João Luciano Amorim Azevedo

# Sugar decolorization - strategies and solutions

Master’s Thesis Project in the scientific area of Chemical Engineering, Supervised by:

Professor Doctor Maria da Graça Bomtempo Vaz Rasteiro, Dr. Julien Arnold (AquaTech)

and Dr. José A. F. Gamelas, and submitted to the Department of Chemical Engineering, Faculty of Science and

Technology of the University of Coimbra

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UNIVERSIDADE DE COIMBRA

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Prof. Dr. Maria da Graça B. V. Rasteiro
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In collaboration with AquaTECH (Switzerland) and RAR (Portugal)

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***“We must accept finite disappointment, but never loose infinite hope.”***

*Martin Luther King Jr*

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Life is a constant pursuit for growth and for fulfillment, and the times we call “student life” is one of the most beautiful stages of someone’s life, for in this period we have open minds, in search for knowledge and for a definition for our lives and, at the same Time, our hearts guide us with the strong flame of hope. I have dreamed a lot and, as life is, had days and nights, fears and times we think about giving up facing the difficulties, but I loved the study and the science field in general, and so, my life in Coimbra provided me much joy and also knowledge, guided by few Professors, who fulfilled my desire for knowledge and consolidated my love for Chemical Engineering, and some other people helped me to keep going and see life as a set of different cultures, objectives and hopes. For that, I want here to express my deepest gratitude and recognition to all of you, but can only name a few.

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# Abstract

Sugar industry comprises mainly of two products: raw and refined sugar. The second one is the most required by the market and consumers, as the requirement for a better quality product for a lower cost and environmental impact is a constant. Refining sugar is a process which main objective is to remove impurities, which normally are related to color compounds, from sucrose. This work was focused in the sugar refining process, more specifically in the color removal by means of precipitation of color compounds from sugar solution in order to separate such compounds by physical means like filtration or clarification. Based on the actual scenario and information obtained in the literature, the study was conducted guided by the use of cationic polymers as color precipitants through flocculation. The study comprises three steps: first is a characterization of the polymers supplied by AquaTech Switzerland, using optical methods, dynamic and static light scattering, to characterize the size and the molecular weight, and electrophoretic light scattering, for zeta potential of the polymers. As second part of the work the laboratorial decolorization tests were conducted in sugar carbonated liquor, supplied by RAR Portugal, testing the different polymers at different dosages, in conditions, pH and temperature, similar to that of the second stage of saturation in carbonatation process, and measuring the decolorization achieved by the treatment with each polymer, following the ICUMSA 420 color characterization method; as third and last part of the work continuous monitoring of flocculation process was performed by using laser diffraction spectroscopy, as technique for following the flocculation kinetics, this way to search for evidences of the flocculation performed by the polymers selected after the laboratorial tests. The study was performed using polymers individually and trying blends of two or three different polymers. Conclusions were that the decolorization achieved was good, reaching levels of 41% of additional color removal over carbonated sugar liquor, in the case of Amber 2009, and Amber2001HMW, Amber 2013 and Amber MetQuat 6, all in the range of 30-40% of decolorization, proving that cationic flocculants are effective decolorization agents when used along the carbonatation process, at pH 8-8.5. The polymer performance is related to its characteristics, needing to perform further studies to find a balance for molecular weight, size of polymer chain and charge to find the most suitable relations in order to achieve the best performance. LDS is used for first time to follow the flocculation kinetics in carbonated sugar liquor using cationic polymers flocculants, and it has proven to be a good tool for monitoring and study performance of the flocculation and the stability of the flocs in the system.

**Key-words:** Sugar Refining, Carbonatation, Color Removal, Cationic Polymer Flocculation, Laser Diffraction Spectroscopy, Light Scattering Spectroscopy.

# Resumo

A indústria do açúcar consiste principalmente em dois produtos: açúcar bruto e refinado. O segundo é o mais procurado pelo mercado e pelos consumidores finais, sendo que a necessidade por um produto de melhor qualidade, por menor custo e impacto ambiental é uma constante. Refinar açúcar é um processo cujo objetivo principal é remover impurezas, que geralmente estão relacionadas a compostos corados, da sacarose. Este trabalho foi focado no processo de refinamento do açúcar, mais especificamente na remoção da cor por meio da precipitação de compostos corados da solução de açúcar, para, então, separar tais compostos por meios físicos, como a filtração ou clarificação. Com base no cenário atual e na informação obtida na literatura, o estudo foi conduzido guiado pelo uso de polímeros catiónicos como agentes precipitantes por meio de floculação. O estudo compreende três etapas: a primeira é uma caracterização dos polímeros fornecidos pela AquaTech Suíça, utilizando métodos óticos, dispersão de luz dinâmica e estática, para caracterizar o tamanho e peso molecular, e dispersão de luz eletroforética para determinar o potencial zeta dos polímeros. A segunda parte do trabalho foi realizada em licor carbonatado de açúcar bruto, fornecido pela RAR Portugal, e assim testando os diferentes polímeros a diferentes dosagens e em condições, pH e temperatura, semelhantes às da segunda fase de saturação no processo de carbonatação e, após a floculação, medindo a descoloração atingida seguindo o método ICUMSA 420 de caracterização de cores de soluções de açúcar; A terceira e a última parte do trabalho foi o monitoramento contínuo do processo de floculação, utilizando a espectroscopia de difração a laser, para o acompanhamento da cinética de floculação, buscando evidências da floculação realizada pelos polímeros selecionados após os testes laboratoriais. O estudo foi realizado usando polímeros individualmente e testando também misturas de dois ou três destes polímeros. As conclusões foram que a descoloração alcançada foi boa, alcançando-se níveis de 41% de remoção de cor adicional sobre o licor de açúcar carbonatado, no caso de Amber 2009 e, no caso do Amber2001HMW, Amber 2013 e Amber MetQuat 6, alcançando níveis de 30-40% de Decoloração, provando que os floculantes catiónicos são agentes de descoloração eficazes quando utilizados ao longo do processo de carbonatação, a pH 8-8,5. O desempenho do polímero está relacionado às suas características, necessitando de mais estudos para encontrar o equilíbrio do peso molecular, tamanho da cadeia de polímero e carga para encontrar as dosagens mais adequadas para alcançar o melhor desempenho. O LDS é uma boa ferramenta para monitorar e estudar a floculação em licor de açúcar carbonatado diluído.

**Palavras-chave:** Refinamento De Açúcar, Carbonatação, Remoção De Cor, Floculação e Polímeros Catiónico, Espectroscopia De Difração Laser, Espectroscopia De Dispersão Da Luz.

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# Nomenclature

| | |
|---|---|
| **$\lambda_0$** | Laser Wavelength |
| **$\mu$** | Dynamic Viscosity |
| **$\varepsilon$** | Dielectric constant |
| **$A_2$** | 2nd Virial Coeficient |
| **C** | concentration |
| **$D_c$** | Translational diffusion coefficient |
| **$D_h$** | Hydrodynamic Diameter |
| **$D_i$** | Hydrodynamic Diameter of Class i |
| **$D_z$** | Average Diameter of the Size Distribution |
| **DLS** | Dynamic Light Scattering |
| **dn/dc** | Differential Refractive Index Increment |
| **ELS** | Electrophoretic Light Scattering |
| **HMW** | High Molecular Weight |
| **$I_A$** | Residual Scattering Intensity of the Analyte |
| **ICUMSA** | International Commission for Uniform Methods for Sugar Analyses |
| **$I_i$** | Scattered Light Intensity of Class i |
| **$I_T$** | Toluene Scattering Intensity |
| **IU** | ICUMSA color Unit |
| **IV** | Index Value |
| **K** | Optical Constant |
| **k** | Boltzmann Constant |
| **LDV** | Laser Doppler Velocimetry |
| **MMW** | Medium Molecular Weight |
| **MW** | Molecular Weight |
| **$N_A$** | Avogadro's Constant |
| **$n_o$** | Solvent Refractive Index |
| **$n_T$** | Toluene Refractive Index |
| **NaCl** | Sodium Chloride |
| **$P_\theta$** | Angular Dependence of the Scattering Intensity |

| | |
|---|---|
| **DADMAC** | Dially Dimethyl Ammonium Chloride |
| **$R_{\theta\_}$** | Rayleigh Ratio |
| **$R_T$** | Rayleigh Ratio of Toluene |
| **RI** | Refractive Index |
| **SLS** | Static Light Scattering |
| **T** | Absolute Temperature |
| **$U_E$** | Electrophoretic Mobility |
| **ZNS** | Zetasizer Nano Series |
| **Z** | Zeta Potential |

# Chapter 1. Introduction

Sugar industry is one of the oldest in the industrial panorama. It had a very important role to play in the development of that which is called the New World, the Americas, and being also very relevant in the scenery of European history, and especially for Portugal itself, during the age of Discovery and mercantilism. According to the sugar history, the cane sugar is originally from India and the southern Asia, where the sugar cane plant comes from and also where it has been first processed to produce the crystals obtained from the sugar cane juice[1]. Centuries later it meets its largest production expansion, in the early 16th century, with the large developments of the sugar mills, when sugar cane became one of the most important luxury commodities to be commercialized in the world, and Portugal at this time became the strongest sugar producer and exporter throughout all Europe. The sugar world production had then a high jump, due mainly to the new American colonies where the sugar cane found favorable conditions of climate and soils to develop its culture, promoting economic development and settling, this way, the age of the new world and the slave system in the world.

