

## Abstract

Coagulation is an essential treatment step in many drinking water treatment plants (DWTP) to remove small particles and certain dissolved natural organic matter (NOM) from water. The coagulation process typically includes promoting the interaction of particles to form larger aggregates, which can then be easily removed in subsequent sedimentation basins. Alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) and iron (III) chloride (FeCl<sub>3</sub>) are the most common coagulants used nowadays in DWTP.

Coagulation is also applied in some DWTPs prior to an ultrafiltration (UF) membrane unit to enhance its performance. By applying such an approach, dissolved NOM that would entirely pass through the UF membrane aggregates with Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> flocs that are retained by the membrane. Optimizing coagulant doses is thus essential to maximize removal of NOM by the membrane. If the applied coagulant dose is too low then a large portion of NOM remains in water and is not removed, while if the applied coagulant dose is too high then Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> flocs accumulate on the membrane leading to fouling problems. Another detrimental effect of an excess of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is that residual Al<sup>3+</sup> remaining in the UF permeate can have detrimental effects on subsequent reverse osmosis (RO) membrane.

The objective of this TFG was to evaluate in bench-scale jar-tests experiments the effect of dosing a Fe- and an Al-based coagulant (separately and together) in the extent of NOM removal from water with the purpose of maximizing NOM removal while ensuring that residual aqueous Al<sup>3+</sup> concentration was kept as low as possible. NOM content in water was analyzed in terms of total dissolved organic carbon (TOC) and absorbance.

NOM is a complex and heterogeneous mixture of compounds often poorly defined from a chemical point of view. Given this complexity, two model organic compounds were used in this study: humic acid (representative of small molecular weight organic compounds) and albumin (representative of high molecular weight organic compounds). Synthetic waters containing single organic compounds or mixtures of both were used, as well as real water collected from the treatment train of the DWTP in Sant Joan Despí.

Because not all organic compounds react with coagulants in the same way and extent, efforts were devoted to characterize NOM with a fluorescence excitation–emission matrix (FEEM) spectrophotometric technique, which allows fractionate NOM in groups or families with similar physicochemical properties. Applying FEEM techniques would allow to differentiate organic components in real complex waters.



## Summary

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# 1. Glossary

Å: Amstrong

BOD: Biochemical Oxygen Demand

BSA: Albumin

COD: Chemical Oxygen Demand

DOC: Dissolved Organic Carbon

DWTP: Drinking Water Treatment Plant

EPS: Extracellular Polymeric Substances

FEEM: Fluorescence Emission Excitation Matrix

HA: Humic acid

IC: Inorganic Carbon

ICP: Inductively Coupled Plasma mass spectrometry

kDa: 1000 Daltons

MF: Microfiltration

NOM: Natural Organic Matter

NF: Nanofiltration

RO: Reverse Osmosis

PARAFAC: PARAllel FACtor

ppb: parts per billion

ppm: parts per million

TFG: Final Project

TOC: Total Organic Carbon

UF: Ultrafiltration

UV: Ultraviolet

## **Chemical nomenclature**

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Al: Aluminum

$\text{Al}_2(\text{SO}_4)_3$ : Aluminum sulphate

$\text{BaSO}_4$ : Barium sulphate

$\text{CaCO}_3$ : Calcium carbonate

$\text{Ca}(\text{PO}_4)_2$ : Calcium phosphate

$\text{CaSO}_4$ : Calcium sulphate

$\text{Cl}_2$ : Chlorine

$\text{CO}_2$ : Carbon dioxide

Fe: Iron

$\text{FeCl}_3$ : Iron chloride (III)

$\text{Fe}_2(\text{SO}_4)_3$ : Iron sulphate (III)

$\text{MgCl}_2$ : Magnesium chloride

$\text{NaHCO}_3$ : Sodium hydrogen carbonate

$\text{O}_3$ : Ozone

PACl: Polyaluminum chloride

PAX18: Polyaluminum sulphate

$\text{SrSO}_4$ : Strontium sulphate

## 2. Foreword

### 2.1. Origin of the project

Over the last years, society has taken care about the origin of all the food and water. Furthermore, the legislation is becoming less permissive and the companies have to adapt to these changes. Also, on this modern era and considering that water is a public good, the economic impact of the water treatment processes have a big weight to the final user. For both of these reasons, there is a company, CETAQUA Barcelona, which tries to improve these processes or to make a research to find new methods to treat the water in Barcelona. CETAQUA Barcelona is composed by members from AGBAR, UPC and CSIC.

One of the projects of CETAQUA Barcelona, and also part of a PhD, is focused on the processes used before reverse osmosis (RO) filtration. This PhD is studying the fouling problems on ultrafiltration (UF) and RO membranes. It also studies some improvement that could be done to prevent the degradation of RO membranes.

This project appears as a part of the CETAQUA project to study the process of coagulation-flocculation done before the ultrafiltration, to prevent the degradation of RO membranes in the DWTP in Sant Joan Despí. This process and also the ultrafiltration are used to prevent the fouling and reduce the damage of RO membranes. Therefore, a good understanding of coagulation-flocculation can reduce these listed problems.

To study this process, some experiments have been planned by means of reproducing the Sant Joan Despí water so as to test different situations.

### 2.2. Motivation

By studying the effect of coagulants on water, the final result could contribute to an improvement in the quality of drinkable water. This can finally mean better healthy conditions for consumers. Also, this project can optimize the process of RO and reduce the final cost of the water treatment, meaning a final reduction of the consumer cost.

Furthermore, for the last years, I have been interested in water treatment methods and have done some projects about this at university. I was working on a water treatment company.

## 3. Introduction

### 3.1. Objectives

The main objective of this TFG is to study the reactivity of iron- and aluminum-based coagulants with dissolved organic matter occurring in the drinkable water treatment plant (DWTP) in Sant Joan Despí. The specific objectives are:

- Study the effectivity of each coagulant in front of the organic matter.
- To evaluate the interaction between these two coagulants when applied together and the influence on their reactivity with organic matter.
- To characterize the organic matter present in the water to be treated (either synthetic water spiked with the model organic compounds or real water containing dissolved organic matter) by means of fluorescence emission-excitation matrix.
- To anticipate the effect of the studied coagulants when applied in the treatment train in the DWTP in Sant Joan Despí.

The process to get all these objectives is based on the preparation of some samples in the laboratory to understand the way that coagulants interact both between them and with organic matter.

All of these main objectives have the goal to improve the operational plant that Sant Joan Despí uses to remove organic matter and aluminum from water.

### 3.2. Scope

This project is part of a PhD, which is focused on the study of Sant Joan Despí reverse osmosis way. This PhD makes a study considering the coagulations pools, sand filtrations, ultrafiltration and reverse osmosis fouling.

This project studies the fouling problems of ultrafiltration membranes. This allows to preview the excess or deficit of coagulant compound that is added to the micro-coagulation before

ultrafiltration membranes. Also, it can be useful to take care of osmosis membranes and consequently to reduce some inversions to buy new membranes.

## 4. Membranes in Sant Joan Despí

### 4.1. Water treatment plant

This project is based on the drinking water plant located in Sant Joan Despí. This plant can treat water coming either from Llobregat river or its aquifer. The operation of the different treatment units will differ depending on the different sources of water used at any moment. The different physical and chemical characteristics must be taken into consideration in order to change the operational parameters. To make plant operation even more complex, the physicochemical characteristics and quantity of the available raw water (in particular groundwater) is greatly influenced also by seasonal variations such as river flow, turbidity, temperature, particle content...

In 1955, the water treatment plant started being operative. Since that moment, the treatments used have changed due to all the changes on the normative and also to the fact that more potable water has had to be produced to supply the increasing demand from different periods of time. This plant had to be set up in order to face the strong industrialization and the increasing population that the metropolitan zone of Barcelona had in the middle of the 20th Century. During the last years before the implementation of the plant, the wells water were overexploited, producing, taking into a count all the wells, close to 275.000 m<sup>3</sup>/day.

From 1955, all upgrades adopted by the DWTP in SJD were implemented in order to increase production of drinking water with higher quality, and it was done by increasing the plant. In 2009, there was an important change to adapt to the legislation on trihalomethanes. This new technology used to produce drinkable water was ultrafiltration and reverse osmosis. By using these technologies the plant can cover the different ways of production without crossing down the sanitary limits. The aim of these technologies is to the remove of all organic and inorganic components.

The overall capacity of the plant is 5,5 m<sup>3</sup>/s, of which 2,5 m<sup>3</sup>/s are from the system of UF- RO described below.

### 4.1.1. Plant's strategy

#### 4.1.1.1. Pre-treatment

Surface water from Llobregat river is conducted by pipes but also going through some filters to eliminate big materials, as sand, rocks... When this first step has been completed, two pumps push the water from the current position to the highest one in the installation. In fact, thanks to the gravity force water can keep on moving through the pipes to reach the next step.

The following state is coagulation. This method is based on the use of aluminum salts (PAX18) which bind particles in order to come apart from water by precipitating. This dosage depends, basically, on the quality of the feed water and its current flow rate. Obviously, these methods are perfectly automatized and for this reason the dosage of coagulant is entirely automatic. After this step, water moves on to agitated pools where chlorine dioxide, which is prepared in situ, is added. This component has two functions. The first one is related to oxidations from different metals and organic matters involved in water. The second one is to disinfect water and make it more pure.

In the next steps water takes part into big pools. These pools reduce the velocity of the water and let the coagulated particles to sediment. There are 88 vertical static tanks, which surface is 100m<sup>2</sup> each. The water is introduced from the bottom of the pool and it keeps moving through a mud's bed where the bind particles are retained. At the same time, big clots sediment at the pool's bottom. The mud's bed has a periodical maintaining depth reduction, in order to guarantee the characteristics of the following water.

A sand filtration is used at the last step water. The aim of this step is to avoid most of the clots which have not precipitated by sand's beds using gravity as unique force. These filtrations are known as open sand filters. The filter consists of 0,6 meters of sand of different diameter, decreasing its dimensions as waters advance. After several operations, it is necessary a cleaning treatment for the sand's bed called backwashing. This consists of flowing air in the opposite direction every 36-48h and water backwashing after every 240 m<sup>3</sup>. All the water that is used in this method is directed to a special treatment plant that has a mud treatment.

After this phase the water from aquifers is added to the pretreated water from the river. If the demand of water increases is necessary to add aquifer water. Also, aquifer's water increases the quality of the water. The aquifers have to be refilled some time to preserve the salinity.

After this first big stage of pretreatment the water is divided in two ways, one with ozone and activated carbon and the other one with ultrafiltration and reverse osmosis.

#### **4.1.1.2. Ozone and activated carbon**

Ozone treatment continued by activated carbon is used to improve the organoleptic conditions of water. The ozone is added with oxygen, and diffused for the contact chambers. The aim is to oxidize and eliminate the microorganisms and organic matter. This treatment is the foundation of activated carbon, which retains all the above mentioned components. At the same time, oxide metals are adhered over the carbon. As anything that retains components, it is necessary a cleaning after some time. This cleaning is done on special ovens and also by backwashing.

#### **4.1.1.3. Ultrafiltration and reverse osmosis**

As stated before, the legislation has, and will have, rigorous levels of components present on drinkable water. As the last explained method way of producing drinkable water is not enough efficient in this aspect, it is necessary to use another technology method to be below the limits. Ultrafiltration and reverse osmosis is known as a membrane technology, and these technologies can obtain very clean water which will eventually be below the limits. Because of this, in 2009, Sant Joan Despí installed this method in the plant.

Ultrafiltration membranes work as a vacuum, of 0,8 bar, with a porous size of 0,02  $\mu\text{m}$ , and it is able to eradicate all bacteria, remove some big molecules but can not eliminate the viruses. Aluminum, one of the coagulants used on the first steps and very harmful for reverse osmosis, presents a low solubility point on acid pH, and for this reason sulfuric acid is added before UF helping the remove it. Also, another coagulant is added (ferric chloride,  $\text{FeCl}_3$ ) which tries to remove aluminum too. UF system is built as a group of pools, with UF membrane modules, specifically 4104 membranes modules are used to filtrate the 2,5  $\text{m}^3/\text{s}$ ., Again, backwash cleaning is required, but it is not only with water. It is a more complex process that depends on some different parameters, and includes different chemical treatments.

After this first filtration the water is conducted to another part composed by two stages of UV radiation, and one of cartridge filtration (which porous' size are 5  $\mu\text{m}$ ) to protect the RO membranes. This part is formed as (UV-cartridge-UV) and it is composed by 132 lamps per system.

To filtrate by RO it is necessary a big pressure, depending on the feed it will oscillate from 8 till 16 bars. On the other hand, the concentrated water, which has not crossed the membrane, is evoked on brine conducts. RO system is composed by 11.060 RO membranes on total, and its backwashing, as UF system, requires more steps and it has more dependent variables to control it.

When the water goes through the RO membranes, the water becomes too pure for human use, and it has to be remineralized. The remineralization is done by  $\text{CaCO}_3$ , with calcite beds and also adding  $\text{CO}_2$ .

After all these steps the two different waters are mixed. The final step is the chlorination that will eradicate all ammonium and will disinfect the water. (Aigües de Barcelona)

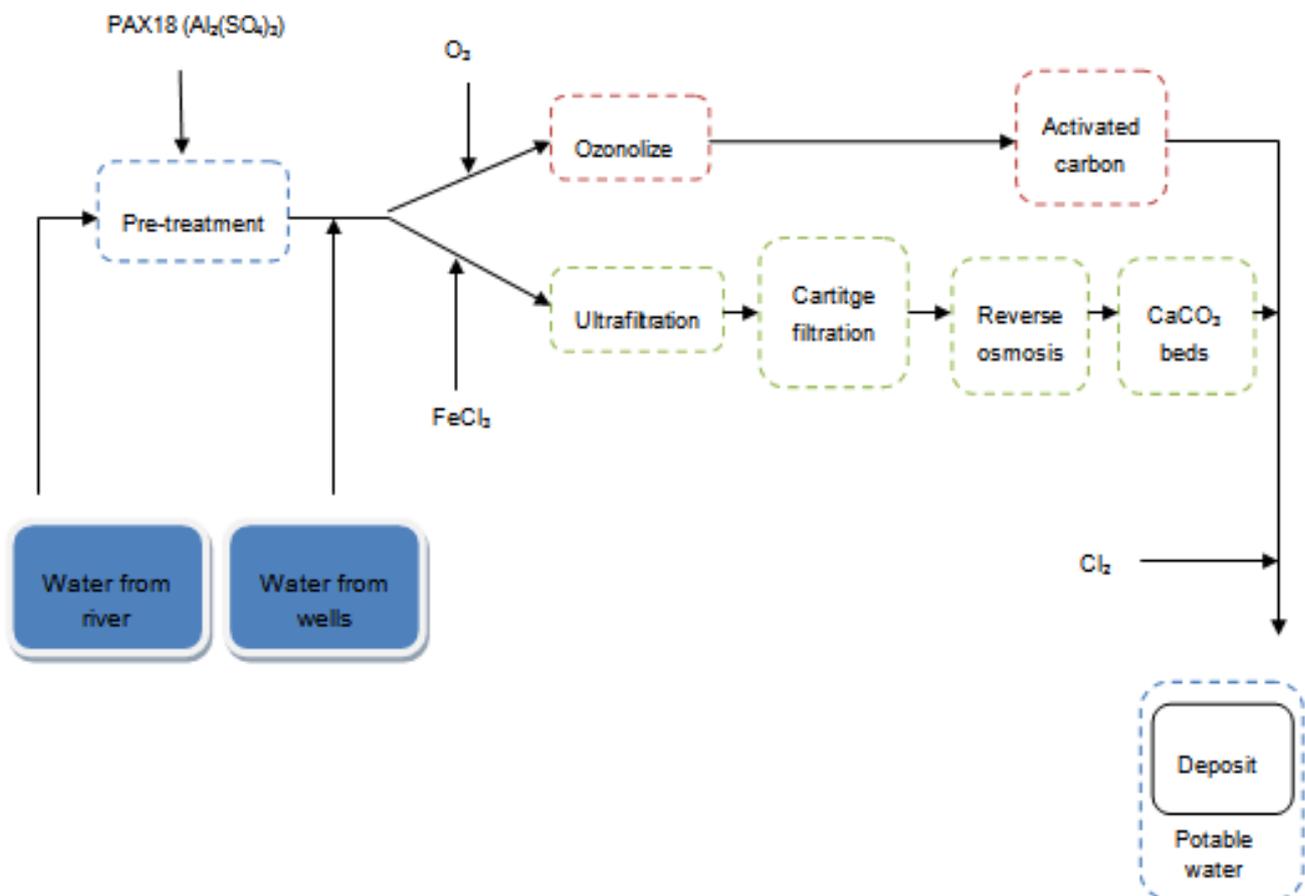


Figure 1: Sant Joan Despí plant (own source)

## 4.2. Theoretical framework

### 4.2.1. Classification

A membrane is a thin semi-permeable layer capable to restrict movement of certain components and particles selectively through it when driving forces are applied. Membranes filter water because its components have a larger size than their porous and consequently those components are blocked up and they can not go through them.

