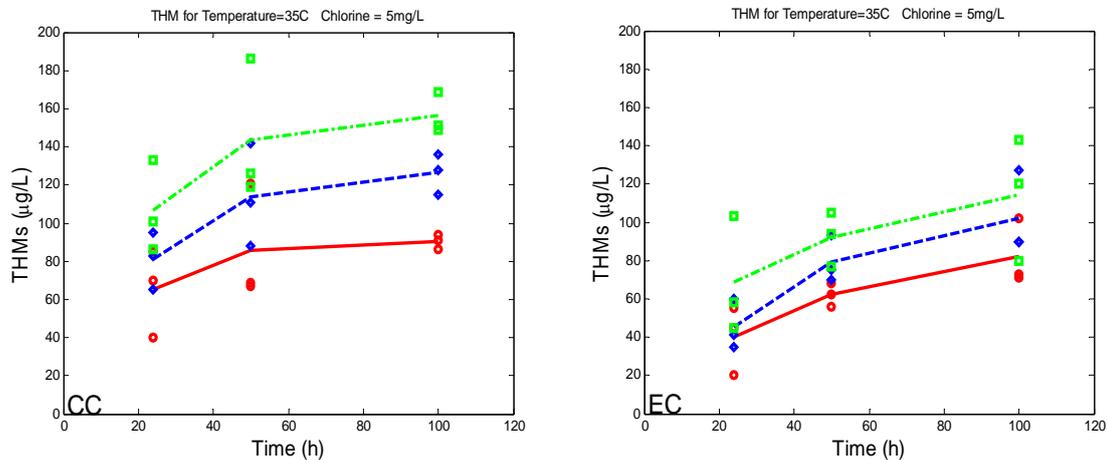

Figure 4.21 THM formation as a function of time for chlorine doses of 5 mg/L and at pH 5 (red solid line), pH 7 (blue dashed line) and pH 10 (green dash-dotted line).

Total Exposure Cancer Risk

Table 4.23 presents the exposure cancer risk for ingestion, inhalation and dermal intake calculated for mean THMs concentration of 0.0575 mg/L with CC and 0.0122 mg/L with EC. This table shows that the risk is five times greater for conventional than for enhanced coagulation, that oral ingestion is the most important way compared with the risk of the other exposure routes, and that the total risk is greater in females than in males. However, males have a higher risk than females in the inhalation route. Wang *et al.* (2007) reported the same behaviour and explained that it is due to the fact that males have a higher inhalation rate than females. The total cancer risk calculated using the mean concentration did not exceed the value 1.0×10^{-5} established by WHO (2008).

Table 4.23 Individual exposure cancer risk for CC and EC.

Individual	Conventional Coagulation		Enhanced Coagulation	
Exposure Cancer Risk	**Female**	**Male**	**Female**	**Male**
Ingestion	9.4×10^{-6}	8.6×10^{-6}	2.0×10^{-6}	1.8×10^{-6}
Inhalation	1.2×10^{-7}	1.5×10^{-7}	2.7×10^{-8}	3.1×10^{-8}
Dermal Intake	7.1×10^{-7}	6.9×10^{-7}	1.5×10^{-7}	1.5×10^{-7}
Total Risk	$\mathbf{1.0 \times 10^{-5}}$	$\mathbf{9.5 \times 10^{-6}}$	$\mathbf{2.2 \times 10^{-6}}$	$\mathbf{2.0 \times 10^{-6}}$