Till nowadays sugar is still of great importance for the economy in many Countries around the World. It plays a very important role in the food industry either as a direct consumer product or as raw material for other industries, most of which require high purity white sugar.

The commodity that we call sugar in the everyday language is in truth the chemical compound known as sucrose, a disaccharide formed by the bond of one molecule of glucose with a molecule o fructose. But not only, there is, even if in very small amounts, a very complex mixture of other chemicals in the commercial sugar, most of which are related to the color of the sugar. Sucrose itself is a colorless compound, and the sugar market is mainly divided into raw sugar, produced in the sugar mills and which has a high color index, and refined, or white, sugar [2]. By that relation between color and the purity of sugar, the color removal process plays a very important role in the sugar refining process. In truth the color removal is the main cost and the main goal of a sugar refinery. This way the removal of colored impurities is a major effort of the sugar refineries intending to produce the highest purity product required by the large market but taking into account economic and environmental aspects.

This work objective is centered into the refining process of sugar, mainly in the use of polyelectrolytes as color removal agents that act by flocculation, to enhance the color removal in the refining process with the aim of reducing costs with chemicals and energy, taking into account also environmental issues.

Many studies have been performed in the past decades in the use of polymers flocculants as color removal agents in various different industrial fields, especially in the water treatment and food industry [3]. The use of those materials have been also studied in the sugar industry, both in the raw and refining sugar processes, where it can be observed that the use of these flocculants as color removal agents can really enhance the removal of color compounds in sugar processing.

From the perspective of this work, the starting material is raw sugar, which has a large grade of products, depending on the geographical area, season of the year, the process through which it is produced, among others factors. Thereby the composition of the raw sugar can vary significantly.

The objective of this work is to evaluate the performance of a few novel cationic polymers, provided by AquaTech Switzerland, as flocculants color removal agents in carbonatation process sugar liquor, provided by RAR Portugal, through three main procedures, namely:

1) characterization of the polymers used in the tests;
2) laboratory trials on color removal flocculation;
3) Online flocculation monitoring by laser diffraction spectroscopy, to evaluate the kinetics of flocculation.

This dissertation is then divided into five chapters, as following:

- Chapter one: introduction and main objectives of the work, giving a first view of the problem of color in sugar industry and the importance of finding a suitable solution for that;
- Chapter two: in this an attempt to summarize the technology of color removal in the sugar industry, as well a brief description of sugar refining process, presenting information on previous studies conducted in this subject;
- Chapter three: describes the materials used in the study as well as the methodology and technics through the study was conducted;
- Chapter four: presents the results achieved in this work;

- Chapter five: here the main conclusions reached with the present work are presented, along with a perspective of new directions and complementary studies to be conducted in future works.

# Chapter 2. State of the Art

In this chapter I will try to explain how sugar is processed, its impurities content, how they can be removed, and finally the use of polymers in the sugar industry as mean to promote separations and color and impurities removal throughout the process of refining.

## 2.1 Sugar refining

The process to obtain white sugar from raw sugar is called refining, and it has the objective of removing impurities and colored compounds from the sugar, aiming to achieve a product of as near as possible of 100% purity of sucrose. This process is mainly comprised of a set of unit operations, where the backbone is the clarification and color removal stages, and the specific conditions on which these operations are to be performed depend on the quality and characteristics of the raw sugar to be processed. However, usually the refining process is performed as described in the following block diagram [4]:

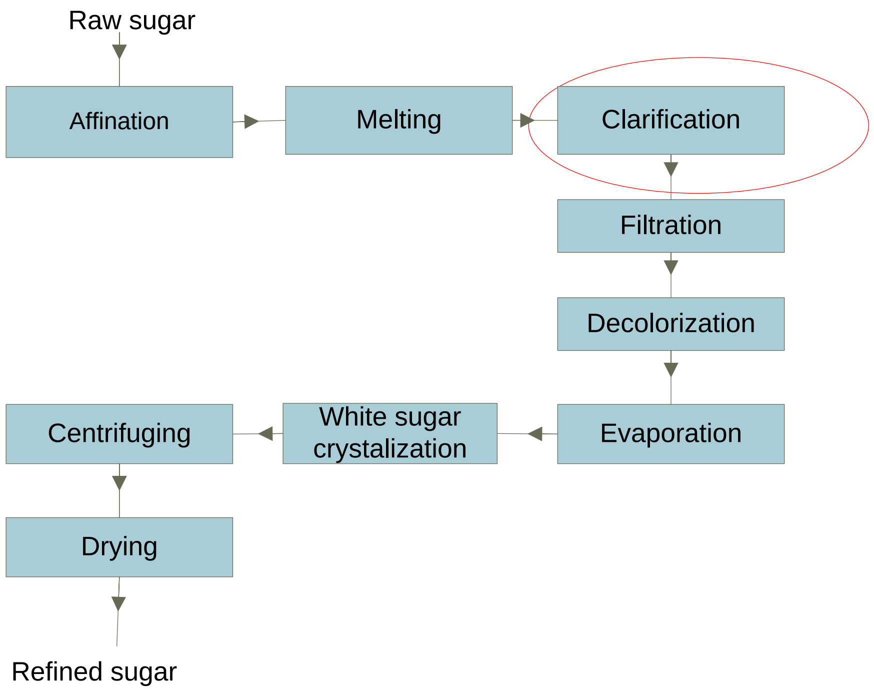


*Figure 2.1: Block diagram representation of sugar refining process. [4]*

## 2.2 Colorants in sugar

The term “Color” in sugar industry is commonly used to refer to a wide range of components that contribute to give color to the sugar. Sucrose, as mentioned before, is colorless although, as it is a natural product, there is a complex mixture of compounds associated with sucrose when extracted from cane, being those compounds associated with color themselves, originated in the cane itself, or acting as precursors of colored compounds formed while processing the sugar. The last ones are the most undesirable impurities in cane sugar production, and the removal of such materials from the sugar is the main goal in order to produce a high quality white sugar [2].

Extensive research in order to identify and characterize those compounds have been performed internationally, so better procedures to remove and avoid their formation could be proposed and tested. Following will be given a brief description of those compounds, dividing it into two main categories: natural colorants- present in the cane itself; and those known as hexose degradation products, formed during the sugar production.

### 2.2.1 Natural colorants

Sugar cane contains plant pigments, and those are present in the juice after milling, some are colored, Chlorophylls and carotenes, others will suffer reactions after milling to form colored compound. Those pigments are mainly phenolics and flavonoids, and they represent up to two thirds of the color present in raw sugar [3]. The phenolic compounds are in general colorless but are oxidized or react with amine or iron forming colorants during the process. The flavonoids are polyphenols present in the cane plant and they suffer enzymatic browning reactions. Those compounds are well removed during clarification or carbonatation, but can also be incorporated into the sugar crystals.