The most common configuration membrane system to filtrate water is described in the figure below ([FIGURE 2](#)). Feed is connected to unit where membrane is set up. From these modules two streams go out, one is clean water flux that has crossed over membrane and does not have any component larger than its porous and the other one is the concentrated flux, which contains all the components that can not have gone through the membrane

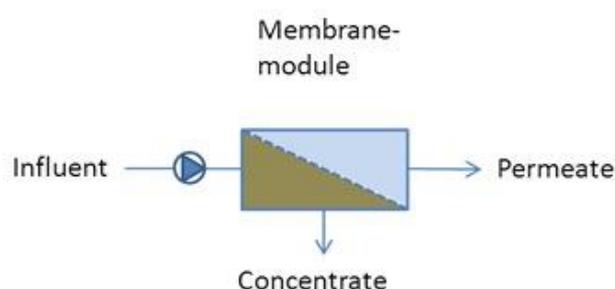


Figure 2: Filtration scheme (<http://www.trevi-env.com>)

Due to an imbalance between input and output streams a new one appears equalize the matter balance. A driving force keeps this imbalance. Depending on which membrane technology is used, this driving force will be a pressure gradient, a voltage gradient, a concentration gradient...The driving force of RO, UF, nano-filtration (NF) and micro-filtration (MF) is a pressure gradient. Therefore, membranes used in Sant Joan Despí have pressure gradient as their driving force. Also depending on their types technology the membranes can retain salts, small organic molecules, macromolecules or particles. Pressure needed varies from few bars (0.5-2) for the most porous membranes (MF) to 10-50 bars for denser membranes (RO).

The differences between all the whole semipermeable membranes are shown in the next figure ([FIGURE 3](#)).

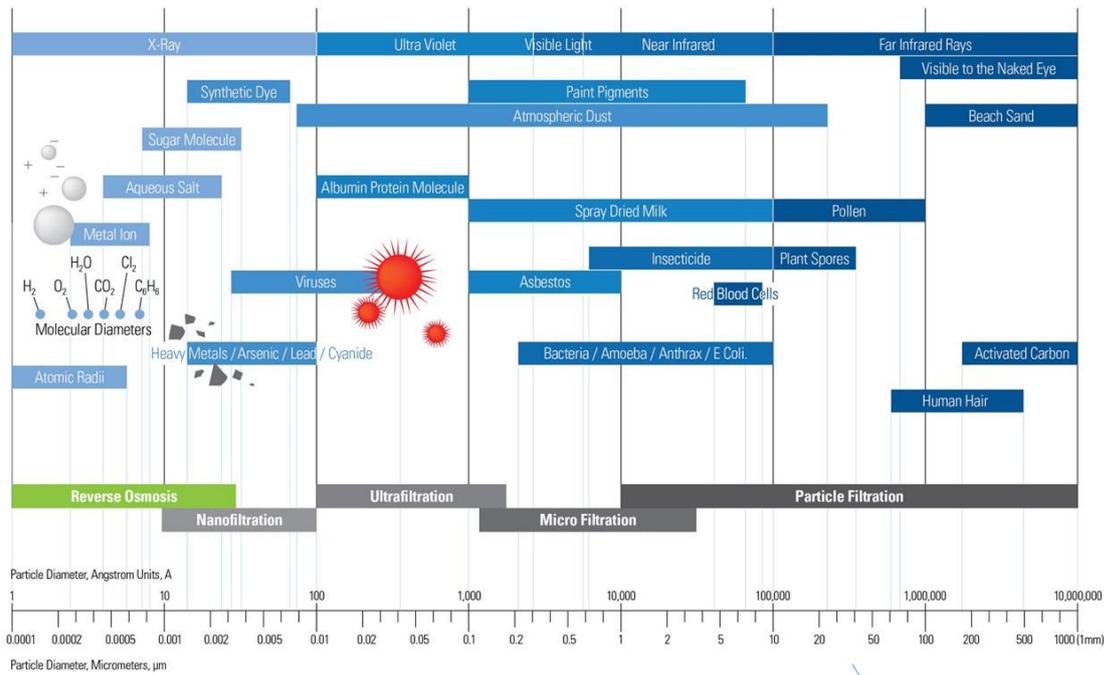


Figure 3: Particle filtration chart ([www.lifesolutions.com.hk](http://www.lifesolutions.com.hk))

The relationship between the applied pressure to the solution and the flux through the membrane are described by Darcy equation ([EQUATION 1](#)).

$$J = \frac{\Delta P}{\mu \cdot R_m} \quad (\text{Equation 1})$$

Where J is the flux (m<sup>3</sup>/s), ΔP is the difference of pressure between feed and permeate (Pa), μ is the viscosity (kg/m·s) and R<sub>m</sub> is the hydraulic resistance of the cleaned membrane (1/m<sup>3</sup>).

The biggest problem of this process is membranes are very sensitive with some dissolved and not dissolved components. The fouling is one of the most important limitations on membranes technology. This fouling may be due to an over added aluminum salts necessary for coagulation but also it may come from deficient pre-filtration systems.

#### **4.2.2. Microfiltration and Ultrafiltration**

The ultrafiltration (UF) and microfiltration (MF) technologies use pressure to lead the separation of solutions. In this case semipermeable membranes with porous size are around 1 to 100 nm are used. The UF systems are used for a wide range of operations. Focused on water cycle they spreading in the market, because the improvements on materials, and the combinations of the systems used make UF membranes a good choice for water treatment plants. Nowadays they are been widely used as a part of non-conventional process of water cycle.

Separation by MF and UF membranes is achieved by sieving mechanisms, i.e. size exclusion. Therefore, these membranes can only retain suspended particles coming from the river water or originated in the treatment train itself during the coagulation process.

Although the use of ultrafiltration technology in water treatment is increasing, membranes fouling remain one of the most complex challenges. On the last years there have been abundant studies on this topic and the behavior of membranes structures considering all components of the filtered solutions. These studies have been done as for external slide as for internal cavities, and its known that it is very sensitive about the changes of the feed's components.

The size of UF porous make this method capable to retain protein molecules, big organic molecules and some salts and only let go throw the membrane water and low molecular weight solutes. A part of those molecules whose cannot go throw are membered on or inside the membrane, causing consequently the fouling in that part.

The water arrives on UF with a few treatments on its back, formed by a peroxidation, coagulation/flocculation, sedimentation/flocculation and then a sand filtration. With all of these pre-treatments the water arrives on UF with a relative low concentration of organic material (<5ppm) but with a too high, relativity, concentration of aluminum (<300ppb) what can cause a problematic degradation on RO membranes.

According to that problematic the uses of UF in Sant Joan Despí DWTP is to eliminate some macromolecules aluminum's complexes, and also reduce free aluminum that can cause several problems in RO if its concentration is over 50 ppb. To eliminate free aluminum it is used iron salts ( $\text{FeCl}_3$ ). So as UF membranes are not able to remove dissolved ions, and aluminum make insoluble complexes with iron it is a good option to prevent damages on RO

membranes. With this micro-coagulation before UF filtration part of this free aluminum can be removed.

Most part of those macromolecules and aluminum make insoluble colloids before UF membrane, and it cause an important fouling problem, which can be reversible (if it is membered on the outside slide and is easy to be removed) or irreversible (if it is membered on the internal porous or cavities and it is impossible to remove it). Irreversible fouling reduce life of the membranes and also increase the chemical cleaning frequency, otherwise reversible fouling can be eradicated by some less aggressive chemical cleanings. Most part of those macromolecules are organic material, assimilated in general as biopolymers, polysaccharides, humic substances, proteins and also colloidal matter can cause fouling on UF membrane. There is not still a good understanding about the effect of those components, and consequently, while there can not be possible to understand the potential of each component there will not be any way to understand the fouling mechanisms on UF membranes to save them from irreversible fouling. However, this fouling has a smaller process and smaller economic impact than the degradation of RO membranes caused by aluminum.

All the processes that use UF membranes require a periodically cleanings, usually known as backwashes. There are some protocols about cleaning stages, there are specified the critical permeability values, determinate the periodicities, concentration of chemical solutions, the different types of solutions used every step and timing of backwash. As has been explained before, the different feeds produce different

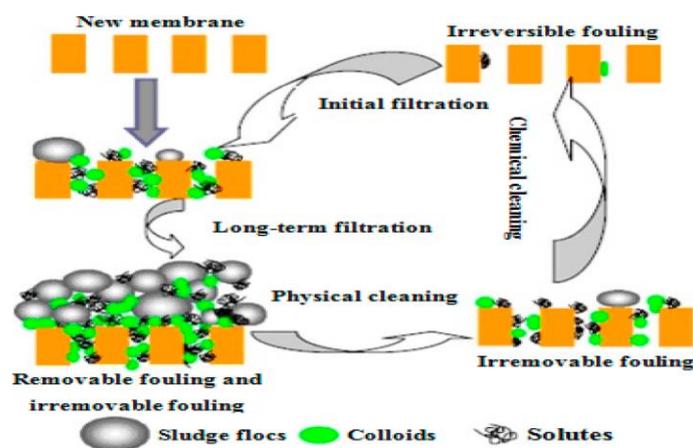


Figure 4: Fouling and cleaning (Petros K. Gkotsis, October 2014)

fouling, and consequently every feed solution should has to have its own protocol. At the moment the general protocols results ineffective in every different feed. To improve the backwash every plant should have to implementation its own protocol, starting with trial and error in the lab, because an improper combination of chemical solutions can accelerate the degradation of those membranes. Also it is not known how degradation affects the internal fibers, on consequence it has not been possible to write a clear strategy that explains how often the membranes should have to be replaced. There are a few points that actually have a long trail to be optimized.

### 4.2.3. Nanofiltration and Reverse osmosis

The reverse osmosis is a physical process which is based on a diffusion phenomenon. The osmosis was discovered by J.A. Nollet whose works about animal membranes were presented on 1748. Later on 1855, A. Fick wrote his laws to describe membranes' diffusion. The first theoretical explanation about osmosis was given by J.A. Van't Hoff on 1887. Finally C.E. Reid and J.E. Breton, of Florida University, tried to desalinate sea water using reverse osmosis, but that project was cancelled due to poor flow rate produced.

Size of porous in RO is roughly 10 Å and provokes that only water can go through the membrane. Therefore, all possible components present in water will not cross the membrane and may precipitate or get stuck on its films (FIGURE 5). Despite the fact that RO and NF uses pressure gradients and concentration gradients to separate the solutions the method is not as UF. In this

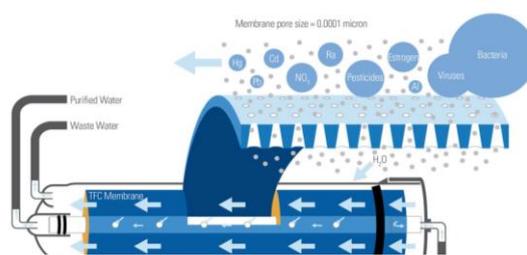
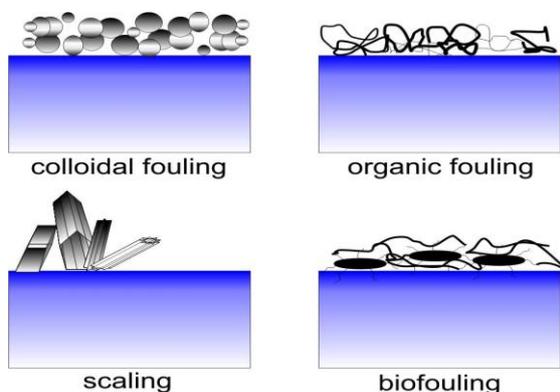


Figure 5: Reverse osmosis process  
 (www.lifefiltration.com.hk)

case the diffusion is the separation mechanism, which is capable to eliminate dissolved ions. The adsorption to the membrane affects to all ions and compounds with the exception of water. Bacteria, viruses and ions don't go through reverse osmosis membrane.

In summary, in most of the DWTPs that use RO filtration have previous stages as micro-coagulation and UF. Therefore, in Sant Joan Despí plant in order to preserve the reverse osmosis membranes they use an iron micro-coagulation to have insoluble colloids of aluminum that can be attached on UF membranes.

### 4.2.4. Membrane fouling



One of the problematic characteristics of ultrafiltration is, as has been exposed on the last episode, the membrane fouling. It can be caused either by organic molecules, or for salts presents on water or also for microorganisms. All these types are showed in the FIGURE 7. All the adsorbed molecules in the membrane, both causing reversible and irreversible fouling, block part of the

Figure 6: Distribution of foulants (LCSC)

porous of the membrane and therefore it decreases the permeability of the membrane, increasing the necessary pressure to filtrate the same flow and also causing a bigger degradation on membrane, shortening its life time.

#### 4.2.4.1. Particulate fouling

Particulate fouling is caused by inorganic or organic particles. Colloids that have gone through the sand filters, with high molecular weight substances and with big volumes are the origins of this fouling. All these compounds can be deposited on the membrane surface, block the pores, or develop a cake layer on the membrane. The structure and mass of the deposited particulate cake layer are affected by the particle-particle forces and by hydrodynamic conditions. The cake layer can be easily removed during cleaning. Therefore, this kind of fouling clogs a big area, but can be removed with a backwashing.

#### 4.2.4.2. Organic fouling

Usually natural organic matter (NOM) is known as the main foulant in water. On the old studies there are some conclusions which suggest that humic substances are the most important NOM-foulants in membranes, where an irreversible fouling is caused by porous plugging and membrane adsorption (D. Jermann, 2007). Although the most recent studies about NOM-fouling have determined that hydrophilic, non-humic, dissolved or colloidal NOM could be the most important NOM-foulant for UF membranes. Also, it has been suggested that polysaccharides can block the membrane (E. Aoustina, 2001). In short, organic fouling includes all kinds of deposit of organic material like grease, oil, surfactants, proteins, polysaccharides, humic substances and other organic biopolymers.

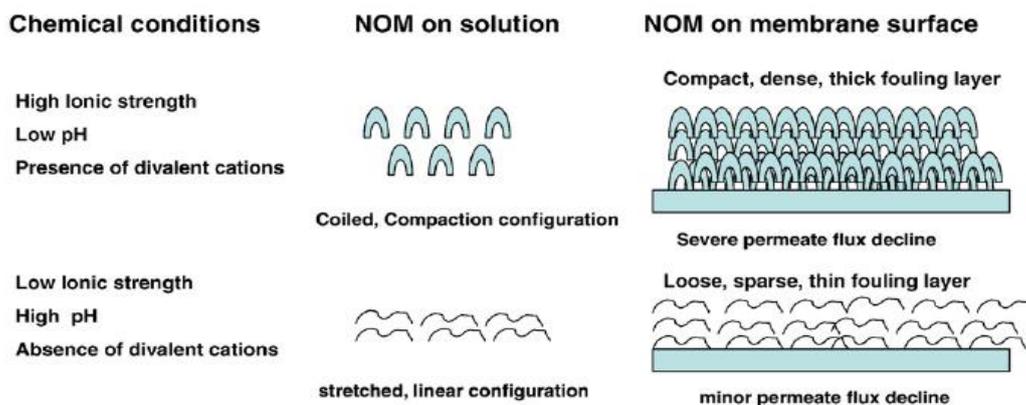


Figure 7: Schematic description of organic fouling

Thorsen showed that the most critical particle sizes for NOM fouling fall in the range 0,1–1,5 µm. In a more detailed study, Hong and Elimelech investigated the role of chemical and physical interactions in NOM fouling of NF membranes. The role of solution ionic strength, pH, and divalent cations in NOM membrane fouling, as well as the fouling mechanisms involved, are reproduced in [FIGURE 8](#). (Al-Amoudi, 2010)

Among the different present compounds, some are thought to have a stronger effect than others. Peiris studied the contribution of protein, like humic, in fouling. By using Fluorescence excitation-emission matrix (FEEM) approach together with principal component analysis (PCA) they found that protein like and humic like compounds were mainly responsible for irreversible fouling. (R. H. Peiris, Sep 2012)

#### **4.2.4.3.       Scaling / Inorganic fouling**

The term ‘membrane scaling’ is commonly used when the precipitate formed is a hard scale. Scaling usually refers to the formation of deposits of inverse-solubility salts such as CaCO<sub>3</sub>, CaSO<sub>4</sub>·xH<sub>2</sub>O, and calcium phosphate. Inorganic scale formation can even lead to physical damage of the UF or RO membranes. It is difficult to restore these membranes performance due to the difficulties of scale removal and irreversible membrane pore plugging. Another potential scaling species are BaSO<sub>4</sub>, SrSO<sub>4</sub>, Ca(PO<sub>4</sub>)<sub>2</sub>, ferric and aluminum hydroxides. Aluminum oxide, inorganic salts, clays, and sand can also act as suitable substrate for crystallization. Minerals precipitation in UF modules leads to a great reduction of the permeate flux, membrane rejection coefficients and life expectancy. (Al-Amoudi, 2010)

#### **4.2.4.4.       Biofouling**

On the first stages of producing drinkable treatment it is pretty common to have a presence of microorganisms as bacteria, viruses or algae. Extracellular Polymeric Substances (EPS) are present outside and inside these microbial cells. They are secretions from microorganisms, and the products of cellular lysis and hydrolysis of macromolecules. If these EPS arrives till UF membranes they can build colonies and block the water flow. This kind of fouling is quite resistant from removing by usual backwashing. They constitute a matrix of high molecular weight molecules (Sheng, et al., 2010). These colonies are extracellular substances, formed by proteins and carbohydrates, which can be adhered over membranes surface as a biofilm. Biofilm matrix is a secondary membrane that participates in the separation process, which means that an extra hydraulic resistance will be added to the membrane, increasing the energy

consumption, decreasing the salt rejection and causing a reduction of permeate production.  
(Flemming, Aug 1996) (Petros K. Gkotsis, October 2014)

## 5. Aluminum

Aluminum is used in the water treatment industry as a coagulant. In DWTP conventional coagulation is often carried out in a separate unit followed by a sedimentation basin. When UF membranes also form part of the treatment train, coagulation can also be carried out by applying small doses of coagulant just prior the UF membrane (giving rise to the so-called micro-coagulation). Some of dissolved species that could go through the UF membranes are retained on the aluminum particle. This final insoluble particle can be retained on the UF membrane. By making insoluble these dissolved components is possible to work with less dense membranes thus reducing the pressure gradient that is needed.