Figures 4.22 shows the total exposure cancer risk (R_T) calculated for Boaco water treated by conventional or enhanced coagulation after it has been disinfected with sodium hypochlorite. The total exposure cancer risks were calculated using the maximum, mean and minimum values of the measured THM concentrations. The figure shows that the total exposure cancer risk is slightly higher in females than males due to the lower body weight (BW) values used for females, which impacts the total exposure cancer risk calculation.
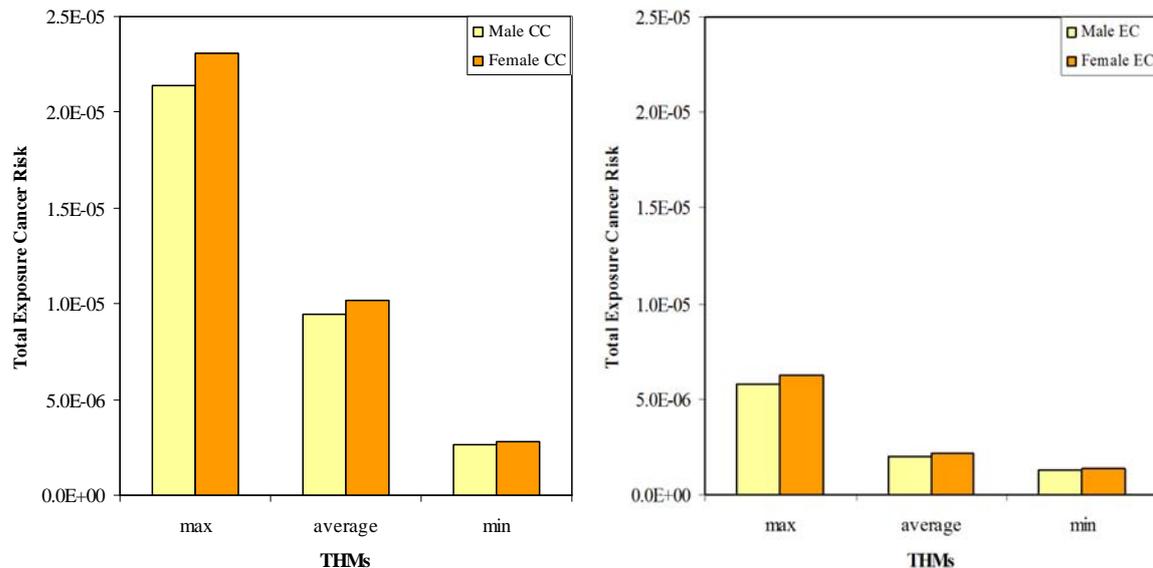

Figure 4.22 Total exposure cancer risks after conventional or enhanced coagulation.

It also be observed that the total exposure cancer risk at the maximum trihalomethane concentration with conventional coagulation (CC) exceeded the lifetime cancer risk of 1.0 x 10^{-5} for chloroform settled by WHO (2008) for Group 2B of possible carcinogenic compounds for humans. The individual exposure cancer risk for ingestion was 2.12 x 10^{-5} for females and 1.96 x 10^{-5} for males at the maximum THMs concentration. This was not reached for the average and minimum THM concentrations with CC and in any cases of enhanced coagulation, due to the lower THM concentrations. Thus, complementary treatment such as enhanced coagulation can greatly help to reduce the cancer risk to the consumers of this facility.

Chapter 5

Conclusions

The removal of natural organic matter was studied in order to reduce the generation of chlorination by-products in the disinfection step. Experiments using conventional coagulation, enhanced coagulation and adsorption were performed to show how they can improve the removal of NOM in the waters before disinfection. Tests using chitosan, a green compound obtained from shrimp shells, were carried out to find out whether this compound can be applied as coagulant and flocculant in the drinking water plants of Nicaragua. This compound could replace the traditionally used aluminium sulphate, which is a threat to human health due to the aluminium residues released to the water bodies. In addition, several parameters influencing the formation of trihalomethanes were investigated. A summary of the findings obtained is presented below.

- Conventional coagulation with aluminium sulphate is unable to sufficiently reduce the presence of natural organic matter and the maximum contaminant level criterion (MCL-USEPA) for trihalomethanes is therefore exceeded after the disinfection step.

- Enhanced coagulation treatment of the water considerably removes the natural organic matter. However, there is a significant amount that cannot be removed and high trihalomethane concentrations, close to the MCL-USEPA criterion, were measured after the disinfection step.