### 2.2.2 Colorants formed during sugar processing.

Many colorants can be formed during sugar processing, either in sugar mills or during the refining process, being those compounds formed from precursors molecules present in the sugar cane that undergo a complex range of reactions to form the colored compounds. In addition to that, the degradation of hexoses, during the process due to high or low pH and temperature conditions, and enhanced by the presence of amino and inorganic compounds in sugar liquors, can lead to degradation products of the hexoses, which are highly colored compounds. Furthermore, sucrose can be hydrolyzed to form inverted sugars, glucose and fructose, which also can be degraded forming highly reactive compounds which can go further reactions to form high molecular mass colored compounds. There are four main types of colored products that can be distinguished depending on the mechanism by which they are formed [4, 5]:

- **Melanins:** those colorants are the result of the enzymatic oxidation, or enzymatic browning, of the phenolic compounds originally present in the sugar cane. These compounds can be formed at temperatures from -18ºC to 55ºC and a pH range from 4.5 to 8 [4]. The formation of melanins is higher during the milling stage, after which it can be stopped, due to the denaturation of the enzymes at the higher temperatures of following stages of the process.
- **Melanoidins:** produced by the condensation reaction between compounds having in its chemical structure carbonyl groups and those having amino groups. In sugar solutions the presence of inverted sugars is the main source of carbonyl compounds while amino groups are related with the presence of proteins, amino acids and ammonia, etc. those are high molecular mass compounds, with intense color.
- **Caramels:** it is the product of the thermal degradation of sucrose, comprising low anionic charge compounds, having high molecular weight that increases with time and temperature as a result of increasing polymerization degree, giving highly colored compounds. Normally, caramel formation is slow and occurs at temperatures normally much higher than those at which the process is performed, although it can happen due to contact with higher temperatures or be catalyzed by inorganic compounds and other sub products of inverted sugars;
- **Hexose Alkaline Degradation Products (HADP):** those are polymeric brownish yellow compounds formed by the decomposition of monosaccharides in alkaline conditions.

The following table (Table 2.1) summarizes the main color compounds present in sugar process [4].

*Table 2-1: Type of sugar colorants present in sugar [4].*

| | **Sugarcane colorants** | **HDAP** | **Melanin** | **Melanoidins** | **Caramels** |
|---|---|---|---|---|---|
| **Molecular Mass** | Monomeric, <1200 | Intermediate <10000 | Very high, >250000 | Polymeric, >10000 | Polymeric, >10000 |
| *Origin* | Flavonoids and other phenolics from cane stalk. Iron complexes with phenols | Reactions of hexoses at high pH (>8.0) | Enzymatic browning of phenols and reactions with amino acids. | In the process by reactions involving amino acids and inverted sugars. | Thermal decomposition of sucrose at high temperatures. |
| **Degree of ionization** | Ionized at high pH and neutral at Low pH's | Cationic below pH 5, anionic above pH 6. | Anionic | Cationic below pH 5, anionic above pH 6. | Slightly charged. |

## 2.3 Measurement of color in sugar

Color in sugar products is usually measured according to the International Commission for Uniform Methods for Sugar Analyses, known by its initials, ICUMSA. The color index is then given in ICUMSA units, IU, and is measured by the method that involves measuring the light absorbance of the sugar solution at 420nm and pH adjusted to 7.0 at 20°C, after filtration though a 0.45µm membrane [4]. The absorbance value obtained is then adjusted to the thickness of the measuring cell and expressed relatively to the concentration of solids dissolved in the liquid solution, brix of the solution, the color index value is then calculated by equation 2.1 [4] presented below:

$$IU = \frac{A_{420} \times 1000}{\delta \times c} \tag{2.1}$$

Where $\delta$ is the measurement cell length and $c$ is the dissolved solids concentration in g/mL.

It is important here to notice that the pore size of the membrane is important as well as the pH at measurements conditions, since they will both affect the result significantly. The membrane filter retains high molecular weight color compounds which affect significantly the color measured and the pH is of great importance since different colorants will present different behavior related to pH changes, exhibiting sometimes a great variation on the color as result of small changes on the pH of the solution.

The behavior of the colored substances in relation to variations in the pH is used as a mean of differentiating between types of colorants, and this relation is what gives rise to what is called Indicator Value, IV, which is an important parameter to characterize the types of colorants present in certain sugar products. The indicator value is obtained by the ratio of the color measured at pH 9 and the color measured at pH 4, or simplifying we can use the relation of color to absorbance by the previous method to obtain the color index, leading to the following equation (equation 2.2) [4]:

$$IV = \frac{A_{pH=9}}{A_{pH=4}} \tag{2.2}$$

Notice that the color index calculated as well as the indicator value don't give complete information of the color present in the product, and one important contribute for the color characterization in sugar industry was given by Bento [5, 6] by measuring the indicator value in the ultraviolet zone.

## 2.4 Decolorization process

In order to achieve the desired degree of decolorization many refineries perform a two stages decolorization process. The first stage is performed in a clarification process and there are mainly two processes in use in the sugar refineries, carbonatation and phosphatation, there is also a process called sulphitation but it is not usual in refineries, being more performed in sugar mills and in unities of plantation white sugar. The secondary stage of the decolorization process is an adsorption process, and can be adsorption in bone char, granular or powdered activated carbon, or by it can be an ion exchange process. Or, as normally occur in the refineries, the two processes are used as secondary decolorization, mainly ion exchange followed by adsorption in granular activated carbon.

In this work it is of interest the understanding of the primary decolorization processes, where is aimed the use of polymers flocculants and color precipitants targeting the reduction of color of the liquor in order to prevent higher expenses in the secondary decolorization step.

## 2.5 Primary decolorization process

The choice of the primary decolorization process depends on the quality of the raw sugar to be refined, but not only, is it also dependent on the overall refining process and the target quality product to be obtained. It also has a great influence in the configuration of the next operation steps, like filtration, flotation, centrifugation and the technology employed for the secondary decolorization, when needed. The main objective in the primary decolorization is to reduce the color of the liquor to an average of 200-250 IU, to avoid higher expenses in secondary color removal to achieve the 45 IU, which is targeted in refining sugar [4].

### 2.5.1 Phosphatation

Phosphatation is a process in which lime and phosphoric acid are added to the sugar liquor in a reaction vessel, being the neutralization reaction described by the following equation:

$$2H_3PO_4 + 3Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 + 6H_2O \tag{2.3}$$

This process the anionic impurities are attached to the salt formed, Calcium Phosphate,, and relies on a flocculation process to remove impurities, by the addition of flocculants that captures the fine colloidal colored compounds and then removing it by flotation with dissolved air. In this process the scums contain normally from 3 up to 7% of sugar, what leads to the need of a process of desweetening the scums [4]. This is one of the strongest disadvantages of phosphatation along with the lower color removal compared to that obtained by carbonatation process, but it can be improved by the addition of cationic surfactants [7, 8].

### 2.5.2 Carbonatation

This is the most utilized process in sugar refineries, and was extensively studied by many authors like Bennett [9, 10], that performed studies to describe the mechanism of this process and it was concluded that the impurities are trapped within the crystals of calcium carbonate rather than its adsorption onto the surface after precipitation. It was observed that any color body with anionic character could be able to form a linkage with calcium, and so get incorporated into the precipitated salt. For this reason the extension of color removal is not particularly sensitive to the precipitated surface area, being more related to a function of the rate of growth of the crystals, making possible the impurities to be incorporated in the salt. The conditions of operation in the carbonatation process, temperature around 80°C and high pH, between 8.5 and 9.5, avoid the problems of inverted sugars as well as the enzymatic browning while promoting the denaturation of the enzymes in this conditions [4].

In this process lime is added to the melted sugar liquor in saturators where a gas containing carbon dioxide is then bubbled in a saturation process, undergoing the following reaction (equation 2.4), where the calcium carbonate is formed:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{2.4}$$

The carbonatation is performed normally in two or three stages. The first stage is the larger and the pH value is kept around 9.5, being in this stage where most of the gas absorption occurs.

In the final stage the exiting liquor is at a pH value around 8.5 [4]. One of the issues of the carbonatation process is the filterability of the liquor that exit the saturators, which depends very much in the structure of the crystals formed during the carbonation, making very important to find the condition in order to achieve a bigger and more compact crystal, to enable the pressure filtration to be well performed.

### 2.5.3 Sulphitation

Sulphitation has proved to be more effective in color formation suppressing than as a mean of removing color already formed in the sugar liquor [3], This was explained stating that the sulphite ions can react with unsaturated carbonyl groups in the color molecules, shifting the light absorption wavelength out of the visible zone. However, those new compounds formed remain in the sugar liquor and can go further reactions later to form highly colored compounds. The process avoids the formation of caramels and moreover the formation of melanoidins. This process is more used in sugar juice clarification in the production of raw sugar, or in white sugar produced in sugar mills, plantation white sugar. In refineries is sometime used after carbonatation process as pH-adjusting, and maybe adding 10% more color reduction to the liquor [4].