### 5.1. Aluminum solubility

Aluminum once added in a stirred vessel dissolves instantly, and depending of pH solution and the temperature, the dissolved ions of aluminum are different, such as Al<sup>3+</sup>, Al(OH)<sup>2+</sup>, Al(OH)<sub>2</sub><sup>+</sup>... and Al(OH)<sub>3</sub> as a precipitate.

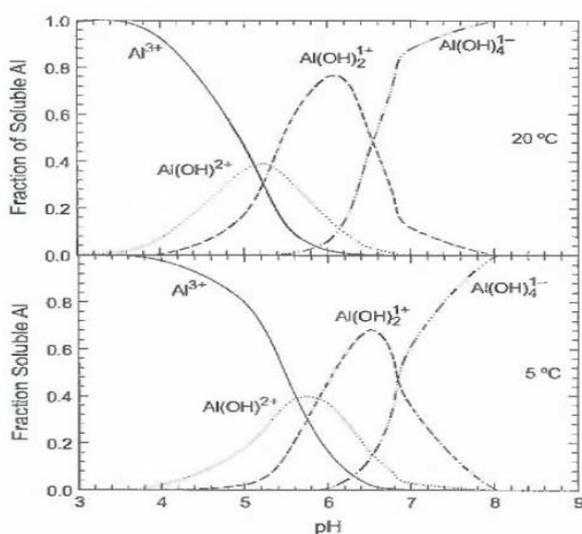


Figure 8: Aluminum ions distribution (Edzwald, 2006)

As it can be seen in [FIGURE 8](#) predominant ions in the pH of the water treated by RO membranes in Sant Joan Despí (6,7) are Al(OH)<sub>4</sub><sup>1-</sup> and Al(OH)<sub>2</sub><sup>1+</sup>. It is important to take in account the temperature too, as can be seen in [FIGURE 8](#). When temperature is low there is a predominance of ions charged more positively. It is noteworthy that solubility values plotted in Figure 8 are calculated for synthetic water and on a thermodynamic basis, which obviously is a simplification of the real environmental solutions found in full-scale DWTP (where, other constituents such as organic matter or other ions may be present)



To conclude this introduction of aluminum should be highlight that the solubility of aluminum depends on whether it is done with aluminum or otherwise is done with poly-aluminum salts. According to different studies it has been observed that precipitates from the solution of the two components mentioned above are different. In order to differentiate them it is common to use an \* in the precipitate from solutions of poly-aluminum. (Edzwald, 2006)

In the case of the plant of Sant Joan Despí they are using poly-aluminum salts, specifically PAX18, which is a specific poly-aluminum that contains sulfates.

## 5.2. Aluminum as a coagulant

With regards to the use of aluminum-based coagulants, it must be underlined that two ways of coagulation mechanism coexist. The prevalence of one mechanism over the other one depends on pH, alkalinity and concentrations of Al. One mechanism consists of the neutralization of the negatively charged particles using aluminum cations, while the second one one consists of the formation of the colloid Al(OH)<sub>3</sub> where the organic particles can get stuck on, eventually this final coagula precipitates.

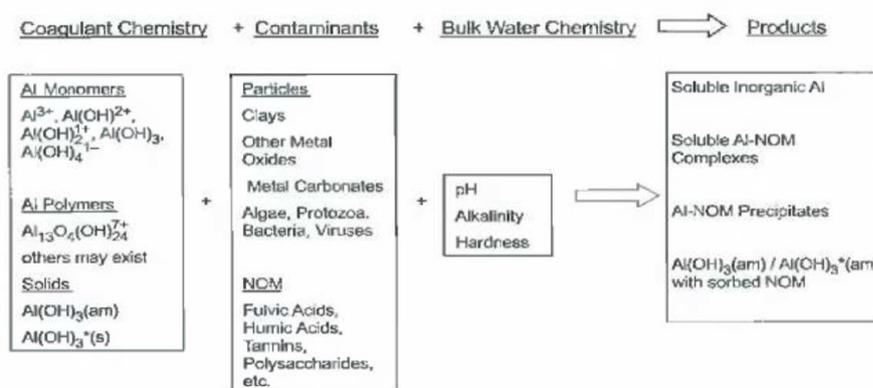


Figure 10: Conceptual view of coagulation reaction (Edzwald, 2006)

As shown in the next figure (FIGURE 12), there is a set of variables in solutions that can make various molecules to precipitate. Under the operation conditions of the plant in Sant Joan Despí, pH 6.5 to 7 makes organic species (NOM) have negative charge, which can be used to coagulate them by means of neutralization. Furthermore, in the operating range of pH on the DWTP, the solubility of aluminum is the minimum, as it can be seen in (FIGURE11: PACl solubility (Edzwald, 2006)). The formation of Al(OH)<sub>3</sub>\* coagulates (formed from poly-aluminum) the particles according to the second way explained before (Edzwald, 2006).

Recent studies have been able to conclude that depending on the size of the coagulant of poly-aluminum salts, the dissolution gets a different precipitate. Aluminum compounds  $AlCl_3$ ,  $Al_{13}$  and  $Al_{30}$  are used in the experiments to show the products from their reaction with NOM. All these products were analyzed after the reactions.

When the first aluminum salt is added ( $AlCl_3$ ), the species that react with NOM are monomeric, dimers or trimers ( $Al^{3+}$ ,  $Al_2(OH)_2^{4+}$  ...), all under 1 kDa and they need less than 1 minute to react as coagulant. When the coagulant is  $Al_{13}$ , the reacting species have greater size; they are polymeric structures that range between 1-3 kDa, and the time to make all the coagulant react goes from 1 till 120 minutes. These species are the most effective coagulant to precipitate NOM. The study of the species that have reacted, when  $Al_{30}$  is used, show that their dimensions are larger than 3 kDa, and is needed more than 2 hours to get the most of them reacted.

It is also necessary to calculate the residual aluminum that remains after coagulation, which is important to take into consideration for the danger that it has towards life and other membranes stages. Once filtered through 0,45  $\mu m$  filters, it is shown how the coagulated compounds coming from  $AlCl_3$  are too small to get attached on the filter. However, the precipitates of other species of coagulants, which are much bigger, are retained in the filter and let permeate water have a lower concentration of Al. But consequently, as mentioned in the above section, solubility pH has a very important role in the final concentration of aluminum in solution. It has been observed that once filtered, the solutions with pH between 6-8 have a much lower concentration of Al because the solubility of aluminum salt  $Al(OH)_3$  (from poly-aluminum salts, which are bigger) is minor in these ranges. This is shown in [FIGURE 13](#).

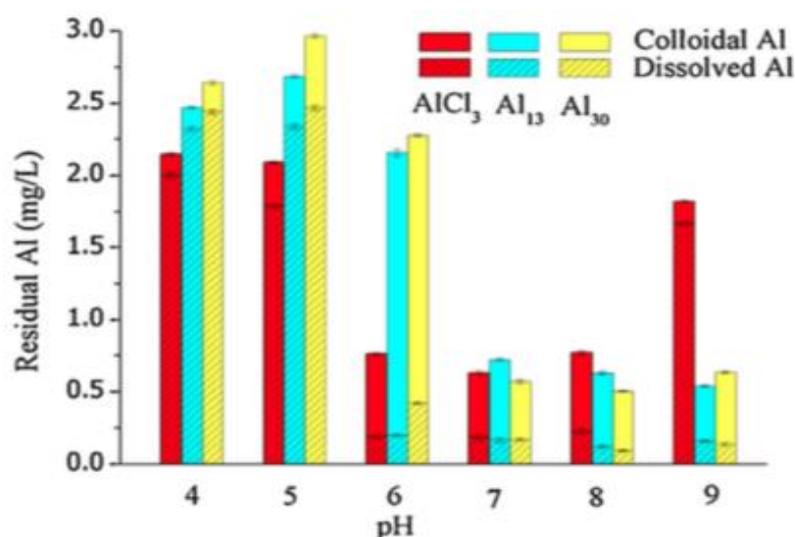


Figure 11: pH effect of dissolved Al (Duan Shu-xuana, 2014)

Therefore, the coagulation with  $\text{AlCl}_3$ , despite being very fast, is inefficient because it generates a final dissolution with high aluminum content. It could also be taken into consideration that using bulky species as  $\text{Al}_{13}$  and  $\text{Al}_{30}$  reduce the amount of coagulant present in the final solution. Moreover, in the case of the  $\text{Al}_{13}$  the minor clotting time is also an advantage. In order to understand this, the following diagram (FIGURE 14) show how the different coagulants react with the NOM (Duan Shu-xuana, 2014).

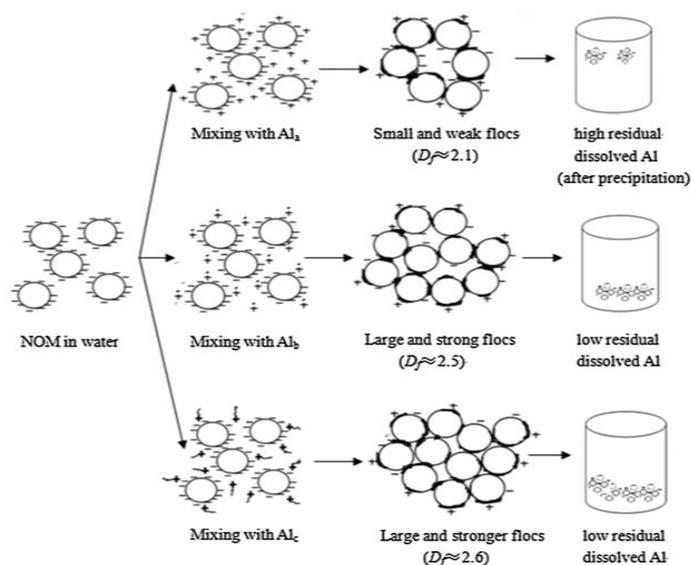


Figure 12: The schematic figure of Al coagulation (Duan Shu-xuana, 2014)

### 5.3. Iron-based for the removal of aluminum

To reduce the damage that aluminum cause on RO membranes, as it has been described before, it is common to use a micro-coagulation with an UF filtration before RO. Iron ions coagulate part of the dissolved aluminum, and the formed colloids adhere on the UF membranes reducing the concentration of Al on the permeate solution.

#### 5.3.1. Fe as a coagulant, $\text{FeCl}_3$

This iron salt is dissolved in water under normal conditions. Naturally, there are some species that are insoluble on water as iron oxide, iron hydroxide and iron carbide.

Ferric chloride is a chemical with a high versatility. It may form floccules and thanks to this, it is widely used in the field of wastewater, industrial or drinking water treatment. Over the years, its use in water treatment has increased because it presents technical and economic advantages in comparison to other coagulants. The salt production is very simple, it is obtained by a reaction between iron oxide and hydrochloric acid, with the following addition of chlorine. Its use becomes one of the important stages prior to filtration, for sludge conditioning, to reduce suspended solids, to make metals precipitate, to reduce turbidity and also to reduce significantly the concentration of organic matter.

Coagulation by  $\text{FeCl}_3$  is not carried out by  $\text{Fe}^{3+}$ , but by a combination of this ion with  $\text{H}^+$  and  $\text{OH}^-$  groups, is possible to be polymerized with other compounds. This  $\text{H}^+$  and  $\text{OH}^-$  groups makes their coagulation function dependent on the pH of the solution. These species of iron coagulate with suspended matter, by neutralizing and destabilizing them. This coagulation is due to the reduction of repulsive forces, as the positive ions of iron and negative ions of suspended materials counteract this force. In the process of flocculation, the coagula become bigger till they precipitate. (OXY Occidental)

### 5.3.2. Differences between aluminum and iron as coagulants

In order to differentiate iron from aluminum coagulants, the first thing that should be defined is the process of coagulation-flocculation. This process consists of several stages by simple physicochemical properties: a mixture of the solution and the coagulant, a stage of coagulation, flocculation and a final decanting of solution to remove colloids.

The mixture is a uniform distribution of the solution in order to spread out all the coagulant in the solvent. Coagulation occurs through the destabilization of colloids and organic matter and they form clots which are bigger or denser and can get attached to the membrane. This process is usually due to the ability to neutralize the negative charge of the molecules suspended in solution, but also because large NOM molecules precipitated with non-solubility specie of coagulant. Flocculation is a soft and constant stirring to make all clots end up precipitating. To finish the process, decantation is done to separate the sludge formed from treated water.

The coagulation-flocculation has an optimum pH, recalling solubility points that coagulator's species have. The optimum point also needs to consider time and the minimum coagulant dose to carry out the process. One point away from the optimum can cause an increase in the dose of coagulant, removing the same NOM, and therefore causing a higher metal concentration on the coagulated water.

(FIGURE 15) shows the difference between the optimum point of the coagulant of aluminum and that of iron. The first coagulant has its optimum pH between 6,8 and 7,7 and the second one has it between 5,5 and 9. This can clearly demonstrate that in this aspect, the iron coagulant has a functionality advantage compared to poly-aluminum coagulant. Despite this difference, the pH range used in DWTP of Sant Joan Despí is between 6.5 and 7.5, which means that this advantage is not significant.

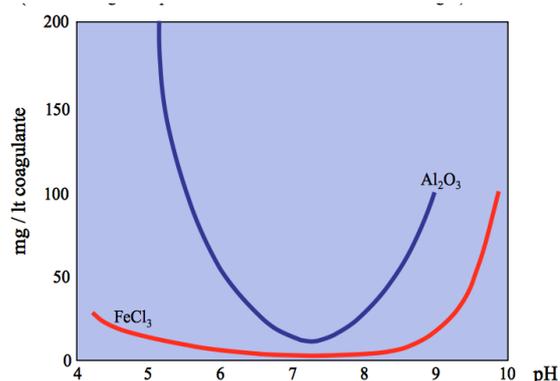


Figure 13: Solubility of coagulants (OXY Occidental)

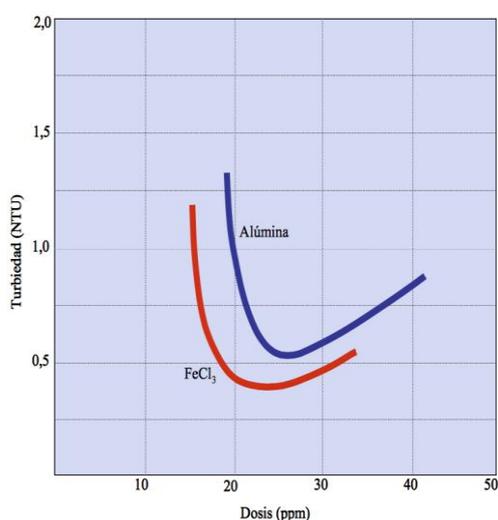


Figure 14: Turbidity removal vs dose of coagulants (OXY Occidental)

Another important parameter is a reduction of turbidity. As shown in the below figure (FIGURE 16) required  $\text{FeCl}_3$  doses are lower than alumina (poly-aluminum) ones to achieve the same results.  $\text{FeCl}_3$  also eliminates the associated color of NOM more easily. (OXY Occidental)

Despite the differences seen in the above analysis, in Sant Joan Despí plant, due to a space configuration and special pipes is not allowed the process of coagulation-flocculation with  $\text{FeCl}_3$ . However, it is used as a coagulant in another stage, basically to remove poly-aluminum coagulant before the ultrafiltration.

## 6. Methodology

The main objective of the present TFG is to get insight into the reactivity between  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  and NOM. The experiments are conducted by a process similar to Jar-test. The water used has similar physicochemical conditions to those of Sant Joan Despí. By adding doses of NOM and coagulants, the results obtained will show coagulation-flocculation process.

From various analysis of Sant Joan Despí DWTP water, it is possible to know the values of several physicochemical parameters and the most common ions concentrations just before UF. These values can be seen in [TABLE 1](#) and [TABLE 2](#). Through these, this study will be based totally on the water from this DWTP.