- Water treated by enhanced coagulation and subsequent adsorption with granular activated carbon achieved high removals; about 80% for total organic carbon (TOC) and dissolved organic carbon (DOC). Trihalomethane concentrations were then below the MCL criterion.

- A comparison of conventional coagulation using aluminium sulphate and chitosan showed that chitosan removes much better the surrogate NOM parameters measured as DOC, colour, UV_{254} and SUVA in river waters. However, aluminium sulphate performs better in lake water, which can be because the lake waters had a lower NOM content and chitosan is a poor coagulant for water with low content of organic matter. Trihalomethanes measured were below the MCL criterion.

- The use of chitosan as flocculant aid in combination with aluminium sulphate was also studied using three different coagulation techniques: conventional coagulation, preformed flocs and two-stage coagulation. The results show that two-stage coagulation with chitosan as flocculant gives a higher NOM removal than the other two techniques. However, the use of two-stage coagulation has the disadvantage that more aluminium may be released into the drinking water. As a consequence,

preformed flocs that exhibited lower removal than two-stage coagulation could be a good option for NOM removal in waters with low NOM content.

- Chitosan has a high adsorption capacity for fulvic and humic acid, measured as DOC, in river, lake and synthetic waters. This trend was more remarkable at pH 4 using chitosan of medium or high molecular weight. The pseudo-second-order model was the best to describe the experimental results indicating that the overall rate is controlled by adsorption reactions and not by mass transport.

- A fractionation of the river and lake waters showed that they are more hydrophobic than hydrophilic and that the surrogates parameters of NOM were higher in the hydrophobic fraction. However, dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN) were higher in the hydrophilic fraction. The fraction showing the highest NOM removals for both waters and coagulants was VHA followed by SHA, CHA and NEU. The lowest removals were found in the hydrophilic fraction (CHA+NEU) which is recalcitrant due to the great solubility.

- The fraction that contributed the most to THM formation was SHA, followed by VHA, CHA and NEU, due to their lower removal compared with VHA. The CHA and NEU fractions that were poorly removed in the coagulation process can also contribute significantly to the formation of THMs.

- Studying the trihalomethane formation as a function of the conditions under which the disinfection is carried out, it was found that the THM formation is greatly increased at high pH, long contact times, high temperatures, and high chlorine doses.

- The total exposure cancer risk was calculated for ingestion, inhalation and dermal intake and it was found that the highest risk is associated with the ingestion exposure route. In addition, higher individual risks were found in the waters treated by conventional coagulation than by enhanced coagulation. When the mean THMs concentrations obtained in this study were used to estimate the individual cancer risk, none of them exceeded the life-time cancer risk determined by the WHO. Nevertheless, when the values for the maximum THMs concentrations with conventional coagulation were used in the calculations, the oral ingestion and the total exposure cancer risk did exceed the life-time cancer risk given by WHO.

- A cost-benefit analysis indicates that the use of chitosan will not increase the cost of the operation. After settling, the chitosan effluent can be released without additional treatment since this coagulant is environment-friendly. Chitosan could therefore be used instead of aluminium salt in the drinking water plants in Nicaragua.

The results of the present research indicate that the application of chitosan as coagulant and/or flocculant may be a good option as a substitute for aluminium sulphate compounds. However, since chitosan does not work properly in the dry season, when the NOM content is low, the use of aluminium sulphate in combination with chitosan should be studied in more detail. A field with a large potential is the modification of the chitosan

structure to increase its capacity for NOM removal and therefore decrease the use of aluminium sulphate. Another advantage of using chitosan is a reduction in the negative impact of shrimp and squat lobster shells on the environment.