## 2.6 Flocculants and color precipitants

It has been over forty years since the publication of some of the most important studies performed in the use of polymer flocculants in sugar industry, which until nowadays are reference to development in the art. That study was written by Michael Camm Bennett, by Tate & Lyle Limited, London [10], but many others authors like Moodley [8] and Dhoerty [11] added new insights to this process. Firstly, must be explained how polymers can induce flocculation in particles suspensions, and so, it will be given next a brief explanation of flocculation mechanisms.

### 2.6.1 Polymer flocculation

Flocculation and coagulation are processes by which colloidal particles dispersed in solution can be induced destabilization, promoting the aggregation of these particles in order to enhance the separation process by physical means such as filtration or sedimentation. The polymers used in flocculation processes can be divided into natural and synthetics, and even more important as anionic, cationic or non-ionic, according to the charge character of the polymer.

There are mainly three mechanisms though which polymer flocculation can occur [12, 13]:

- **Charge neutralization mechanism**: the particle charge neutralization in colloidal suspensions can occur by the addition of polyelectrolytes, through the compression of the double layer, when the ionic strength of the solution is increased, allowing thereafter short-range attractive forces to predominate over the electrostatic repulsive forces. In the presence of opposite charges polyelectrolytes those can neutralize the charges of the particles by adsorption onto its surface, reducing then the double layer repulsion allowing the aggregation to occur due to Van Der Waals forces.
- **Bridging mechanism**: this flocculation mechanism occurs when a long chain polymer is added to a colloidal suspension, the polymer chains are adsorbed onto the particles suspended in a way that one single chain can be attached to two or more particles by kind of "bridging" them together. This mechanism is very much dependent on an optimal polymer dosage, at which it is assured that there are sufficient unoccupied particle surface in order to allow attachment to other particles already attached to different polymer chains, bridging them together. At same time those bridges should be made in a such extension to guarantee that the distance over which particles aggregation is overcome. Following this, too low dosages of polymers might not provide sufficient polymer chains to form good bridging links between particles, but also too high dosages diminish particle surfaces for the bridging attachment and steric repulsion may occur inhibiting aggregation of the flocs.
- **Electrostatic patch mechanism**: this mechanism has been proposed to explain the resulted observation that polymers with high cationic charges added into anionic colloidal suspensions the energy interactions favors a flattened adsorption configuration. The highly charged polymer adsorbs onto the surface of the particle in a way that lead to areas, which seem like "islands" or "patches" of charge, surrounded by areas of opposite charge. Thus,

when the polymer is adsorbed in this manner, it can interact with oppositely-charge areas of a different particle promoting a strong electrostatic attraction between them. This mechanism predominates in systems of anionic colloidal suspensions when cationic polymer is added, even though bridging mechanism may occur if particle concentration is high enough to promote collisions between them in a time similar to that needed for the polymer to form the flattened configuration.

The next drawing (Figure 2.2), represents the bridge and patch mechanisms of flocculation, which are, normally, expected to happen when using polymers flocculation:

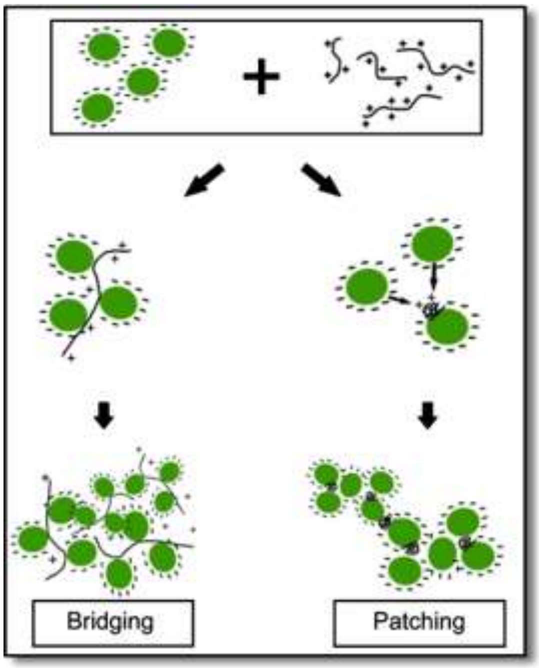


*Figure 2.2: Representation of bridging and patch flocculation, green balls are the anionic impurities and the polymer chains [14].*

## 2.6.2 Anionic flocculants

The first reference flocculants used in sugar industry was the polyacrylamide [3], being that polymer used mainly to improve the separation during the clarification process in the sugar mills, in production of raw sugar, and in refineries using the phosphatation process to enhance the separation of the calcium precipitates from the sugar solution. Those flocculants are normally high molecular weight copolymers of acrylamide and sodium acrylate, with anionic character that react forming a bridge with the calcium ions precipitates, promoting flocculation, increasing the size of the precipitate and so promoting an easier and faster separation by filtration or flotation. This anionic polymers are mostly used in phosphatation process, without that the process is much less rentable, in this case those polyelectrolytes have a major importance [3]. The efficiency of those polymers in the flocculation is very dependent on the molecular mass, the charge density and the structure of the polymer chain. Gorjian [11] performed studies using cationic copolymers as flocculation aids in raw sugar production, in the clarification process where only initially anionic polyacrylamides were used, concluding that dosages 5-10ppms of copolymers containing dimethylaminoethyl acrylate methyl chloride and DADMAC's, enhanced the color removal in sugar cane juice clarification.

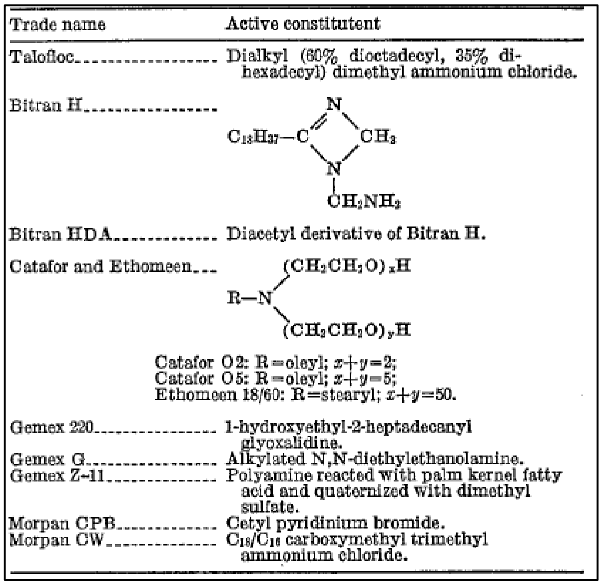
### 2.6.3 Cationic flocculants

As the target color compounds to be removed by precipitation have an anionic character, as concluded by Bennett [10], the surfactants to be used for targeting specifically those colored compounds should have a strong cationic character.

Cationic polymers have been investigated since the 60's in water treatment processes. In the late sixties of the 20th century, Michael Camm Bennett [9,10], for Tate and Lyle Ltd., performed a series of studies and research, on the field of flocculation in sugar solutions, which would compose the basis for the research for the use of polyelectrolytes to enhance color removal in the sugar industries processes. He concluded that the decolorization processes performed in the refineries, namely ion exchange process and adsorption in bone char or activated carbon, were characterized by their ability to remove anionic impurities from the sugar liquor.

Those anionic impurities are compounds that present a strong hydrophilic character, therefore highly water soluble. For that, in order to remove them by physical means, like filtration or clarification processes, those materials should react, forming chemical or physical bonds, with substances which would turn them insoluble in water, and so allowing the separation. Bennett [10] observed that those color compounds were trapped into calcium carbonate crystals during the carbonatation process and that they were also well removed by adsorption process in bone char, which also presents calcium ions, also with the capacity to adsorb negatively charged anionic molecules. Thus he concluded that the most effective way to remove those color impurities was by using materials with a strong cationic character in order to attract and promote the precipitation of the colored compounds. Based on the use of cationic surfactants in water purifications processes, he tested some of these polymers used for water purification in sugar liquor to see if it could perform any decolorization, after what he concluded that flocculation with cationic polymers could be used as a mean of color precipitation in sugar refining process.