Feed UF	Turbidity	pH	Temperature	Aluminum	Iron	TOC
Average	0,41 NTU	6,76	17,61 °C	200 ppb	178,3 ppb	3,8
Standard deviation	0,97	0,14	8	100	74,4	-
UF membrane	Biopolymers	LMW neutral	Humic substances	Building blocks	Humic acids	Albumin
Concentration (ppb)	785	1997	797	966	3,76	785
Percentage (%)	17,3	43,9	17,5	21,3	82,7	17,3

Table 1: Water composition on UF feed

Specie	$\text{Na}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{HCO}_3^-$	$\text{SO}_3^{2-}$	$\text{Cl}^-$	Conductivity
mmol/l	3,04	2,59	1,28	4,82	2,13	3,01	1400 $\mu\text{S}/\text{cm}$

Table 2: Sant Joan Despí water composition

## 6.1. Laboratory material

Materials used are:

1 volumetric flask (3 l)	1 volumetric flask (1 l)	1 volumetric flask (500 ml)
3 beakers (1 l)	1 funnel	1 micro-pipet 10 ml
Agar plates	Spatula	Dropper pipets
Beakers (100 ml)	Vacuum pump	Filter paper (0,45 $\mu\text{m}$ )
Bottles (150 ml)	Buchner funnel	Kitasato beaker
Bottles (1 l)	Stir plate	Stirrers magnets
1 volumetric flask (100 ml)	1 volumetric flask (50 ml)	Balance
pH meter	Conducti-meter	

On the other hand, it is also necessary to mention the following chemical reagents used to carry out this experiments:

NaOH 1 M	HCl 1 M
Humic acid(s)	$\text{FeCl}_3$ (0,5 g/l)
$\text{MgCl}_2$ (s)	$\text{CaSO}_4$ (s)
Milli-Q water	PAX 18 (1 g/l)
Albumin(s)	$\text{NaHCO}_3$ (s)



Figure 15: Stir plate (own source)

In the picture above can be seen all the necessary equipment and reagents situated on the laboratory.

## 6.2. Experimental design

Experiments are carried out for different synthetic solutions of 500 ml prepared in the same laboratory.

A Jar-test is done on the prepared samples. It is a simulating coagulation process and afterward the following filtration of solution. The organization of these experiments is such that, in order to simulate more realistic processes, the samples to simulate the coagulation-flocculation increase their complexity step by step.

The first series of experiments consist of 12 experiments to study the direct relationship between each organic component and each coagulant. To carry out this simulation and knowing that organic matter concentration in the water of Sant Joan Despí, just before UF, is around 5 ppm, the experiments changes the coagulant concentration to study the relationships. Coagulants doses are 0,5, 5 and 15 ppm in the case of iron chloride and are 1,10 and 30 in the case of PAX18. Organic concentration is always maintained at 5 ppm.

1st series of experiments			
0,5 ppm FeCl <sub>3</sub> + 5 ppm Albumin	0,5 ppm FeCl <sub>3</sub> + 5 ppm Humic acid	1 ppm PAX18 + 5 ppm Albumin	1 ppm PAX18 + 5 ppm Humic acid
5 ppm FeCl <sub>3</sub> + 5 ppm Albumin	5 ppm FeCl <sub>3</sub> + 5 ppm Humic acid	15 ppm PAX18 + 5 ppm Albumin	10 ppm PAX18 + 5 ppm Humic acid
15 ppm FeCl <sub>3</sub> + 5 ppm Albumin	15 ppm FeCl <sub>3</sub> + 5 ppm Humic acid	30 ppm PAX18 + 5 ppm Albumin	30 ppm PAX18 + 5 ppm Humic acid

Table 3: 1st series experiments

These samples comes from each experiment, 12 in total.

Once verified that the working range allows the observation of the entire working range of both coagulants it is time to go to next experimental stage. This new stage must be able to show if there is any selectivity between coagulants and different NOM species.

The working range of coagulants shows that doses higher than 10 ppm have already carried out a large coagulation of the organic matter, and therefore an increase of coagulant dose does not provide more benefits. Therefore the new coagulant range was situated between 1

and 10 ppm. In this case the same concentrations scale for each coagulant was used, in order to obtain a faster and a better extrapolation of results.

This new series has also an important characteristic, which is that the studied solutions have a similar composition to that found in Sant Joan Despí. In the plant, just before the UF filtration, concentration of NOM assimilated as humic acid is about 4 times larger than the NOM assimilated as albumin. So taking into account this factor and also criteria of minimum detection of analysis instrument, it is necessary to make an extrapolation and increase components concentration of water. The relation 1ppm : 4ppm of albumin : humic acid is assimilated for this series 4 ppm of albumin and 16 ppm of humic acid.

After the preparation of this concentrated water of NOM a sand filtration is done in order to only have the dissolved components on the final water. With this method it is not possible to know the final concentration of organic matter on this solution and for this reason it is necessary to take a sample of this water to finally know the effectiveness of the coagulant. Therefore one filtration by 0,45 µm but without coagulant is done on this sand filtrated water to afterwards observe if the coagulant makes a big difference. With this new concentration of coagulants and new organic matter concentrations can be done 9 more experiments. These ones will show the effectiveness of coagulation of total NOM by only one coagulant. In the table below can be seen those experiments compositions:

2nd series experiments				
4 ppm Albumin + 16 ppm Humic acid	1 ppm FeCl <sub>3</sub> + 4 ppm Albumin + 16 ppm Humic acid	3 ppm FeCl <sub>3</sub> + 4 ppm Albumin + 16 ppm Humic acid	5 ppm FeCl <sub>3</sub> + 4 ppm Albumin + 16 ppm Humic acid	10 ppm FeCl <sub>3</sub> + 4 ppm Albumin + 16 ppm Humic acid
	1 ppm PAX18 + 4 ppm Albumin + 16 ppm Humic acid	3 ppm PAX18 + 4 ppm Albumin + 16 ppm Humic acid	5 ppm PAX18 + 4 ppm Albumin + 16 ppm Humic acid	10 ppm PAX18 + 4 ppm Albumin + 16 ppm Humic acid

Table 4: 2nd series experiments

On the next figure it is shown the samples of water and the filters coming from each Jar-test when it is used  $\text{FeCl}_3$ . But also can be observed the first sample and its filter, which has not passed a Jar-test. It is only the water coming from the sand filtration with a later vacuum filtration using  $0,45 \mu\text{m}$  filters.



Figure 16: Samples and filters after Jar-Test using  $\text{FeCl}_3$  (own source)

In total are taken 10 samples, 8 coming from the normal Jar-test, 1 from vacuum filtration of sand filtered water and another 1 from only sand filtration.

The next stage of the experimentation is to determinate the influence of the iron chloride in front of real water. This water is bring directly from the DWTP of Sant Joan Despí just after sand filtration and before the ultrafiltration .Therefore this water has the characteristics and compositions that this project tries to simulate, but on this stage of DWTP the aluminum (PAX18) are already added, with a concentration around 200 ppb. The composition of NOM are around 4 ppm, with the same relation between humic : albumin (4:1). On this stage some aliquots of iron chloride are going to be added on the different experiments, to try to elaborate a conclusion about the behavior of iron and aluminum, and also observe if this iron interact with the organic matter that are still dissolved. As on the last series experiment a filtration by  $0,45 \mu\text{m}$  but without an additional coagulant is done to observe if the coagulant makes a big difference.



Figure 17: Samples and filters after Jar-Test using  $\text{FeCl}_3$  (own source)

These third series experiment is composed by 5 experiments; as is shown on the following table only iron is added.

3rd series experiments				
-	1 ppm $\text{FeCl}_3$	3 ppm $\text{FeCl}_3$	5 ppm $\text{FeCl}_3$	10 ppm $\text{FeCl}_3$

Table 5: 3rd series experiments

In total are taken 6 samples, 4 coming from the normal Jar-test, 1 from only filtrated water and another 1 from real water.

### 6.3. Jar-test

Jar-test technique consists adding a growing coagulant dose into solutions to test water. Determine a time of agitation and physicochemical properties of solutions provides the optimal point (optimal coagulated dose).

However, the results of the laboratory tests can not be directly extrapolated to the water treatment plant. There are several factors to take into account among them, such as the amount of coagulant added or water conditions, and also differences in shape and



Figure 18: Jar-test example ([www.hdwalls.xyz](http://www.hdwalls.xyz))

dimensions of decanters, methods of coagulant addition... In order to carry out every Jar-test in the same way, each experiment have the same container, and the same agitation system.

Steps to do a successful Jar-test are described below:

- i. 1 liter beakers are placed on agitation plate, and they are filled by experimental water, which is pre-conditioned, controlled pH and conductivity. Then doses of coagulant are added by a pipette. Then, stirring starts at a set speed around 40-80 rpm.
- ii. After 20 minutes agitation stops and dissolution begins its sedimentation. This process takes 20-30 minutes.
- iii. Once this time of sedimentation is over it is moment to do a decantation of the top part of dissolution in order to make a study of color and turbidity of each sample. It should

also be taken into account the pH of the final solution, and check if its pH has been constant since the beginning of the process. (Consultora de Aguas)

Although the process described above is the theoretical frame of this project, in this one the Jar-test is done in a different way, because the parameters studied goes beyond than turbidity and color of the final sample. The experimental method consists to make the process of coagulation-flocculation as a Jar-test but with a final filtration. This filtration is done in order to observe concentrations of all components of the final solution, as residual coagulant as dissolved organic matter.

## 6.4. Operational protocol

In order to do the experiments with the same method every time it is necessary to set down all steps to follow in lab. Coming up next the protocols are explained in detail.

### 6.4.1. Synthetic water preparation

Synthetic water is just water with similar alkalinity and salt concentrations as water found in the plant of Sant Joan Despí. It lets experiments to have the same background and consequently it allows having another variable under control.

The only known values of Sant Joan Despí water are concentration of the most important species and the conductivity, which is intertwined with the ionic strength. These values are shown in [TABLE 2: SANT JOAN DESPÍ WATER COMPOSITION](#).

This water comes from a synthetic solution by the addition of different salts as  $\text{MgCl}_2$  (s),  $\text{CaSO}_4$  (s) and  $\text{NaHCO}_3$  (s). These salts are added to a volumetric flask whose solvent is Milli-Q water, in order to avoid dissolved organic matter. Milli-Q water guarantees a concentration less than 20 ppb of TOC.

In order to prepare dissolution of 3 liters is necessary to keep concentrations constants, but for stoichiometric reasons that is impossible. So then, it is tried to reproduce proportions of species as accurate as possible, and also it is tried to keep conductivity value as close as it is found in plant. In the table below ([TABLE 6](#)) is shown the mass quantities that are added in order to match this criterion.

These mass values have been calculated by [EQUATION 2](#). The molecular masses (PM) of salts MgCl<sub>2</sub> (s), CaSO<sub>4</sub> (s) and NaHCO<sub>3</sub> (s) are 203.2, 172 and 91 g/mol, respectively. It should take into account that some of them are hydrated.

$$m = \text{mols} * PM$$

(Equation 2)

In order to improve the conductivity simulation of synthetic water 0,2 g of MgCl<sub>2</sub> (s) and also 0,2g of NaHCO<sub>3</sub> (s) are added, thus helping to increase the ionic strength.

Specie	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Conductivity
mmols (in 3L)	9,13	7,78	3,38	14,46	6,38	9,03	1400 μS/cm
0,84 g MgCl <sub>2</sub> (mmols)			4,5			9	
1,21 g CaSO <sub>4</sub> (mmols)		7			7		
0,91 g NaHCO <sub>3</sub> (mmols)	10			10			
Global (mmols)	10	7	4,5	10	7	9	1192 μS/cm

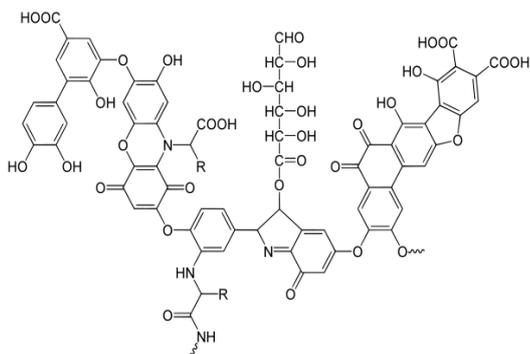
Table 6: Water solution composition

#### 6.4.2. Concentrated solutions of albumin and humic acid preparation

In the preparation of soluble organic matter solutions there is a remarkable fact, the solubility of this matter in water. In the case of albumin there is no problem when solutions with a lower concentration than 500 ppm are prepared, but in the case of humic acid the maximum concentration that can be achieved without having to heat or agitate it is limited to 100 ppm. Consequently, these two values are used to prepare concentrated solutions with the aim of having less added amount of these solutions in the experiments.

##### 6.4.2.1. Humic acid

Humic acid is the main component of humic substances which are the major organic component of soil humus, peat, coal, many water streams, dystrophic lakes and oceans water. It is produced by biodegradation of dead organic matter. This is not a simple acid, it is a complex mixture of many different acids containing carboxyl group and fennel, consequently the mixture has functions as a dibasic acid or, occasionally, as a tribasic acid.



Humic matter is a supramolecular bio-organic structure with a relatively small size and its molecular weight is under 1000 g/mol. Therefore, its small size allows assimilating the low molecular weight organic matter present in water as humic acid and thus facilitating experimentation without much distortion results.

Figure 19: Example of a typical humic acid (www.wikipedia.org)

#### 6.4.2.2. Albumin

Albumin is a protein found in high proportion in the blood plasma, the main blood protein, and one of the most abundant in humans. Thanks to its big 3D structure, as can be seen in [FIGURE 19](#), it lets all the big water compounds be assimilated as albumin. Its molecular weight is around 69.000 g/mol which means that there is a big difference, at least, on the structural behavior between humic acid and albumin.

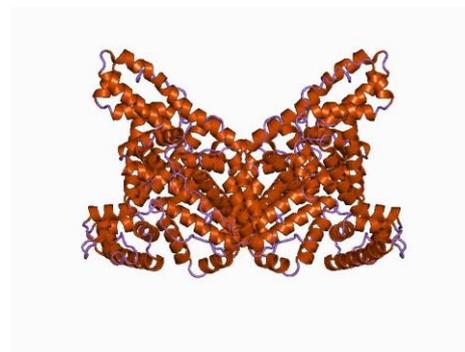


Figure 20: Albumin structure (www.wikipedia.org)

#### 6.4.3. Concentrated solutions of FeCl<sub>3</sub> and PAX18 preparation

Concentrated coagulant solutions come from Sant Joan Despí plant, where they are used. Using conversion factors as can be seen in [EQUATION 3](#) and [EQUATION 4](#), is easy to obtain the desired concentration of coagulant. In whole the experiments the concentrations that will be used will be 1g/l of each coagulant.

$$0,5\text{ l} * \frac{1\text{gFe}}{1\text{ l}} * \frac{162,2\text{FeCl}_3}{55,84\text{gFe}} * \frac{1\text{mlFeCl}_3}{1,42\text{gFeCl}_3} * \frac{100\text{mlreal}}{40\text{mlpure}} = 2,56\text{ ml of FeCl}_3 \quad (\text{Equation 3})$$

$$0,5\text{ l} * \frac{1\text{gPAX18}}{1\text{ l}} * \frac{1\text{lPAX18}}{20\text{gPAX18}} * \frac{1000\text{ml}}{1\text{ l}} = 25\text{ ml of PAX18} \quad (\text{Equation 4})$$

#### 6.4.4. Experiment solution preparation

To prepare the solutions, the set of reagents, both coagulants dissolutions, synthetic water and organic matter dissolutions, have to be already prepared. To measure the volume of the solution, a 500 ml volumetric flask is used. Once the solution has the right volume by filling the flask with synthetic water till the 500 ml line, it is time to pour the solution to the beaker. This beaker has a magnet inside. Then, the stirring begins at the lowest speed that the agitator table allows, which is 200 rpm. As fast as possible, pH is measured and adjusted to 6,7 in order to balance the physicochemical parameter as in plant. This is done using HCl and NaOH both 1 M.

At this point, the difference between the normal Jar-test and the method used in this project is shown. The next step is to stop stirring after 20 minutes.

After 1 hour since agitation started, the beaker is brought to the next step. A hand agitation is done to the beaker to homogenize the solution. In order to analyze a non-filtrate sample, part of the solution that is on the beaker is poured into this corresponding labeled bottle.

The experiments are not carried out simultaneously, they are displaced in time slots between 20 and 30 minutes as the materials have to be cleaned and also the new solution has to be prepared.

#### 6.4.5. Vacuum filtration

The last step of the process carried out in the experimental laboratory is vacuum filtration, which allows the filtration in less time. It is used a Buchner, an Erlenmeyer Kitasato and filters of 0.45 µm. When high amounts of coagulant are used, this precipitates and it is deposited in the filter, thus causing a significant decrease in flow filtration, and therefore using longer time to get the solution filtered.

The filtrated solution obtained at the end of the process goes into another bottle, also labeled in order to take it to analyze. Moreover, filter paper is stored, placing it in the oven for 10 minutes to dry



Figure 21: Vacuum filtration (own source)

and keeping it in Petri dishes in order to analyze the precipitated structures afterwards.

All the bottles goes to the fridge still they are analyses, with the aim of prevent the degradation of the organic matter.

#### 6.4.6. Instruments cleaning

The last but not least important point is the instrument cleaning, which has to be done before and after the experiments. It is necessary to be sure that the instruments used are well cleaned. The cleaning is done by adding an abundant water supply. Then, deionized water is poured to remove debris that may remain. And in the final step, Milli-Q water is added in order to ensure the non-presence of any compound on the instrument.

Buchner funnel and beakers have to be cleaned as well with acid and laboratory paper because the precipitates can be stuck on the glass.