Notations

Latin letters

A_d	Dynamic adsorption	(mg/m^3)
AT	Average exposure time	(day)
BW	Body weight	(kg)
C_o	Initial DOC concentration	(mg/L)
C_1	Concentration of HCl	(M)
C_2	Concentration of NaOH	(M)
C_{air}	THMs concentration in the air	(mg/L)
CDI	Chronic daily intake	(mg/kg-day)
C_e	Effluent concentration	(mg/m^3)
C_i	Influent concentration	(mg/m^3)
C_t	Concentration at time t	(mg/L)
CW	Concentrations of THMs in water	(mg/L)
ED	Exposure duration	(year)
EF	Exposure frequency	(day/year)
$E^o{}_{red}$	Standard potential of reduction	(V)
ET	Exposure time	(min/day)
G	Dry chitosan	(g)
H	Henry's constant	-
IR	Ingestion rate	(L/day)
k_1	Pseudo-first-order rate constant	(1/min)
k_2	Pseudo-second-order rate constant	(g/mg-min)
$K_{OL}A$	Overall mass coefficient for chloroform	(L/min)
N	Coefficient	-
n_{LF}	Langmuir-Freundlich isotherm exponent	-
PC	Permeability coefficient	(m/min)
Q	Volumetric flow	(m^3/min)
Q_L	Water flow rate	(L/min)
Q_G	Air flow rate	(L/min)
q	Adsorption capacity	(mg/g)
q_e	Equilibrium adsorption capacity	(mg/g)
q_t	Adsorption capacity at time t	(mg/g)
SA	Skin surface area	(m^2)
SP	Slope factor for chloroform	(kg-day/mg)
t	Time	(min)
V	Volume of the solution	(L)
V	Volume of activated carbon	(m^3)

V_1	Volume of HCl	(mL)
V_2	Volume of NaOH	(mL)
VR	Ventilation rate	(L/min)
V_s	Bathroom volume	(m^3)
w	Weight of chitosan	(g)
W	Moisture content of chitosan	(%)
Y_{si}	Initial THM concentration as chloroform	(mg/L)
$Y_s(t)$	THM concentration as chloroform at time t	(mg/L)

Abbreviations

AS	Aluminium Sulphate
C	Carbon
Ch	Chitosan
CAPRE	Regional Committee for Drinking Water Institution and Sanitation for Central America, Panamá and Dominican Republic
CBPs	Chlorination By-products
CC	Conventional Coagulation
CHA	Charged Hydrophilic Acid
Da	Dalton
DBPR	Disinfection By-products Rule
DBPs	Disinfection By-products
DCCA	Dichloroacetic Acid
DD	Degree of Deacetylation
DIN	Dissolved Inorganic Nitrogen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
EC	Enhanced Coagulation
FA	Fulvic Acid
GAC	Granular Activated Carbon
HA	Humic Acid
HAAs	Haloacetic Acids
HANs	Acetronile Acids
HMW	High Molecular Weight
HOBr	Hypobromous Acid
HOCl	Hypochlorous Acid
LMW	Low Molecular Weight
M	Molar
MCLs	Maximum Contaminant Levels
MDGs	Millennium Development Goals
MINSA	Nicaragua Health Department
MMW	Medium Molecular Weight
N	Nitrogen
NaOCl	Sodium Hypochlorite
N-CBPs	Nitrogen Chlorination By-products
N-DBPs	Nitrogen Disinfection By-products
NEU	Neutral Hydrophilic

NOM	Natural Organic Matter
PACls	Polyaluminium Chloride
PF	Preformed Flocs
POM	Particulate Organic Matter
Pt	Platinum
RW	Raw Water
SC	Two-stage Coagulation
SHA	Slightly Hydrophobic Acid
SM	Standard Method
SUVA	Specific Ultraviolet Absorbance
TCAA	Trichloroacetic Acid
TDN	Total Dissolved Nitrogen
THMs	Trihalomethanes
TOC	Total Organic Carbon
TOX	Total Organic Halide
TSUVA	Specific Ultraviolet Absorbance based on Total Organic Carbon
TTHM	Total Trihalomethane
USA	United States of America
USEPA	United States Environmental Protection Agency
UV_{254}	Ultraviolet Absorbance at 254 nm
VHA	Very Hydrophobic Acid
WHO	World Health Organization

Acknowledgments

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