Bennett [10] tested many cationic polymers, after these he concluded that those presenting the best performance as color precipitants were those ones containing a cationic center configured by a quaternary ammonium, attached to long or cyclic hydrocarbon chains, in this way the ammonium cationic center would attract and bind to the anionic impurity while the hydrophobic hydrocarbon chains proportionate the means to precipitate the complex formed, as it is insoluble in water. He concluded by that time that the reaction between the polymer and the impurities has an ionic character being, so, very fast reactions. He proposed that the chain length should be the ones containing sixteen or eighteen carbon atoms, as it is present in the structure of the surfactant named Talofloc (a trademark of Tate and Lyle Ltd., London), that is the dialkyl dimethyl ammonium chloride, with the alky group containing eighteen carbon atoms. Below is an image (Figure 2.2), containing the name and structure of cationic surfactants tested by Bennett in his trials for the application of his patent submitted in 1972, which inspires the study of color precipitants in sugar industry until nowadays.



| Trade name | Active constitutent |
|---|---|
| Talofloc | Dialkyl (60% dioctadecyl, 35% dihexadecyl) dimethyl ammonium chloride. |
| Bitran H | |
| Bitran HDA | Diacetyl derivative of Bitran H. |
| Catafor and Ethomeen | Catafor O2: R=oleyl; $x+y=2$;<br>Catafor O5: R=oleyl; $x+y=5$;<br>Ethomeen 18/60: R=stearyl; $x+y=50$. |
| Gemex 220 | 1-hydroxyethyl-2-heptadecanyl glyoxalidine. |
| Gemex G | Alkylated N,N-diethylethanolamine. |
| Gemex Z-11 | Polyamine reacted with palm kernel fatty acid and quaternized with dimethyl sulfate. |
| Morpan CPB | Cetyl pyridinium bromide. |
| Morpan CW | $C_{18}/C_{16}$ carboxymethyl trimethyl ammonium chloride. |

*Figure 2.3: Polymers tested By Bennett in his work (1971) adapted from [10].*

After testing the polymers he concluded that the best one was the Talofloc. Bennett also found that those anionic color compounds present in the sugar liquor could be precipitated from water solutions with primary or secondary amines [15]. The figure presented next (figure 2.3) shows the model of interaction through which the surfactant Talofloc interacts with the color bodies in the sugar liquor.

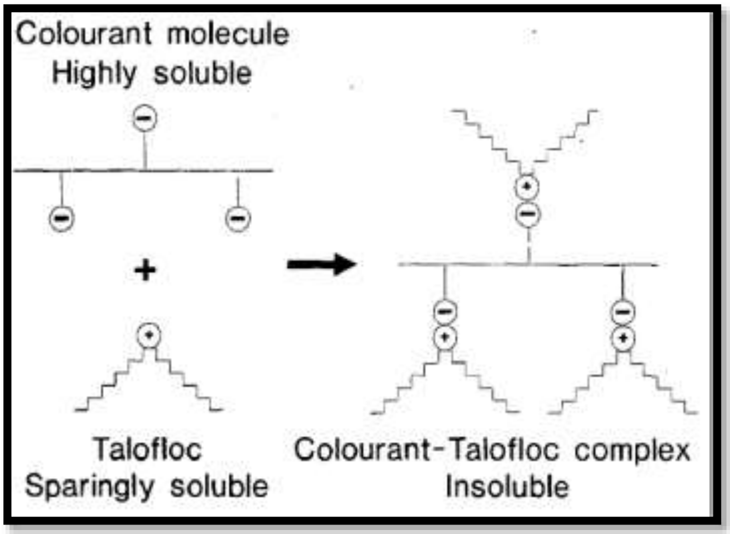


*Figure 2.4: Representation of the interaction between surfactant and anionic color impurity, adapted form [8]*

Talomel [3], an acyclic dimethyl amine polymer,  which was reported initially to have its use more largely applied in the production of mill white sugar, or plantation sugar, has been reported to increase the decolorization by 20-30% in a clarifying sugar syrup [16] by adding 100-200 ppm of the polymer to the clarifying syrup. Talomel is in truth a Diallyldimethyl Ammonium Chloride polymer, or as it is called, a poly (DADMAC). Another polymer, Talocarb, an Epichlorohydrin-methylamine copolymer, approved by the FDA to use as color precipitant, was also reported that adding 200ppms of this surfactant on brix of the sugar liquor, added immediately before filtration, increased the decolorization by 25-30% in a carbonated liquor. Talofloc and Talocarb were the two most used polymers in sugar decolorization process for a time, followed by the poly (Diallyldimethyl ammonium chloride).

Talofloc was very successfully used in phosphatation refineries, because of its structure that promotes very small flocs to be precipitated, which were difficult to be removed by filtration, while used alone, but further studies proved that when used in a phosphatation process, it improved the process and enhanced the color removal, jumping from an initial decolorization, promoted by the phosphatation process alone, in the order of 25 %, to a total decolorization of 70%, when phosphatation is performed using Talofloc during process. Additionally, using polyacrylamide in the phosphatation, it has enhanced the flotation process, by promoting the formation of larger aerated flocs [7]. But Talofloc has not been so successful in the carbonatation process, because it is a wax at room temperature, difficult to handle and dosage. Besides, as carbonatation normally uses pressure filtration as next step in the process it was not so useful, as it created a filtration problem, due to large pressure drops during filtration.

The newer polymer Talocarb works as a color precipitant the can be used in carbonatation refineries, which has proved to be effective in the process when added after the second stage of carbonatation, along with the calcium carbonate precipitated. Also, it didn’t present major problems for the filtration process and improved the decolorization performance of carbonatation alone by the additional removal of color impurities till up to 300 IU [7].

M. Moodley [8], performed also tests in decolorization with commercial surfactants, Bulab 5031, a polyamine, Talocarb, dimethyl amine polymer, Primco 144, a polyamine and Ultrafloc 5000, also a polyamine, performing these tests in different plants, one using carbonatation and other using phosphatation as clarification process. In his study, he proved the effective performance of cationic surfactants as color removal agents, enhancing the clarification process by promoting an additional color removal of 20 to 30% in the process, when adding around 200ppms of the polymers. He concluded that polyamines could be added to carbonated liquor before filtration, while in phosphatation refineries it should be added in raw melted liquor before the phosphatation unity [3].

Runggas [16], performed some relevant studies in the sugar milling institute, university of Natal, South Africa, which were presented in the proceedings of the Southern African sugar technologists association, using a range of cationic flocculants in carbonatation refining process. The polymers tested were produced locally, but various commercial polymers were also tested, from trademarks like Talofloc, Flocotan, and a set of Superfloc trademark surfactants, which were poly(DADMAC)’s of low, medium and high molecular weight, other comercial poly(amines), and Basefloc C45, used in water clarification. This study conducted tests on color removal, turbidity, ashes, starch and gums removal as well as on the influence in the filterability of the carbonated liquor after polymer treatment. He concluded that the optimal color removal addition point of the polymer in the process was after saturation, at a point prior to filtration. The most effective dosages were 50ppm’s of polymer on sugar liquor brix. The Superfloc grade (a poly (DADMAC) of medium molecular weight) had the best color removal performance. Additionally those surfactants had good performance in gums and starch removal, as well as in the removal of suspended particles, reducing the turbidity of the liquor. One important conclusion is also that for those cationic polymers, the dosage have to be well tuned. This factor affects very much the performance: a low dosage might not be so effective but high dosages can reverse the colored bodies bond to the polymer, being prejudicial to the color removal, sending the color molecules back to the sugar liquor. Furthermore, high dosages can produce foams in the liquor, what would be a big problem in the next steps, the filtration and even in the secondary color removal process.

## 2.7 Secondary color removal technics

The final color in refined white sugar sometimes has to be below 60 IU, and for some markets the requirement is that of 45 IU, and purity superior to 99.9% of sucrose [4]. The color achieved normally by the primary decolorization process is in the range of 200-300 IU, so a secondary decolorization is required, which can be mainly one or more of the following processes:

- ✓ Bone char adsorption;
- ✓ Granular or powdered activated carbon adsorption;
- ✓ Ion exchange.

A brief explanation of those decolorization processes is given in the next subsections.

### 2.7.1 Bone char

The adsorption in bone char has been the main decolorization process for many years in the sugar industry, until the development of ion exchange and granular activated carbon use in the refineries to take place. It consists of a high surface area material, constituted basically calcium phosphate, hydroxyapatite, which is coated with carbon. It comprises of only 10-12% carbon in total. This kind of adsorption is no longer in use, mainly because of the disadvantage of large and expensive unitis, along with the need of large char inventory as, with time operation, char degrades and pores are blocked, increasing its density, in a way that it needs to be replaced. So it is not any more cost effective [4, 17].