### 6.5. Analytical methods

#### 6.5.1. Metal analysis in aqueous samples

The ICP (Inductively Coupled Plasma mass spectrometry) is a technical analysis for inorganic matter. It is very sensitive and able to determine a range of metals and non-metals at various concentrations below one ppb. It is based on coupling inductively coupled plasma as a method to produce ions (ionization) with a mass spectrometer as a method for separating and detecting ions. This technique is used for both qualitative and quantitative inorganic analysis. This method has advantages as its high speed, precision and sensitivity compared to the techniques of atomic absorption spectroscopy.

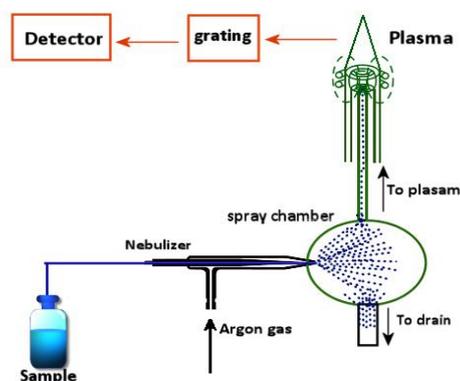


Figure 22: ICP scheme  
(www.chemiasoft.com)

Detection range in the metals used in this project, aluminum and iron, have their low limit on 45 ppb and 6.2 ppb respectively.

All those analysis are done on an external department, and they provide the results by its respective report. These reports describe metal concentrations found in the samples.

### 6.5.2. Total organic carbon

The measurement of the amount of organic matter found in a solution can be set directly using a total organic carbon (TOC) method. This method is faster than other systems, such as DQO or DBO, and it also has a direct measurement of organic carbon as it does not consider the possible links between nitrogen, hydrogens and inorganic species.

The method used is a catalytic oxidation at 680 °C. Among the products of combustion, this method is interested on carbon dioxide particularly, both coming from the inorganic and organic carbon. With the use of an infrared detector (NDIR) it would be possible to know the total carbon concentration. Then, an acidification with phosphoric acid is done, and it forms CO<sub>2</sub>, and by NDIR the IC is revealed. The IC is the carbon dioxide dissolved in the water as carbonates or bicarbonates. Therefore, using a difference between total carbon and the IC will get the TOC of the sample.

Again, all those analysis are done on an external department, and they provide the results by its respective report. They are done in CETAQUA-UPC. These reports describe the total organic carbon concentrations found in the samples. It is not a direct measure for this project but it helps to corroborate the values that come from the FEEM.

### 6.5.3. Florescence emission-excitation

Fluorescence spectroscopy is a type of electromagnetic spectroscopy that analyzes the fluorescence of a sample. Commonly ultraviolet and visible light is used with the intention to excite electrons from the molecules of certain components and cause the emission of a photon, usually as visible light. Its complementary technique is the absorption spectroscopy.

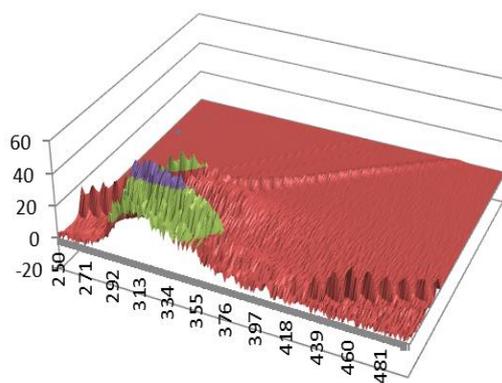


Figure 23: FEEM example (Own source)

In fluorescence spectroscopy, species are excited by a photon beam. These photons carry the electrons of these molecules to the vibrational states of excited electronic states. Then, the molecule returns to its ground state, releasing a photon with a different intensity. In consequence of the existence of various levels of excitation there is a set of wavelengths from photons emitted.

Through this series of data from the various excitation-emission signals, three dimensions graphs are represented (FEEM). Afterwards, through data processing, known as PARAFAC, it is easy to draw some quantitative conclusions. These excitation-emission signals consist of wavelength range, selected between 250 and 500 nm for excitation and 200 to 400 nm for emission.

To do all these tests, a quartz cuvette I used. Prior to any experiment, it is cleaned with Milli-Q water, and then filled with the sample. This process is done for each sample, and it gives a big data table.

FEEM analyses are performed in the Analytical Chemistry Department of the Physics and Chemistry Faculty in the University of Barcelona (UB).

#### **6.5.3.1. PARAFAC**

PARAllel FACtor analysis (PARAFAC) is used in the chemical sciences to decompose trilinear multi-way data arrays and facilitate the identification and quantification of independent underlying signals, termed 'components'.

Important assumptions for successfully decomposing a multi-way dataset using PARAFAC include:

- (1) Variability: two chemical components can not have a perfect covering fluorescence intensities or identical spectra.
- (2) Trilinearity: the same number of components underlies the chemical variation in each mode (dimension) of the dataset. For FEEMs, this means that emission spectra are invariant across excitation wavelengths, excitation spectra are invariant across emission wavelengths, and fluorescence increases approximately linearly with concentration.
- (3) Additivity: the total signal is due to the linear superposition of a fixed number of components. (Kathleen R. Murphy, Desember 2013)

With this mathematical method is possible to relate the global 3D spectrum, composed by all compounds characteristics, to with a different evolution of these compounds. Finally, this parameter is related with the compounds concentration and is possible to study their evolution.

#### **6.5.4. Colorimetry analysis**

A colorimetry analysis is done by spectrophotometer instrument. It is possible by the propriety that some compounds have. This propriety is its color that changes with their concentration. Once is known the concentration function in front of color it is easy to study this characteristic using a spectrophotometer.

If is desired to study one element that have not this color propriety is possible to combine it with another one and obtain one final compound that can be analyzed by this technique.

In this project with the aim to study the concentration of iron and aluminum it is also done a colorimetric analyze. To analyze the metals are used different compounds. These final solutions give a characteristic color, which can be traduced to a concentration using the spectrophotometer.

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## 7. Experimental results

### 7.1. Model organic compounds vs PAX18 or FeCl<sub>3</sub>

This section reports the NOM removal percentages after the addition of the coagulants of interest during the jar-test experiments. in front of only 0,45 µm filtration. Once the data from FEMM are treated by PARAFAC, and the final concentrations of iron and aluminum are analyzed too it is possible to proceed with the following results.

#### 7.1.1. Albumin vs PAX18 or FeCl<sub>3</sub>

Table 7 gives a relative concentration extracted by PARAFAC analyses. This relative concentration is the parameter (C1) that uses FEEM and PARAFAC to analyze the compounds concentrations of the samples. There is also the absorbance, the TOC and the percentage of BSA (albumin) removed. The different rows represent all the experiments done with BSA 5ppm and the different PAX18 and FeCl<sub>3</sub> concentrations (+ C xx/xx ppm, respectively).

PAX18	C1	Absorbance	TOC (mg/L)	% removed
BSA 5	1269	0,025	2,992	0
BSA 5 + PAX18 1	1044	0,011	2,932	17,72
BSA 5 + PAX18 10	371	0,002	2,94	70,71
BSA 5 + PAX18 30	235	0	2,101	81,41
FeCl <sub>3</sub>	C1	Absorbance	TOC (mg/L)	% removed
BSA 5	1274	0,025	2,992	0
BSA 5 + FeCl <sub>3</sub> 0,5	997	0,011	2,336	21,74
BSA 5 + FeCl <sub>3</sub> 5	272	0,008	0,451	78,62
BSA 5 + FeCl <sub>3</sub> 15	323	0,045	2,097	74,65

Table 7: Albumin + C (ppm)

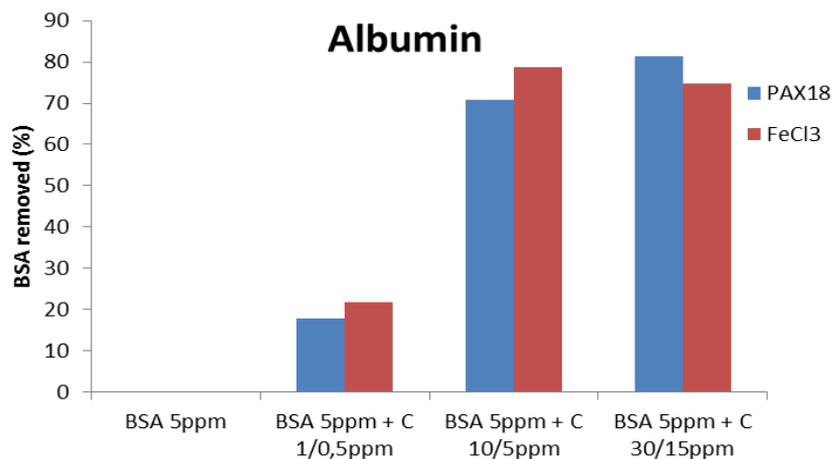


Figure 24: Albumin + C

In the last graphic, it can be seen that FeCl<sub>3</sub> coagulant has more effectiveness than PAX18, because with half the concentration it removes the same quantity of NOM than PAX18. There can also be seen that increasing the concentration of the coagulants over 10 ppm of PAX18 and over 5 ppm of FeCl<sub>3</sub> does not improve the BSA removal significantly.

Otherwise, it is shown that the BSA removal increases up to 90% of NOM removed versus a simple filtration.

The following graphic displays the concentrations of BSA on each experiment.

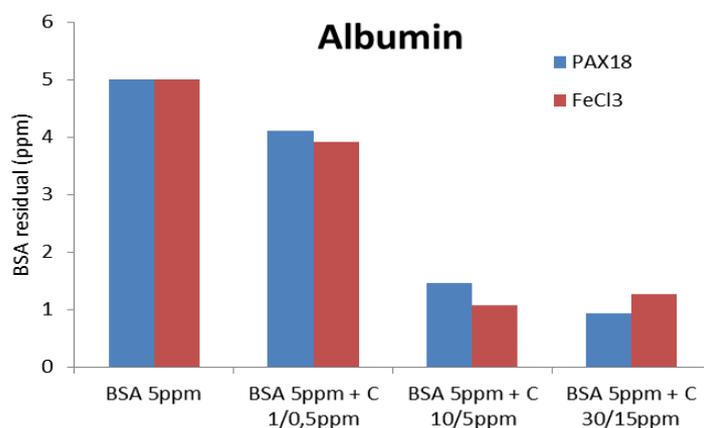


Figure 25: Albumin + C (concentration)

This shows that finally the concentration of albumin decreases to approximately 1 ppm.

### 7.1.2. Humic Acid vs PAX18 or FeCl<sub>3</sub>

Table 8 shows the relative concentration extracted by PARAFAC analyses. This relative concentration is again the parameter (C1) that uses FEEM and PARAFAC to analyze the compounds concentrations of the samples. It also shows the absorbance, the TOC and the percentage of HA (humic acid) removed. The different rows represent all the experiments done with HA 5 ppm and the different PAX18 and FeCl<sub>3</sub> concentrations (+ C xx/xx ppm, respectively).

PAX18	C1	Absorbance	TOC (mg/L)	% removed
HA 5	845	0,365	3,932	0
HA 5 + PAX18 1	748	0,146	2,992	11,46
HA 5 + PAX18 10	534	0,06	1,401	36,74
HA 5 + PAX18 30	413	0,03	2,449	51,06
FeCl <sub>3</sub>	C1	Absorbance	TOC (mg/L)	% removed
HA 5	842	0,365	3,932	0
HA 5 + FeCl <sub>3</sub> 0,5	687	0,1	1,401	18,33
HA 5 + FeCl <sub>3</sub> 5	433	0,018	2,449	48,55
HA 5 + FeCl <sub>3</sub> 15	386	0,022	2,574	54,09

Table 8: Humic Acid + C

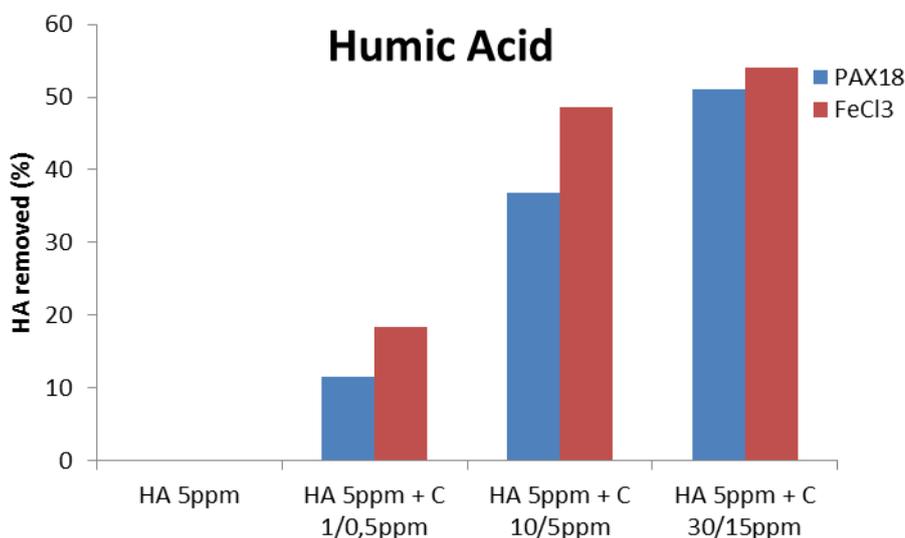


Figure 26: Humic Acid + C

In the last graphic, it can be seen that FeCl<sub>3</sub> coagulant has again more effectiveness than PAX18, because half the concentration removes more NOM percentage than PAX18. The

effectiveness of these coagulants continues increasing by adding more coagulant to the solutions, but only a little.

Otherwise, it is shown the HA removal increases up to 50% of NOM removed compared to simple filtration.

In the following graphic, there is a display of the concentrations of BSA of each experiment.

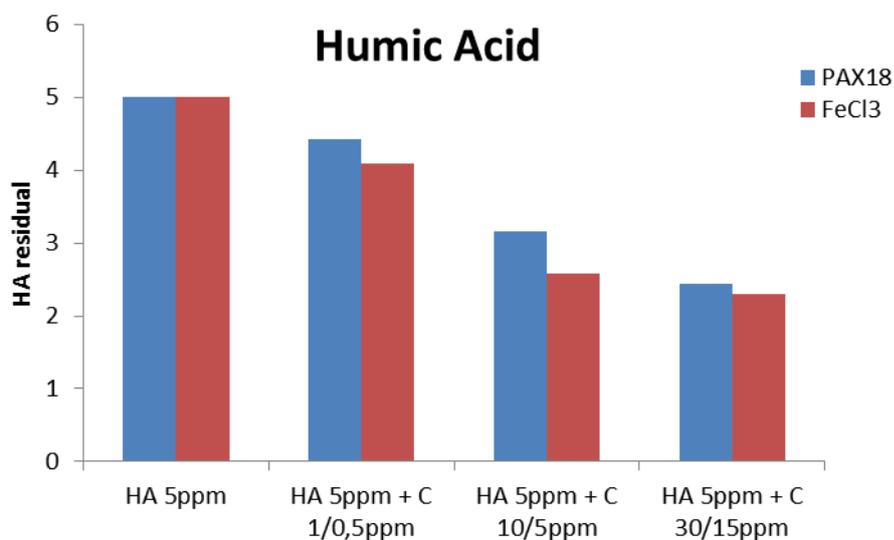


Figure 27: Humic Acid + C (concentration)

This shows that finally the concentration of humic acid decreases to approximately 2,5 ppm.

On the other hand, an important data that was not a variable at the beginning of the project has become an important part that could be studied further in the future. This is the time needed to do the vacuum filtration, which increases significantly when the coagulants dosages rise. This information would be important when fouling and flow rate evolution want to be studied and modeled.

Both coagulants present a constant effectiveness for both humic acid and albumin when the coagulant concentrations are over 10 ppm. This has determined that, as stated in the methodology, the working range that coagulants work without saturation is between 1 and 10 ppm.

### 7.1.3. FeCl<sub>3</sub> vs Humic Acid or Albumin

Figure 30 shows the selectivity of FeCl<sub>3</sub> coagulant versus the different NOM.

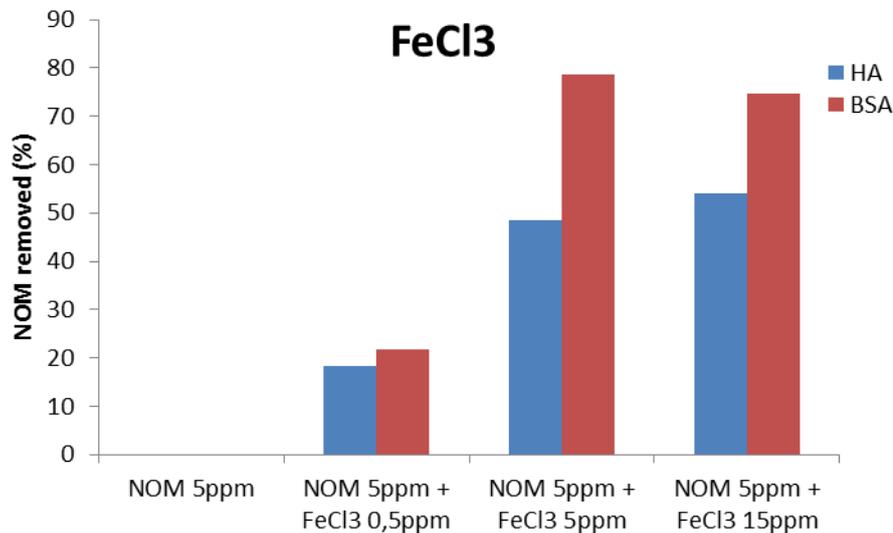


Figure 28: NOM + FeCl<sub>3</sub>

The most representative tendency of FeCl<sub>3</sub>, seen in this last graphic, is its major preference to remove BSA. There is a difference of 20%-30% between each NOM. These differences are shown when the amount of removed NOM is meaningful. Also, its effectiveness stops when reaching the 70% or 50% of removal of its respective NOM when the concentration of FeCl<sub>3</sub> goes over 5 ppm.