### 2.7.2 Activated carbon

Activated carbon is a non-polar highly porous material, with very large surface area, which is used as color removal aid, by physical adsorption mechanism [4], where strong attraction between the carbon surface and sugar molecules present in sugar liquor, promoted by van der Waal's or London forces, so occurs and the color molecules are held against many points in the large surface of the activated carbon, thus being strongly adsorbed on it.

The color removal is mainly physical, but chemisorption may occur due to the activated carbon still containing oxygenated functional groups which will adsorb polar molecules. It is not specific to remove any type of colorant, giving a high overall decolorization, of around 80%, which may go up to 90% [4]. It is very good to remove flavonoids and phenolic colorants [3]. Normally granular activated carbon is used but powdered activated carbon may be used for small through output applications. Besides, the use of granulated carbon adsorption allows the removal of odorous compounds present in the sugar liquor.

One of the drawbacks of the use of activated carbon may be the sucrose losses by pH drop and inversion reaction, which can be avoided by adding magnesite to the system during revivification of the granular activated carbon [17]. One of the advantages of the use of activated carbon instead of bone char is the impact in energy consumption for the decolorization process, which dropped to 50% of that needed when used bone char [4].

### 2.7.3 Ion exchange

In this process, polymeric resins in macro reticular form and with strong basic character are used to remove anionic colorants from the sugar liquor through ionic bounds with the cationic center of the resin along with hydrophobic interactions with the resin matrix [4], if a styrenic resin is used. Besides the styrenic, acrylic resins are used in ion exchange columns, and even though the acrylic are generally able to remove more colorants they are more prone to fouling, thus, sometimes the two resins are used in combination, with the styrenic ahead of the acrylic one, in a way that the first one provides protection to the second.

Those resins are characterized by their high molecular weight, as well as a high degree of cross-linking, presenting a quaternary ammonium functional group in their chemical structure. The acrylic resins are less selective in the process than the styrenic, but on the other hand its regeneration process is easier and more complete, this way they show slower rate of deterioration.

The main mechanism of this process is the ion exchange between the chloride ions to be displaced from the resin matrix, which will be replaced by the anionic groups on the color compounds.  Competitive exchange occurs during the process [3], by smaller organic molecules, sometimes not color related, or inorganic molecules, which may also occupy the active sites leading to the exclusion of color molecules. In this process, besides the functional groups of the color bodies, the size of those compounds also affect the performance of the process.

# Chapter 3. Materials and Methods

This section refers to the methods by which the laboratory trials were performed, as well as the main materials utilized for that purpose. The tests were divided into four stages: decolorization, indicator valor evaluation, polymers characterization and last the monitoring of flocculation process performance by the most effective polymers used.

## 3.1 Materials

### 3.1.1 Sugar

The starting point of the work is the raw sugar to be decolorized, that is sugar from sugarcane, and it is important to mention that the raw sugar has different compositions in terms of color bodies present on it, depending on its geographic origin, climate and soil conditions, season of harvesting and process through which the raw sugar was produced, among other factors and aspects that may influence the composition of raw sugar (the sugar used had its origin in central America).

The next figure represents the configuration of the carbonatation unity, from which the sugar liquor was harvest, consistent of three saturators, where the major part of the calcium carbonate is formed, representing the first stage of the carbonatation and where the liquor has an average pH of 9.5, followed then by a second stage saturator, where the pH range will be in the order of 8.5. It is at this point that it is normally added the flocculants, as normally those polymers are pH sensitive and it is known to be at this point that they are most effective in the carbonatation process [3, 6]. The sample collecting, to be used in the present study, is made then in the saturator B, pointed in the diagram below by the red circle, before the before the polymer is added in the industrial process conducted by RAR Portugal.

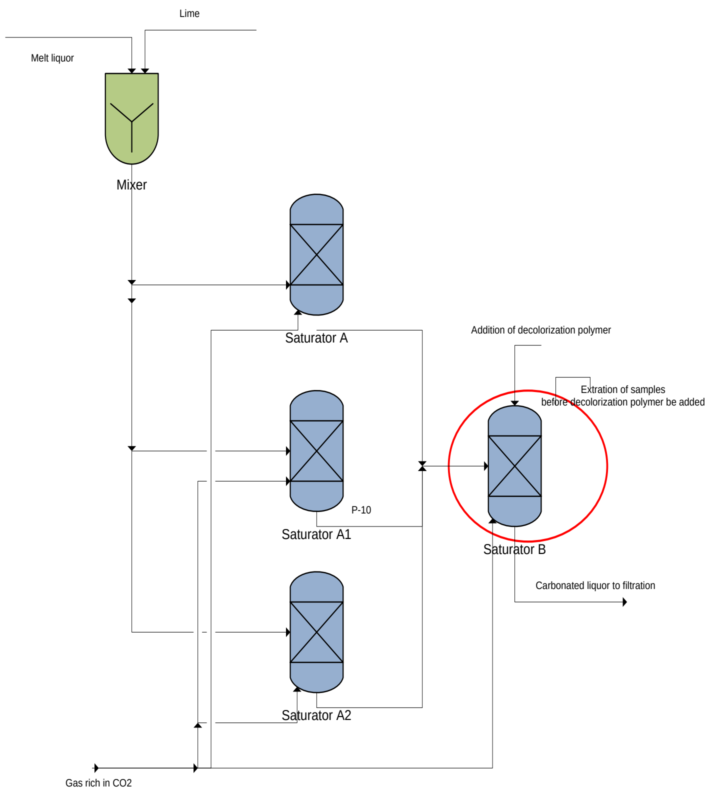


*Figure 3.1: Carbonatation process diagram, red circle represents point of sample extraction for the laboratorial trail ( the scheme represents the unit of RAR).*

For all the tests performed in this work the sugar source was raw sugar liquor collected in the installations of the sugar refinery RAR, being the samples of 12 liters collected at the second stage of the carbonatation process, where the normal conditions of the liquor are around 80°C and the pH is 8-8.5 and with a degree of Brix( concentration of solids in the liquor) of approximately 65°Brix, and prior to the dosage of color precipitants that is added normally at this second stage, and before the pressure filtration unit. The samples were immediately cooled in order to stop the carbonatation process, which was still going on at the collecting time of the liquor. The sugar carbonated liquor was then transported in thermal protection container, after what it was kept in a refrigerator at temperatures close to zero, for the use in the decolorization tests planned in the laboratory. The same process of collecting samples and storage was performed one second time, to collect more liquor to perform tests of flocculation monitoring in the LDS (Laser Diffraction Spectroscopy) system.

### 3.1.2 Polymers

After the research in the literature on the previous studies performed in color removal with polyelectrolytes, and taking into account that the colored materials to be removed have an anionic character it was decided to use cationic surfactants, which were provided by AquaTech Switzerland.

Knowing that the most effective polymers to precipitate the color impurities present in the sugar liquor are those with strongly cationic functional group [9, 3] to attract the anionic impurities, and that those cationic centers must be bonded with hydrocarbon chains to provide the hydrophobic character in order to allow the precipitation, and that, according to Bennett [10] the most effective cationic character was provided by polymers containing quaternary ammonium compounds. Following those information, it has been decided to test a set of polyamines and poly (diallyl dimethyl ammonium chloride), or poly (DADMAC) as it is known. In addition, the novel polymer poly [(2-methacryloxy) ethyl trimethyl ammonium chloride], commercial name Amber MetQuat 6. Those polymers were provided as solution with the concentrations given in weight of polymer by volume of solution. The complete list of polymers used are shown next (Table 3.1).

*Table 3-1: List of Polymers used in the present study, provided by AquaTech Switzerland.*

| **Polymer** | **Form, concentration(%w)** | **Chemistry** | **Viscosity(MPas)** |
|---|---|---|---|
| Amber 2001HMW | Liquid, 50% | Polyamine | 2000-3000 |
| Amber 2002 | Liquid, 50% | Polyamine | 400-700 |
| Amber 2006 | Liquid, 50% | Polyamine | 100-300 |
| Amber 2008 | Liquid, 40% | Poly(DADMAC) | 500-1000 |
| Amber 2008HMW | Liquid, 40% | Poly(DADMAC) | 1000-2000 |
| Amber 2009 | Liquid, 40% | Poly(DADMAC) | 2000-3000 |
| Amber 2010 | Liquid, 40% | Poly(DADMAC) | 1000-3000 |
| Amber 2013 | Liquid, 35% | Poly(DADMAC) | >9000 |
| Amber 2014 | Liquid, 50% | Poly(DADMAC) | >10000 |
| Amber MetQuat 6 | Liquid, 40% | MetQuat 6 | 1200 |

## 3.2 Methods

### 3.2.1 Preparation of the polymer solutions

The polymers to be used in the decolorization procedures were first prepared in solutions of 1% (w/V) in ultrapure water. For each test, a solution of 50ml of polymer was prepared and kept under agitation at 400 rpm's in stirring plates for twelve hours, covered with parafilm to avoid contamination with air particles. The solutions that were prepared took into account the concentration of polymer by weight in the original solution provided by AquaTech.