### 7.1.4. PAX18 vs Humic Acid or Albumin

This graphic shows the selectivity of PAX18 coagulant against the different NOM.

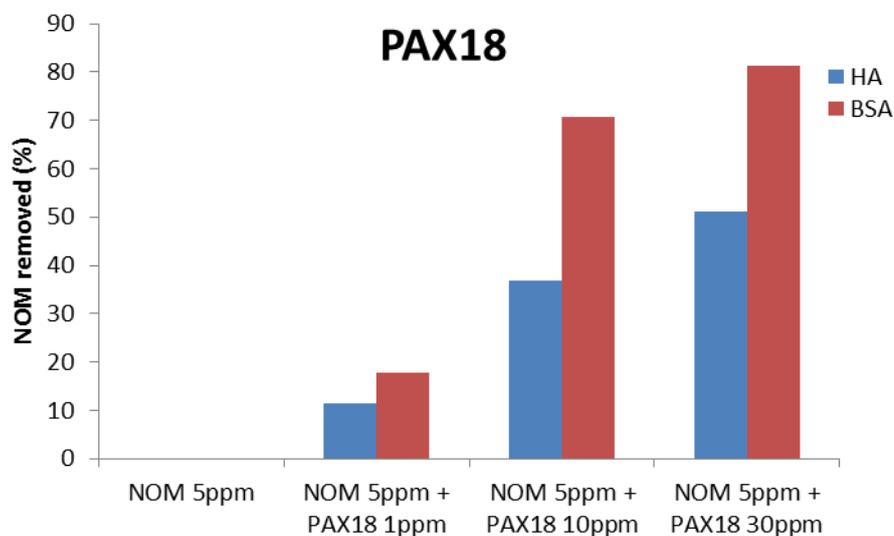


Figure 29: NOM + PAX18

The most representative tendency of PAX18 is again its preference to remove BSA. This could be caused by the different sizes that these two organic matters have. BSA has a quite bigger size, and with the addition of the coagulants the effectiveness of these could be affected. Also, its effectiveness increases with concentrations over 10 ppm, although only slightly. There are again differences of 20-30% between each NOM.

## 7.2. Mixtures of model organic compounds vs PAX18 or FeCl<sub>3</sub>

In this stage there are different percentages represented. The NOM percentages that are removed on each experiment are displayed in the graphics in comparison to simple filtrated water, with the aim to show the removal effectiveness that coagulant adds in this Jar-test.

In this part, it is possible to see whether the coagulants have different selectivity when they find different organic matters in the same solution. The experiments are done with 16 ppm of humic acid and 4 ppm of albumin, and this time the same concentrations of coagulants are used; 1, 3, 5 and 10 ppm. Because of the samples from 5 ppm have not given a coherent numbers they do not appear on the graphics and tables.

Furthermore, some modified FEEM are shown to see the differences between some final compositions. There are also exposed the metal concentration on the samples.

### 7.2.1. Albumin

In the following graphic, there are the concentrations that are found once the dissolution has been filtered with coagulant or without it. (C means coagulant)

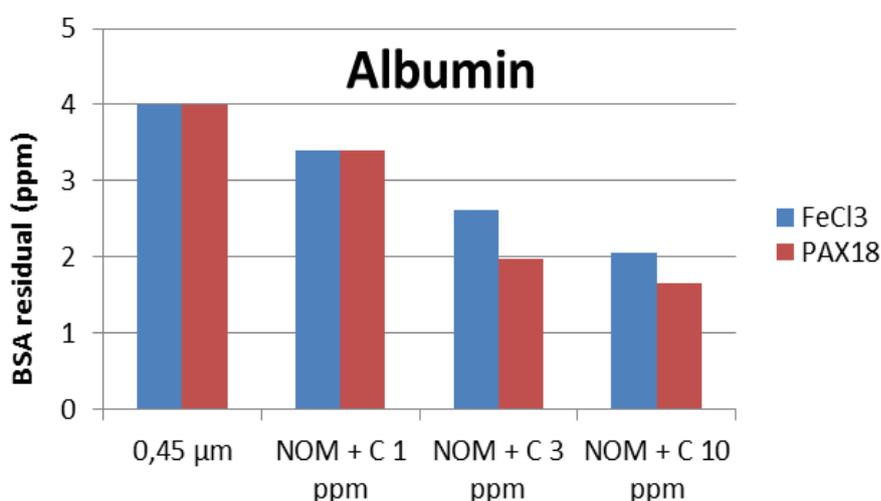


Figure 30: Albumin + C (water with HA&BSA)

From this last graphic, it can be extracted that PAX18 has a greater effectiveness in front of  $\text{FeCl}_3$ . This selectivity tendency is little but clear in this range, and shows that this NOM can be reduced more than 50 % with 10 ppm of PAX18.

### 7.2.2. Humic acid

In the following graphic, there is a display of the concentrations that are found once the dissolution has been filtered with coagulant or without it. (C means coagulant)

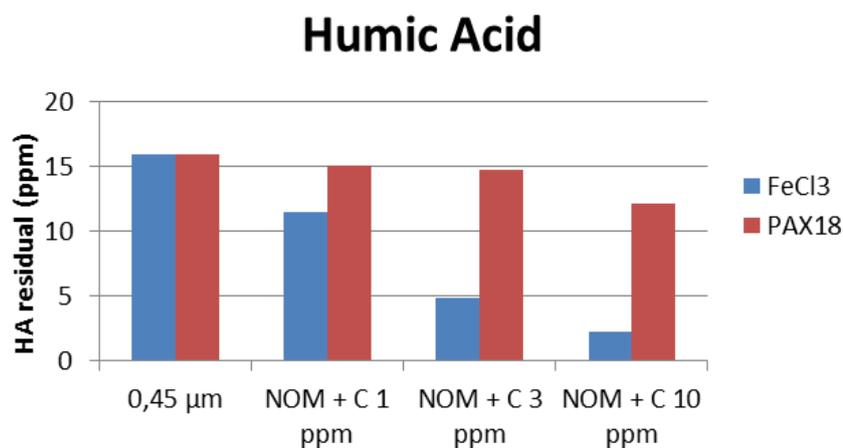


Figure 31: Humic Acid + C (water with HA&BSA)

In this last graphic, the differences of humic acid versus albumin can be seen. The molecular size of humic acid in front of albumin can change the effectiveness of each coagulant. When studying humic acid, it can be seen that  $\text{FeCl}_3$  removes more humic acid than PAX18 with the same concentration. The percentage reduction rises up to 80 % or even higher.

The same as with albumin, the effectiveness of both coagulants does not decrease meaningfully while its concentration rises up. The final concentration of both organic matters decreases to 2 ppm when their best coagulant is used.

Once again, the time of vacuum filtration has been an important data that has been featured. It has increased a lot when the coagulants have been used. The fouling problems show that the coagulant does its work, but on the other hand it blocks the porous of the membrane and the permeate flow is reduced drastically.

### 7.2.3. FeCl<sub>3</sub>

In the following table different parameters like NOM concentrations, absorbance and the percentages of NOM removed are exposed.

	HA (ppm)	BSA (ppm)	Absorbance	HA removed (%)	BSA removed (%)
0,45 μm	16	4	0,445	0	0
FeCl <sub>3</sub> 1 ppm	11,45	3,39	0,288	28,45	15,14
FeCl <sub>3</sub> 3 ppm	4,86	2,61	0,078	69,60	34,85
FeCl <sub>3</sub> 10 ppm	2,32	2,05	0,043	85,51	48,68

Table 9: NOM + FeCl<sub>3</sub> (water with HA&BSA)

So as to get a better visual result, the next graph shows the different effectiveness that this coagulant (FeCl<sub>3</sub>) has with each organic matter. From this figure some significant results can be extracted. FeCl<sub>3</sub> has greater removal selectivity of humic acid than of albumin.

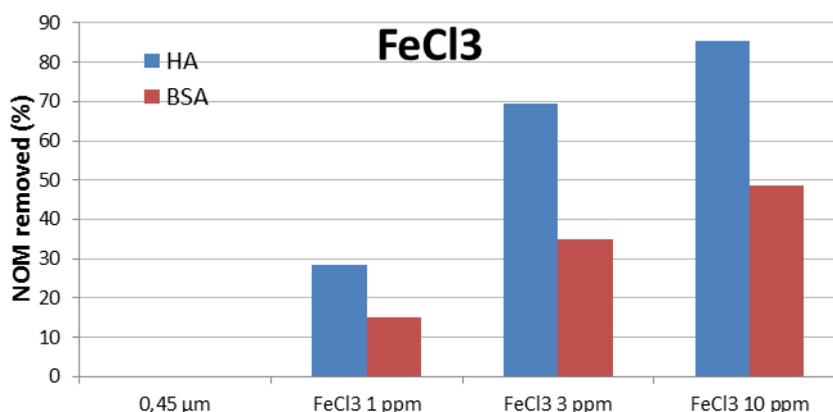


Figure 32: NOM + FeCl<sub>3</sub> (water with HA&BSA)

To show the evolution that this water has in front of this coagulant, some three-dimensional graphics are represented. On the first column, the FEEMs of fluorescence emission-excitation technique are shown. On the second column, there is the removed NOM that each experiment has eliminated.

The diagonal line that can be seen on the graphics does not interact with the results, it is only a physic phenomenon that has this technique.

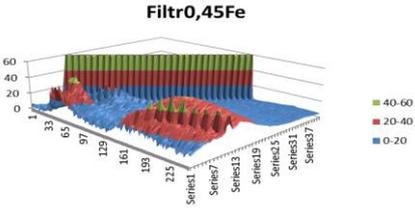
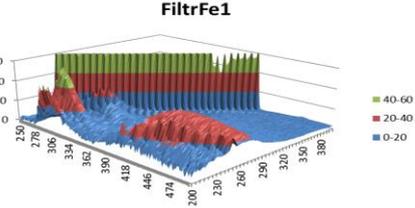
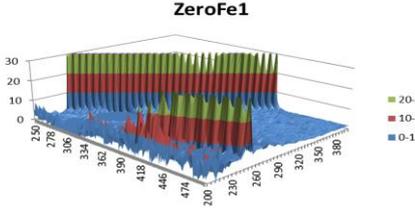
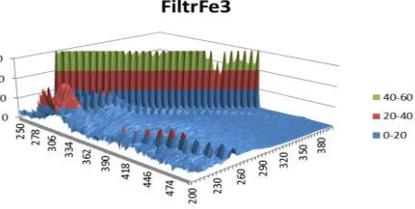
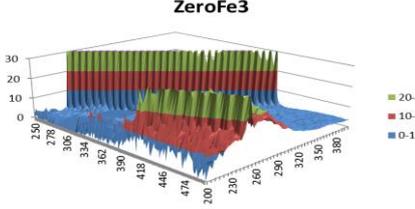
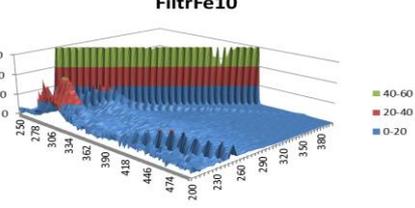
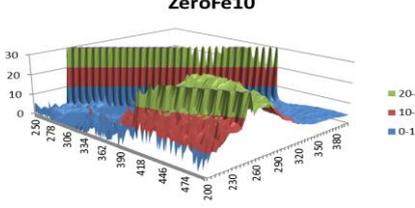
	FEEM of sample	FEEM of not coagulated sample – FEEM of sample = FEEM of organic matter removed
0,45 µm		
FeCl <sub>3</sub> 1 ppm		
FeCl <sub>3</sub> 3 ppm		
FeCl <sub>3</sub> 10 ppm		

Table 10: FEEM using FeCl<sub>3</sub>

The high areas of the graphic in the first column are equivalent to the concentration of NOM. The elevated areas decrease when the dosage of coagulant increases. This is because the NOM concentration is reduced after the vacuum filtration. These areas are formed by albumin and humic acid fluorescence.

It is easy to see on the second column that by adding FeCl<sub>3</sub>, the elevation of these areas increases. This elevation is now equivalent to the removed NOM concentration.



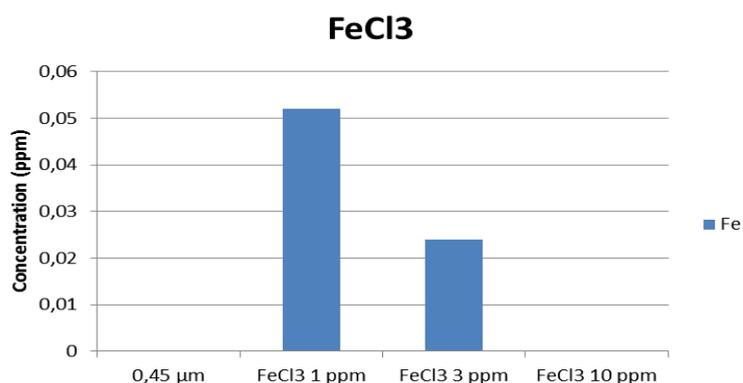


Figure 33: FeCl<sub>3</sub> concentration

This last graphic represents the concentrations of iron, equivalent to FeCl<sub>3</sub> coagulant, in the different samples. It shows an interesting tendency: when the coagulant concentration rises up, the coagulant left after filtration decreases to <0,005 ppm (colorimetric limit). This could be a great tendency, because this would mean that the permeate water has less metal concentration. Because of this unexpected tendency, these experiments should have to be corroborated doing some other tries.

#### 7.2.4. PAX18

In the following table, different parameters like NOM concentrations, absorbance and the percentages of NOM removed are represented.

	HA (ppm)	BSA (ppm)	Absorbance	HA removed (%)	BSA removed (%)
0,45 µ	16	4	0,501	0	0
PAX18 1 ppm	15,10	3,39	0,45	5,61	15,31
PAX18 3 ppm	14,80	1,97	0,3	7,47	50,75
PAX18 10 ppm	12,11	1,65	0,185	24,29	58,67

Table 11: NOM + PAX18 (water with HA&BSA)

Again, so as to get a better visual result, the next graphic shows the different effectiveness that this coagulant (PAX18) has with each organic matter. From this some significant results can be extracted. PAX18 has greater removal selectivity of albumin than of humic acid. This different tendency shows a very significant data to take into account, because this finally means that each coagulant has more affinity with a different organic matter.

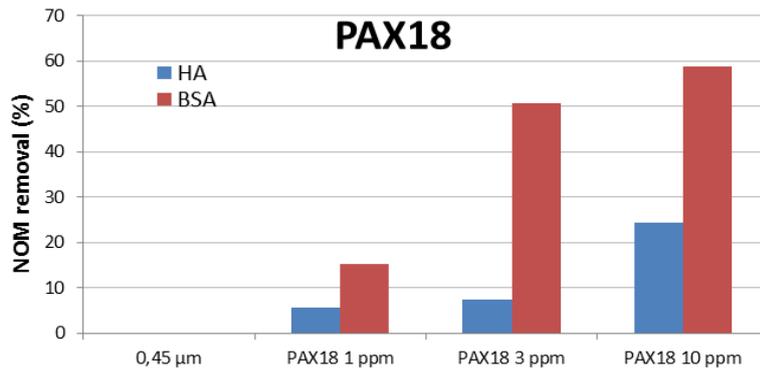


Figure 34: NOM + PAX18 (water with HA&BSA)

To show the evolution that this water has in front of this coagulant, some three-dimensional graphics are represented. On the first column, the FEEM of fluorescence emission-excitation technique are displayed. On the second column, there is the removed NOM that each experiment has eliminated.

The diagonal line that can be seen on the graphics does not interact with the results, it is only a physic phenomenon that has this technique.

	FEEM of sample	FEEM of not coagulated sample – FEEM of sample = FEEM of organic matter removed
0,45 µm		
PAX18 1 ppm		

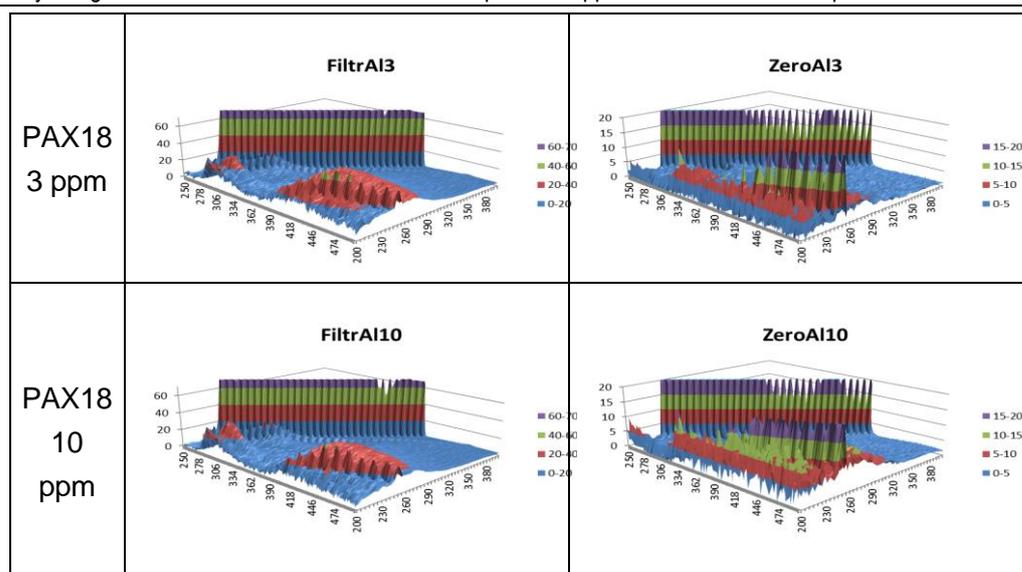


Table 12: FEEM using PAX18

There can be seen again that the elevated areas of these graphics decrease when the coagulant dosage increases. These areas are formed again by albumin and humic acid fluorescence.

The elevated areas in the graphics of the second column shows the NOM removed when PAX18 is added. With this coagulant, the decrease of the elevated areas is more difficult to. Despite this fact, with this little difference PARAFAC is able to study the reduction of the NOM.

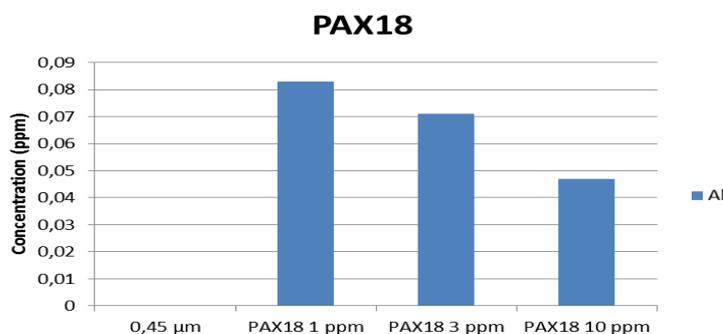


Figure 35: Al concentration

This last graphic represents the concentrations of aluminum, equivalent to PAX18 coagulant, in the different samples. It shows again an interesting tendency: when the added coagulant concentration rises up, the coagulant present after filtration decreases roughly 50%. It could be a great tendency again, because it means that the permeate water has less metal

concentration, but again, this unexpected result should have to be corroborated repeating these experiments.

### 7.3. Real water vs PAX 18 or FeCl<sub>3</sub>

Once both coagulants have been studied separately is time to study the effectiveness of coagulants in real water. This real water has been taken directly from the DWTP of Sant Joan Despí just before the ultrafiltration systems.

At this stage of the DWTP the aluminum coagulant has been already added, and because of this, only FeCl<sub>3</sub> has been added in all these analyses. Therefore, in this series of experiment the effectiveness of iron coagulant has been studied once aluminum has been added.

These results show the effectiveness that iron coagulant has versus real water and also versus simple filtration (using 0,45 µm filter). The concentration that each different NOM has on the samples and the percentages that have been removed are shown in the table below. Therefore, at this stage it is possible to compare clearly the effectiveness of the coagulant, both against real water and against a simple filtration process. These results would be able to show if the amount of NOM removed increases meaningfully when the coagulant is added in front of simple filtration. This gives again the possibility for further studies, if this increase of the NOM removed is worth.

The FEEMs that fluorescence technique has obtained are displayed bellow to show the differences between each sample. The metal concentrations are exposed too.

In the following table the NOM concentration, the absorbance and the removal percentage of each organic matter in front of different samples or coagulant concentrations are shown.

	HA (ppm)	BSA (ppm)	Absorbance	HA removed (%)	BSA removed (%)
Real water	3,7	0,4	0,331		
0,45 µm	3,45	0,382	0,328	6,71	4,30
FeCl <sub>3</sub> 1 ppm	3,27	0,383	0,288	11,74	4,12
FeCl <sub>3</sub> 3 ppm	2,99	0,382	0,26	19,23	4,53
FeCl <sub>3</sub> 5 ppm	2,79	0,380	0,242	24,65	4,80
FeCl <sub>3</sub> 10 ppm	2,57	0,379	0,235	30,66	5,17

Table 13: Real water + FeCl<sub>3</sub>

The following graphic shows the NOM concentration of the different samples of this series.

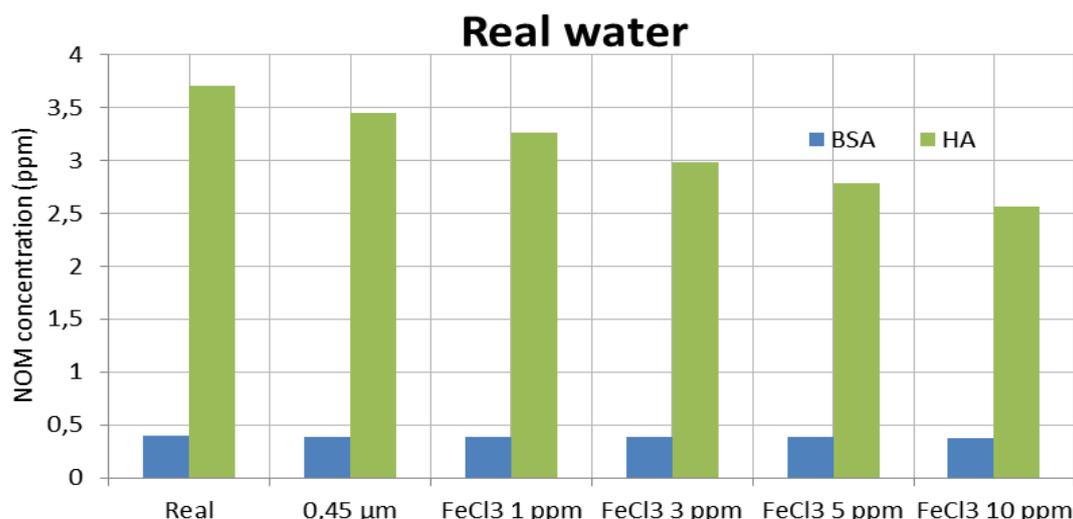


Figure 36: Real water concentrations

In this graphic it is only possible to see the evolution of the humic acid. It decreases when the iron coagulant is added. It is also true that it is not possible to see if the albumin decrease with the same percentage in this graphic, but this is studied in [FIGURE 39](#).

The last series experiment showed that iron coagulant has double effectiveness with HA than with BSA. In addition, the HA concentration is much higher than BSA so the difference is even clearer. In [FIGURE 39](#) the percentages of NOM removed are shown. The differences between simple filtration and coagulated samples can be observed. It shows that the coagulants are a great advantage against simple filtration.

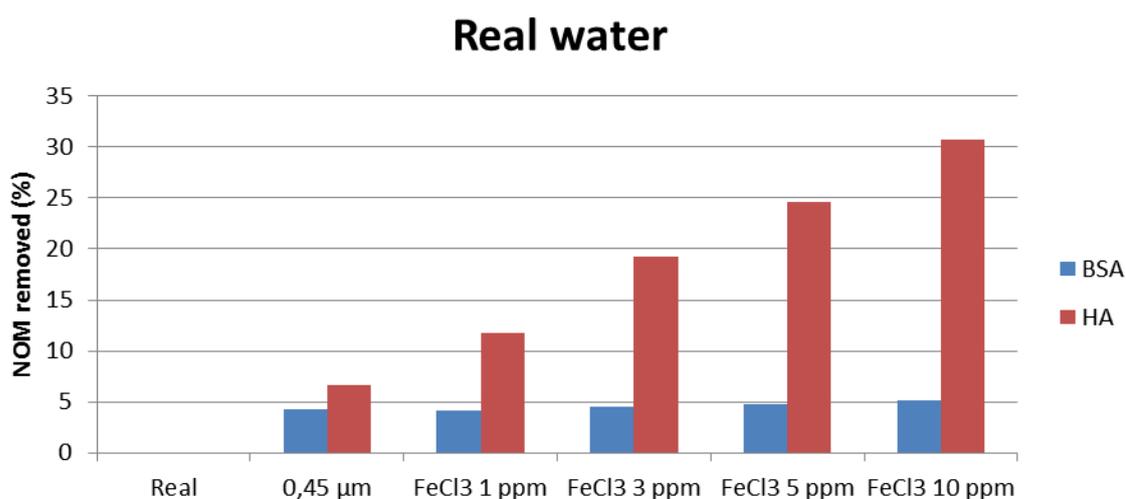


Figure 37: NOM removal in real water

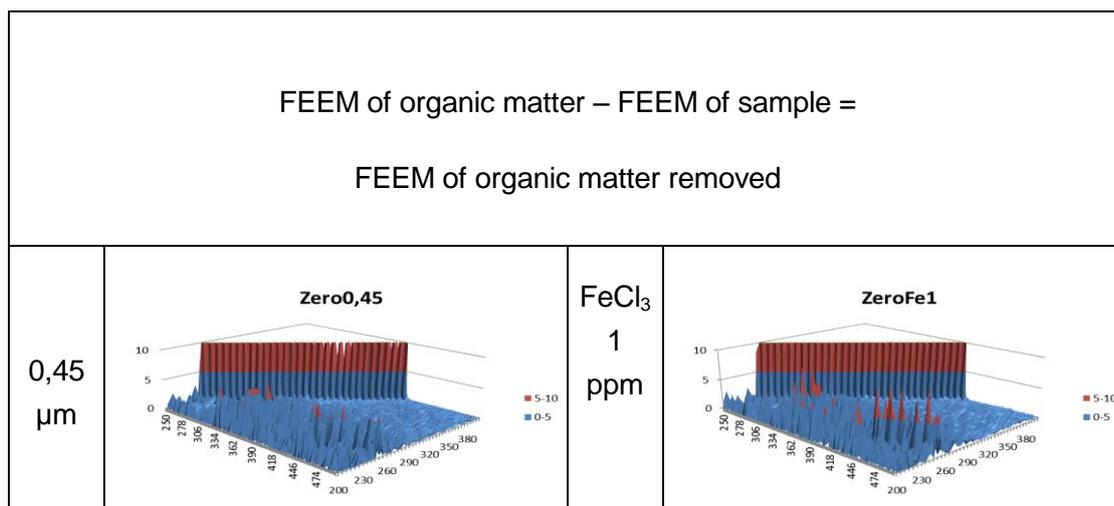
From this last graphic some interesting data can be extracted. Taking in account that these results are from the plant of Sant Joan Despí,  $\text{FeCl}_3$  has a useless effectiveness to remove BSA. This coagulant only increases less than 1 % of the BSA removal in front of simple filtration (using 0,45  $\mu\text{m}$ ).

On the other hand, the effectiveness of this coagulant with HA has a great removal percentage, increasing it near 25% of HA removal in front of simple filtration. This fact can be assumed as an important point because it helps to eliminate near a third of this organic matter.

Moreover, in such case, the time needed to do the vacuum filtration has not been a remarkable data. This filtration time has not increased as much as in the other series experiments. Here, due to the low organic matter concentration, the final coagulated compounds that iron or aluminum coagulants could do has been reduced. The coagulated compound could be both new iron colloids and old aluminum colloids that were already coagulated.

Therefore, it shows that when working with small organic matter concentrations, the removal effectiveness is reduced. On the other hand, it is important to remember that iron coagulant can also make aluminum insoluble, reducing the NOM removal effectivity as a possible consequence.

To show the analyzed data, represented on three-dimensional graphics, the organic matter that has been removed is shown on the following table. It is easy to see that the elevation of the highlighted areas is lower than in the other cases. It is because the removed NOM is lower in this case.



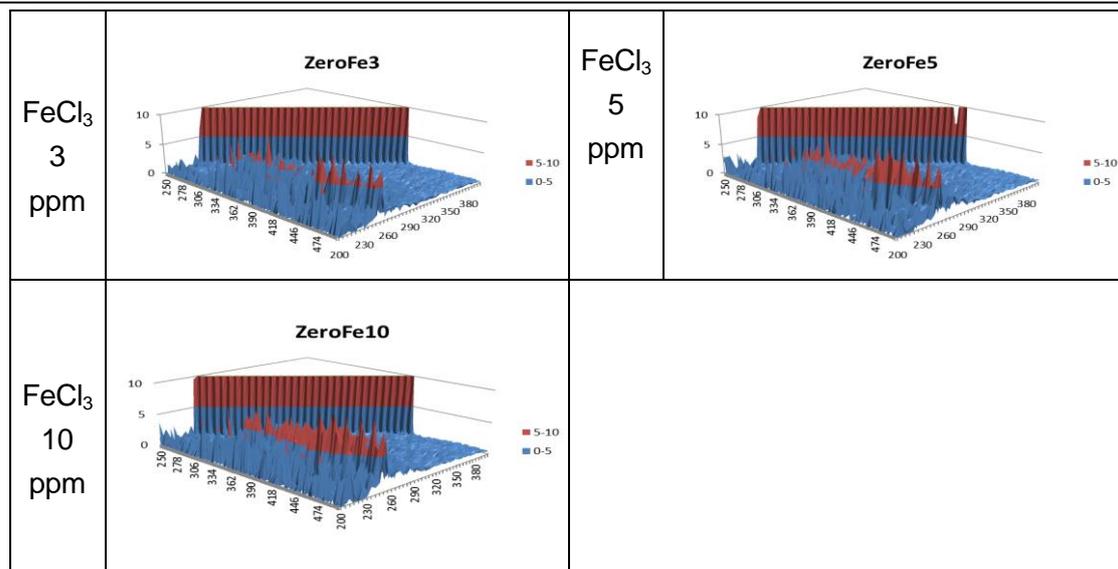


Table 14: FEEM of organic matter removed

Finally, it is shown that iron coagulant removes more organic matter when its dosage is increased. Moreover, the selectivity of this last mentioned coagulant has been demonstrated again when both HA and BSA are in the same dissolution.

Also, it is important to note that when the NOM concentration is small the fouling problems are reduced drastically. This has been observed on the filtrations times of each experiment.

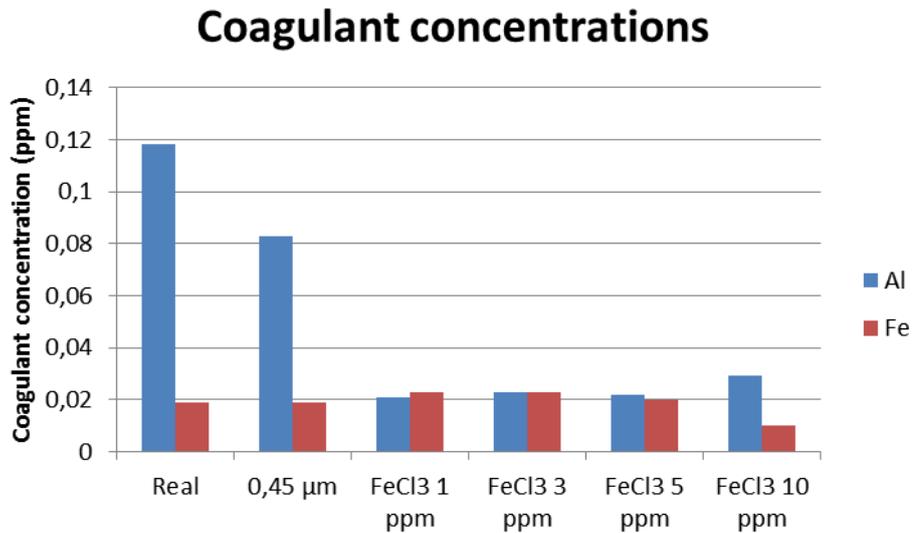


Figure 38: Coagulants concentrations

This last graphic finally shows the effectiveness of iron coagulant in front on PAX18. Here are represented the metal concentrations, which are directly associated with their coagulants concentrations. The first column is composed by aluminum added before UF and also by  $\text{FeCl}_3$  added on the pre-treatment in the DWTP in Sant Joan Despí.

It is shown that only with simple filtration de aluminum concentration decreases. This data shows how iron coagulant is able to reduce more than 80% the aluminum concentration. Iron concentration is reduced both due to the formation of aluminum complexes and to the formation of NOM colloids, which generate insoluble compounds. The aluminum concentration decreases to 30 ppb, enough to avoid a problematic fouling in RO membranes.

## 8. Schedule

In [TABLE 15](#), there is the chronology of the activities that have been carried on during this project. It is done by a Gantt diagram.

During the first weeks, some bibliographical research about the coagulation and about the DWTP in Sant Joan Despí has been done. After some weeks, the series of experiments started, increasing the level of complexity in every stage. This project includes 32 experiments, with a total of 64 samples. Besides, 7 concentrated solutions of organic matter have to be included; finally this project has a total of 71 samples.

The first series of experiments has been done to test the concentrations range that allows to work according to the techniques working ranges. Once the concentrations ranges have been determined, the experiments continued its development, step by step, ending with a coagulation test with real water from DWTP.

Once all the samples have been analyzed and treated by mathematical methods, the results have been analyzed and collected on this project.