### 3.2.2 Decolorization tests

The decolorization tests were performed using the carbonated sugar liquor brought from RAR.

First the liquor was taken from the refrigerator were it has been kept, agitated and then taken 50 ml of the liquor measured in a graduated cylinder, and then transferred to a 100ml beaker which was after covered with aluminum foil and then taken into a thermic bath, with a thermal sensor placed inside the liquor to monitor and control the temperature, then it was heated to the temperature of 80°C, in the intuit of lead to similar conditions of the carbonatation system. When the temperature of the liquor reached 75°C the prepared polymer solution was then added with one micrometric pipet, the volume of solution added to the system was that reached by calculations of the referent ppm's aimed to be used, those calculations were referent to the solids content in the liquor, or as it is said in the sugar industry, based on the brix of the liquor.

In the literature [3, 8, 15] has been reported dosages from 10-600 ppm's on brix for polymers, some authors used the range till 150, in the work the tests were performed for: 25, 50, 100, 150, 200 and 250 ppm's of polymers based on the brix of the liquor. After addition of the polymer the system was kept at temperature maxim of 80°C, in agitation at 400 rpm's for 10 minutes counting from the addition of the polymer solution to the carbonating liquor.

After the ten minutes the agitations and heating are stopped, the liquor was diluted in one part of liquor to two parts of ultrapure water, after what it was then cooled to temperatures around 20°C, proceeding then to the vacuum filtration with aid of a 0.45µm membrane filter. After that, the filtrated was leaded to pH and temperature adjust for 20°C and pH 7.0, according to the ICUMSA requirements for color measurement in sugar solutions. After this the measurement of the absorbance at 420nm was carried out in three times for two solutions inserted in the measuring covet, performing six absorbance measurements, from which an average absorbance was calculated. After that the measurement of the Brix of the solution was performed in a refractometer. After all that done, with the absorbance value, dimension of the cell, 1cm, and the brix, of the solution, all measured at 20°C and pH 7.0 ± 0.02, the ICUMSA color index of the filtrated solution was then calculated using the ICUMSA 420 method, by means of the equation 2.1 mentioned previously.

The figure presented next (Figure 3.2), shows in block diagram the flow of the trial procedure:

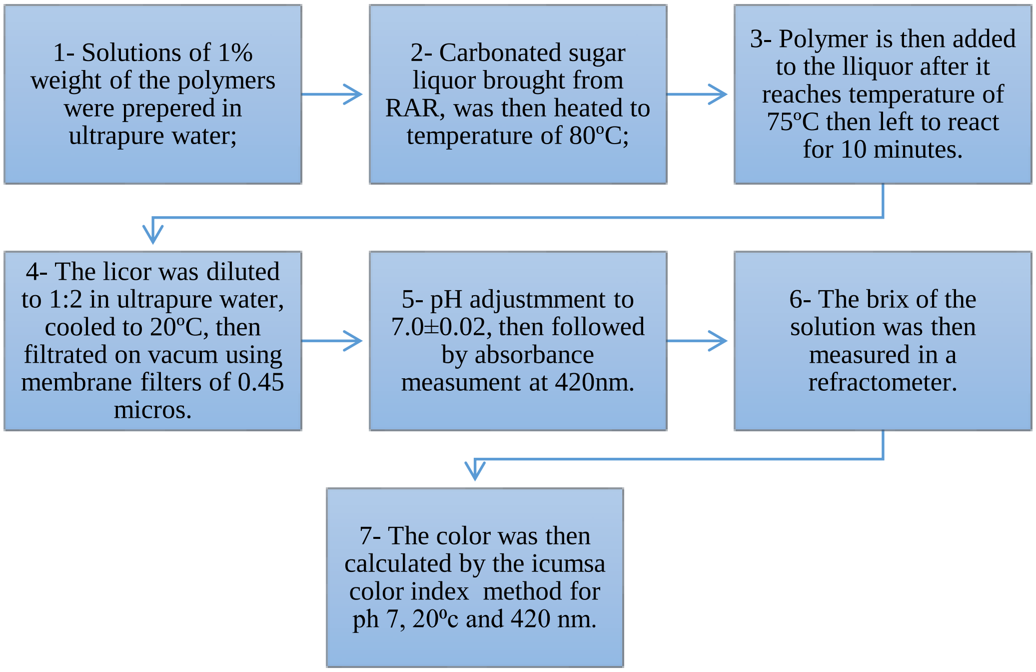


*Figure 3.2: Schematic representation in flux diagram of the procedure for decolorization laboratorial tests performed.*

It has to be mentioned that at same time that the liquor was submitted to the decolorization process with the polyelectrolyte, another beaker with liquor from the same collected sample was taken and submitted to the same steps, but without addition of polymer. This second sample will be referred as the blank of the test, to compare to the one to which the polymer was added. The decolorization percentage for the test is then calculated based in the following formula (equation 3.1):

$$\left(\frac{(C_{IUblank} - C_{IUsample})}{C_{IUblank}}\right) x\ 100 = \%_{decolorization} \tag{3.1}$$

Where:

- $C_{IUblank}$ is the color of the sample without polymer decolorization, or blank of the test, in ICUMSA unities, which is the color of the filtrated liquor after carbonatation process;
- $C_{IUsample}$ is the color of the liquor submitted to the decolorization through flocculation process with the polymers, in ICUMSA unities,
- $\%_{decolorization}$ is the percentage of decolorization achieved.

All the procedure described above were repeated for all the tests of decolorization, which were performed for each polymer and for each dosage of polymer tested individually.

In addition to the individual polymer decolorization tests, tests were also performed mixing two and three of previous polymers simultaneously. The polymers having shown the best performance in the individual decolorization tests have been chosen for using in the blending.

## 3.4 Evaluation of IV on decolorization

After the polymer decolorization tests in order to understand if the impurities removed by this process were those characterized by high, medium or low molecular weight, evaluation of changes in the Indicator Value( IV) were conducted. In order to do that, the procedure for individual decolorization test was performed and the liquor submitted to the reaction with the polymer was, after the filtration, split into two parts, both at 20°C temperature. The pH was adjusted to 7.0 in one sample, which was again splinted in two parts, and the absorbance was measured for one of those parts at the pH 7.0, the other part adjusted to pH 4.0, after which the absorbance was measured. The other half of the filtrated liquor was adjusted to pH 9.0, and then the absorbance at this pH was measured. As explained in the previous chapter, the indicator value (IV) can be calculated by the ratio of the absorbance of the sugar solution at pH 9.0 and absorbance at pH 4.0, or alternatively by the equation 3.2 [4]:

$$IV = \frac{color_{pH=9}}{color_{pH=4}} \tag{3.2}$$

## 3.5 Polymers characterization

Characterization of the polymers used in the decolorization tests was also conducted to try to understand their activity. It was decided to perform tests to determine three important aspects that have influence in the flocculation process: the hydrodynamic diameter of the polymer (determined by dynamic light scattering), the zeta potential of the polymer chains in deionized water (electrophoretic light scattering), and the molecular weight of the polymers (static light scattering). In order to perform the molecular weight measurement the determination of the refractive index of the polymer solution was also measured.

The equipment used to perform the characterization of the polyelectrolytes was the high performance Zetasizer Nano ZS (ZSN) commercialized by Malvern, installed in the facilities of the solids technology laboratory, in the chemical engineering department of the university of Coimbra.

*Figure 3.3: Zeta Nano Sizer ZSN by Malvern. [18].*

### 3.5.1 Hydrodynamic diameter

When referring to a hydrodynamic radius or diameter, this dimension is a hypothetical dimension, considering that the easier shape to characterize three dimensionally a particle is a sphere because its diameter is enough to determine the size of the particle. Following this idea the hydrodynamic diameter determined by the Zetasizer is that one of the sphere that diffuses at same speed as the particle that is being characterized. This parameter is determined using dynamic light scattering (DLS), and the size is determined based on the Brownian motion of the particles in the sample relating it to the measurement of the scattering light intensity fluctuation, when a laser beam is projected into the sample [18].