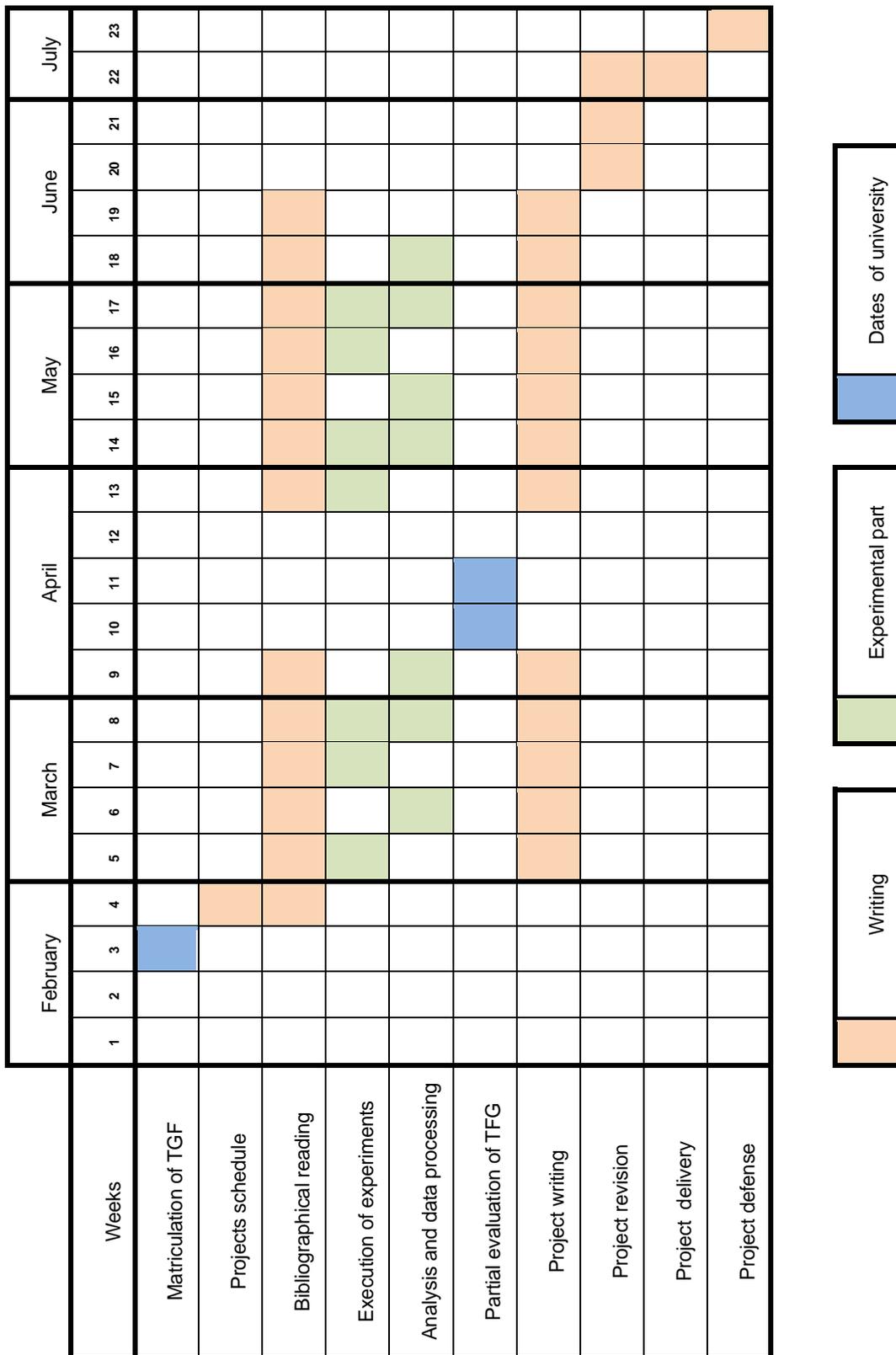


Table 15: Gantt diagram

## 9. Costs of the project

The economic evaluation of this project can be splitted into materials and humans resources.

### 9.1. Material resources

Material resources includes a wide category of items such as all chemicals consumed during the project, laboratory equipment and devices needed for the successful performance of all tasks of the project, and utility services such as water are detailed in [TABLE 16](#).

Reactive	Concept	Quantity	Price	Cost
Humic acid	Dissolution	0,4 g	50€/kg	0,02 €
Albumin	Dissolution	1 g	96€/kg	0,10 €
MgCl <sub>2</sub>	Dissolution	4,16 g	70€/kg	0,29 €
CaCO <sub>3</sub>	Dissolution	4,84 g	1€/kg	0,01€
Na(HCO <sub>3</sub> )	Dissolution	4,44 g	35€/kg	0,16€
HCl	pH control	60 cm <sup>3</sup>	12€/L	0,72 €
NaOH	pH control	5 cm <sup>3</sup>	15€/L	0,08 €
Milli-Q	Dissolutions and cleaning	23 L	1,1 €/L	25,30 €
Deionized water	Cleaning	32 L	1 €/L	32 €
Tap water	Cleaning	128 L	1,8 €/m <sup>3</sup>	0,28 €
0,45 µm filters	Vacuum filtration	46	120 €/100	55,20 €
Pasteur pipets	-	16	1 €/625 pipets	0,03 €
Latex gloves	-	7 pairs	5 €/100 gloves	0,70 €
Parafilm	-	1	12€/u	12 €
Dropper pipets	-	14	12€/100	1,68 €
Volumetric flask 3 dm <sup>3</sup>	-	1	38€/u	38 €
Volumetric flask 1 dm <sup>3</sup>	-	1	17,50€/u	17,50 €
Volumetric flask 0,5 dm <sup>3</sup>	-	1	12,5€/u	12,50 €
Volumetric flask 0,1 dm <sup>3</sup>	-	1	3,35€/u	3,55 €
Volumetric flask 50 cm <sup>3</sup>	-	1	2,55€/u	2,55 €
Beakers 1 dm <sup>3</sup>	-	3	5,25€/u	15,75 €
Beakers 0,1 dm <sup>3</sup>	-	5	2,5€/u	12,50 €
Funnel	-	1	5,30 €/u	5,30 €
Sitters magnets	-	3	3,29 €/u	9,87 €
TOTAL				246,09 €

Table 16:Material resources

When an equipment resource is purchased, amortization must be calculated and the costs associated to the project quantified following [EQUATION 5](#).

$$\text{Amortization} = \frac{\text{AcquisitionCost}}{\text{UsefulLife}} * \text{UsedTime} \quad (\text{Equation 5})$$

Some equipment such as balance, pH meter, conducti meter are considered amortized.

Equipment	Price	Useful life	Quantity	Used time	Cost
Vacuum machine	599 €	2 years	1	20 days	16,41 €
Micropipette 0,1-10 cm <sup>3</sup>	160 €	2 years	1	30 days	2,03 €
Vacuum material	300 €	2 years	1	20 days	8,22 €
Stir plate	1200 €	5 years	1	30 days	19,72 €
TOTAL					46,65 €

Table 17: Amortized material

## 9.2. Human resources

Human resources include all people, including laboratory services, which have taken part in some way in the project. [TABLE 18](#) provides costs associated to laboratory analyses.

Analyzes	Quantity	Price	Cost
ICP	16	15 €/analyze	240 €
Absorbance	50	1,20 €/analyze	60 €
TOC	50	18,80 €/analyze	940 €
Fluorescence	50	8 €/analyze	400 €
Colorimetry	8	2,25 €/analyze	18 €
TOTAL			1658 €

Table 18: Analyzes costs

[TABLE 19](#) gives costs associated to personal involved in the execution of the project tasks, mostly the practicum student (responsible for the bibliographic research, the design and the performance of the experiments, the interpretation of results, and the thesis writing) assisted

when required by the supervisor of university. The unit costs of the practicum student is based on the “*Federació Empresarial de la Indústria Química Espanyola*” guidelines and is fixed at 10€/hour. The people who has correct the thesis and did the data analyses have a superior university degree and the last mentioned guidelines fix its minimum at 20 €/hour, the fix price/hour is the double.

Analyzes	Quantity (h)	Price	Cost
Bibliographic research	95	10	950 €
Experimentation	95	10	950 €
Data analyze	65	40	2600 €
Data treatment	50	10	500 €
Thesis writing	252	10	2520 €
Thesis correction	45	40	1800 €
TOTAL			9320 €

Table 19: Personal costs

The overall costs of the project, based on the previous calculation, can be summarized as shown in [TABLE 20](#).

Concept	Cost
Materials and analyzes costs	1950,74 €
Personal cost	9320 €
IVA	2366,86 €
TOTAL	13637,60 €

Table 20: Total costs

In total the cost of this project rises up to **13 637,60 €**.

## 10. Environmental impact

This project consists of a series of experiments in a laboratory scale. Therefore, the environmental impact is only based on the tasks needed to do the experiments.

### 10.1. Environment

This project has been carried out entirely in the laboratories of Chemical Department from ETSEIB (UPC). These installations have been used for 4 months. The levels of the environmental quality in the near areas have not changed much as a result of the experiments.

### 10.2. Identification and actuation of environmental impacts

During the project, care has had to be taken into account during the experiments in the laboratory. For instance, all the metal dissolutions have to be carefully put into special residual bottles and all the acid/basic solutions poured into another special bottle. Also, when working in a laboratory, responsible behaviour is needed when using all the resources such as water, electricity and raw material.

Although the real aim of the project has a strong link with the improvement of the environmental impact, the carrying out of this project has both negative and positive impacts. It uses natural resources and does some residual compound. But on the other hand, it creates a positive impact, improving the understanding of the water treatment processes.

## Conclusions

The conclusions of this project could be described from different points of view, the first of them is the interaction of coagulants when the organic matter is dissolved. The interaction that these compounds have with the most components in DWTP of Sant Joan Despí has showed that it is possible to reduce significantly the organic concentrations. It has also shown that the insoluble colloids that are formed obstruct the membrane reducing the flow rate of the membranes.

It has shown that  $\text{FeCl}_3$  coagulant has a great effectiveness to reduce organic matter in water, but the infrastructure of Sant Joan Despí plant does not allow the use of  $\text{FeCl}_3$ . PAX18 coagulant, used in Sant Joan Despí plant, also presents a good behavior in front these organic matters.

When doing the experiments with only one coagulant and only one NOM, the result is that the coagulants have a saturation point where its effectiveness does not increase by adding more coagulant, but at least it is not reduced. This shows that dosage has to be set before the saturation point, because a dosage increase would not mean a better effectiveness. But on the contrary, the global cost of the filtration would increase, and also the membranes could have faster fouling problems.

As a second point, it is important to remark that each coagulant has a different selectivity.  $\text{FeCl}_3$  has a better behavior with humic acid, making more insoluble compounds of this organic matter, thing that it is necessary to remove during the filtration. On the other hand, it has been tested that PAX18 has a better behavior with BSA.

The results have showed that these coagulants help to reduce these organic matters in a different way. This selectivity could come from the molecular weight differences that exist with these two organic matters.

When a high concentration of NOM (20 ppm) is used, the high effectiveness of the coagulants make a lot of insoluble colloids that block the membranes and reduce the flow rate. This conclusion has been extracted after a long time needed to do the vacuum filtration. It is an important conclusion, which could show that the removal of NOM using a micro-coagulation before UF could damage the membranes dangerously. It is important to

note that if this organic condition is reproduced on DWTP it could become an important fouling problem.

Also, there has been an unexpected tendency when the coagulant concentration has been increased in the experiments. The metal concentrations, which remain once the Jar-test and vacuum filtration have been done, decrease while the concentrations of coagulant added increase. It could mean that the coagulants have an auto-coagulating behavior and helps each other to interact with the NOM. This could also mean that the residual metal in the permeate water could have a minimum value. This minimum could be possible because it is known that by increasing the dosage of coagulant, at the end, the remaining metal concentration in permeate water increases. This could be a new thing to study, but first of all this series of experiments should be repeated to corroborate this unexpected tendency.

Finally, the last point this project has dealt with is the organic effectiveness of micro-filtration before UF membranes in DWTP in Sant Joan Despí. This has been studied in the last series of experiments. These experiments have shown some data that can get to a conclusion. That is, that the effectiveness of the coagulants is reduced while the concentration of NOM is reduced, because with the same concentration the removal effectiveness of  $\text{FeCl}_3$  goes down from 50% to 30%. This decline is also because the aluminum coagulates with iron.

The effectiveness that  $\text{FeCl}_3$  has to remove NOM, once PAX18 is added, is not negligible. This could reduce considerably the fouling problems that RO membranes could have.

Another part of the study is that: PAX18, added on the water before UF filtration, interacts with  $\text{FeCl}_3$ . It reduces the iron coagulant concentration, which consequently reduces its power to remove NOM. The interaction of  $\text{FeCl}_3$  with PAX18 means that the purpose of reducing aluminum concentration using iron coagulants works, reducing more than 80% its concentration with only 1 ppm of  $\text{FeCl}_3$ . Finally, the aluminum concentration decreases to 30 ppb, a value under the problematic limit of 50 ppb that could cause a harmful damage to RO membranes.

It is also important to conclude that the fouling problems that showed the other series of experiments have been minimized, at least from a general point of view, because the time to do vacuum filtration has not been as long as other stages.

To conclude,  $\text{FeCl}_3$  has a good effectiveness with aluminum coagulant, reducing significantly its concentration and reducing the possible damage to RO membranes. Also, that the fouling problems decrease when the NOM concentration is small. And finally, that  $\text{FeCl}_3$  also helps to remove part of NOM that PAX18 has not been able to make insoluble.



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## Bibliography

**Aigües de Barcelona** [www.aiguesdebarcelona.cat](http://www.aiguesdebarcelona.cat) [Online]. - March 9, 2015. - <http://www.aiguesdebarcelona.cat/documents/10540/21743/monograf%C3%ADa.pdf/cd3f9d97-4d40-4a55-801f-f62695e790b3>.

**Al-Amoudi Saleh A.** Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: A review [Journal] // Desalination. - [s.l.] : Desalination, 2010. - Vol. 259. - pp. 1-10.

**Aoustina E. Schäfera A.I, Fanea A.G. , Waiteb T.D.** Ultrafiltration of natural organic matter [Journal] // Separation and Purification Technology. - [s.l.] : Separation and Purification Technology, 2001. - Vols. 22-23. - pp. 63-71.

**B.V. Lenntech** Iron and water [Online]// Lanntech. - March 20, 2015. - <http://www.lenntech.com/periodic/water/iron/iron-and-water.htm#ixzz3VljkwiCX>.

**Consultora de Aguas** Consultora de Aguas [Online]. - March 29, 2015. - [http://www.cdaguas.com.ar/pdf/aguas/14\\_Ensayo\\_de\\_coagulacion.pdf](http://www.cdaguas.com.ar/pdf/aguas/14_Ensayo_de_coagulacion.pdf).

**Edzwald David J. Pernitsky and James K.** Selection of alum and polualuminum coagulants: principles and applications. [Journal] // Journal of Water Supply: Research and Technology-AQUA. - [s.l.] : AQUA, 2006. - Vol. 55.2. - pp. 121-141.

**F. Hans-Curt** Reverse Osmosis Membrane Biofouling [Journal] // Experimental Thermal and Fluid Science 1997. - [s.l.] : Experimental Thermal and Fluid Science, 1996. - Vol. 14. - pp. 382-391.

**Genesys International** Genesys International [Online]. - March 25, 2015. - <http://www.genesysro.com/ro-membrane-antiscalant-cleaning-chemicals.php>.

**J. Glater** The early history of reverse osmosis membrane development [Journal] // Desalination. - [s.l.] : Desalination, 1998. - Vol. 117. - pp. 297-308.

**Jermann D. Pronk W., Meylan S., Boller M.** Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production [Revista] // Water Research. - [s.l.] : Water Research, April 2007. - Vol. 41. - p. 1713-1722.

**Kathleen R. Colin A., Graeber D. and Brod R.** Fluorescence spectroscopy and multi-way techniques [Journal] // Analytical Methods. - [s.l.] : Analytical Methods, 2013. - Vol. 23. - pp. 6541–6882.

**Lenntech B.V** Lenntech [Online]. - March 20, 2015. - <http://www.lenntech.es/periodica/elementos/al.htm>.

**OXY OCCIDENTAL CHEMICAL CHILE LIMITADA** MANUAL CLORURO FÉRRICO. - Providencia : [s.n.].

**Peiris RH. Ignagni N., Budman H., Moresoli C., Legge RL.** Characterizing natural colloidal/particulate-protein interactions using fluorescence-based techniques and principal component analysis. [Journal] // Talanta vol 99. - [s.l.] : Talanta, 2012. - Vol. 99. - pp. 457-463.

**Petros K. Dimitra Ch., Efrosini N. , Anastasios I. and Petros E.** Fouling Issues in Membrane Bioreactors (MBRs) for Wastewater Treatment: Major Mechanisms, Prevention and Control Strategies. [Journal]. - [s.l.] : Processes, 2014. - Vol. 2. - pp. 795-866.

**Sheng G.P., Yu H.Q. and Li X.Y.** Extracellular polymeric substances (EPS) of microbial aggregates in biological wastewater treatment systems: A review [Journal]. - [s.l.] : Biotechnol, 2010. - Vol. 20. - pp. 882–894.

**Shu-xuana D. Huia X., Fenga X., Dong-shenga W., Chang-qingb Y.** Effects of Al species on coagulation efficiency, residual Al and floc properties in surface water treatment [Journal] // Colloids and Surfaces A: Physicochemical and Engineering Aspects. - 2014. - Vol. 459. - pp. 14-21.