The particles, below micrometric dimension, dispersed in a liquid solution are consider not at rest, but in continuous Brownian motion, that is a motion due to the constant collision between the particles and the molecule of the liquid that surrounds the particle. The speed of the particle in this movement is dependent on the size of the particle, the larger is the particle slower it moves. When a light source, in this case a laser beam, crosses the solution it will hit the particles and the light will be scattered by them in all directions. Being the particles in constant motion, the scattering pattern will change over time, presenting an intensity fluctuation as a function of time. The small particles move quickly, producing a higher intensity fluctuation, on the other hand the larger particles should move slower, presenting also lower intensity fluctuation. This intensity fluctuation signal detected is then sent to a digital correlator, present within the Zetasizer equipment, which will convert this signal into a particle size [18]. The intensity of two consecutive signals is higher than two separated signals, so, the smaller the particles, the faster they move and the correlation between the signals over time will decrease. The next figure is the graph that represents the correlation functions on which the DLS is based in the Nano Sizer equipment (Figure 3.4).

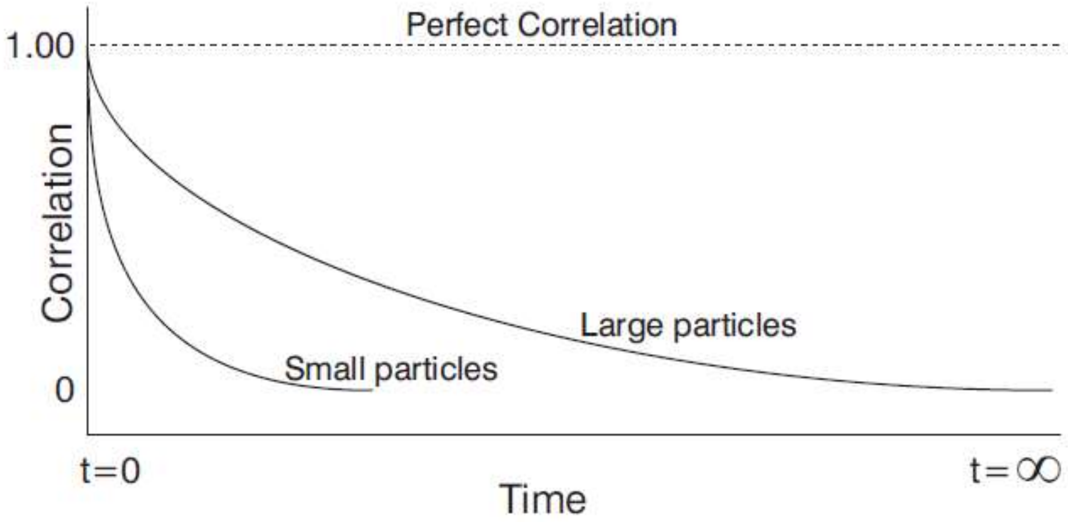


*Figure 3.4: Graphic representation of the correlation functions used in DLS treatment by the Nano Sizer equipment [18].*

The equipment software relies in two algorithms to obtain a diameter value: Cumulants analysis, that fits the correlation curve to an exponential function, or the CONTIN method, based on the approximation of the correlation curve to a sum of exponential functions, which is more adequate to complex multidisperse sample analysis. By one of those two algorithms the distribution of the diffusion coefficient, $D_c$ can be calculated, and for each value of $D_c$ the hydrodynamic diameter is calculated though the Stokes-Einstein equation presented below (equation 3.3) [18]:

$$D_c = \frac{kT}{3\pi\mu D_h} \tag{3.3}$$

Where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\mu$ is the dynamic viscosity, and $D_h$ is the hydrodynamic diameter of the particle. From this calculation a distribution of diameters is obtained from which an average diameter $D_z$ is then calculated by the Zeta Sizer software, assuming that the particles light scattering obey the Rayleigh theory. The average diameter $D_z$ is calculated by equation 3.4 [18] below:

$$D_z = \frac{\sum I_i}{\sum \frac{I_i}{D_i}} \tag{3.4}$$

Where $I_i$ is the scattered light intensity of the class i, and $D_i$ is the hydrodynamic diameter of the same class $i$.

In the procedure for the measurements, some factors had to be considered, mainly preparation and handling of the samples to be analyzed. The solution preparation had to take into account first the concentrations of polymer in solution in order to have the adequate concentration to perform the measurements, which has to be very low, but high enough to be clean the noise signal, but also not too high that could cause aggregation of the particles or multiple scattering effects.

The polymer solutions were prepared in ultrapure water with addition of 0.05M of Sodium Chloride, and concentrations of polymer from 0.1%to 0.01 % (w/V). The starting solution was prepared in the day before, covered with parafilm, to avoid contamination, and left under agitation through the night, being the dilutions prepared early in the morning and also left in agitation for at least one hour before any measurement being performed. All the samples measured were filtrated though a 0.45µm membrane filter before proceeding to measurements. In the present work, the filling of the measurement cell was performed using a 5ml syringe coupled to the 0.45µm membrane filter. After initial trials it has been concluded that the best concentration range for the size measurement was that in the range between 0.02-0.1% w/V.

### 3.5.2 Zeta potential measurement

Zeta potential, or electrokinetic potential of colloidal particles is an important parameter used to characterize electrochemical equilibrium on interfaces, and it is a very important key to the stability of a particle suspension or solution. In the case of large molecules, zeta potential supplies an indication of the charge of the molecules.

The zeta potential is a way to express the degree of electrostatic repulsion between particles adjacent and similarly charged in a colloidal suspension, it is measured in mV (millivolts), thus suspensions with high zeta potential, either negative or positive, are considered stable thus the high repulsion between particles in the suspension.

To characterize the polyelectrolytes used in the present study, one important aspect was the measurement of the zeta potential of the polymers in suspension, which was performed using the equipment mentioned in previous topics, the Zetasizer Nano ZS, which is provided with electrophoretic light scattering (ELS).

The ZSN equipment performs the sample's zeta potential measurement based on the electrophoretic mobility of the charged particles in the suspension when an electric field is applied to the suspension, causing those charged particles to move towards the electrode of opposite charge, and the velocity at which this migration occurs is measured by Laser Doppler Velocimetry, included in the ZSN equipment. The velocity in measured will depend on the following factors [18]:

- The strength of the electric field applied or voltage gradient;
- The dielectric constant of the suspension medium;
- Viscosity of the suspension;
- The related zeta potential.

The velocity of migration, so referred as electrophoretic mobility, is measured and the software calculates the zeta potential by the Henry's equation [18] (equation 3.5):

$$U_E = \frac{2\varepsilon z f(ka)}{3\mu} \tag{3.5}$$

where $U_E$ is the electrophoretic mobility, $\varepsilon$ is dielectric constant, z is the zeta potential, μ is the medium viscosity and *f(ka)* is the Henry's function, which may assume two approximation values- 1.0 or 1.5, depending on the liquid media. In the case of this study since the suspensions were prepared in ultrapure water, the value of 1.5 was used, which is called Smoluchowski approximation [18].

For the trials the polymers were prepared in ultrapure water in concentrations similar to those used to measure the particle size. The zeta software analysis reported as good quality measurements those made at concentrations on the range of 0.02-0.1% w/V. In this case the, an initial solution was prepared in the day before and left under continuous agitation at 400 rpm, over a period of twelve hours, then dilutions were made and left for also under agitation, for a minimum of one hour before proceeding to the measurements. The solutions were submitted to ultrasound treatment for two minutes prior to cell filling. Here the filling of the measurement cells were also conducted using a 5ml syringe coupled to a membrane filter of 0.45µm.

### 3.5.3 Molecular weight

The measurement of the molecular weight (MW) of the polyelectrolytes used in the study has been performed seeking to understand the influence of this variable on the performance of those polymers as color precipitants in the sugar liquor. It is known that the MW of the polymer, along with the charge density and the molecule's architecture and its length [10, 16] are some of the major parameters that may influence the flocculation mechanism and performance of such materials.

The molecular weight of the polymers was measured by means of the Static Light Scattering spectroscopy technique, which is one of the most widely used procedures to obtain absolute molecular weight of macromolecules [13]. In this technique, the particles in a diluted suspension are illuminated by a source of light, such as a laser, being then the light scattered by the particles in all directions. But in this case, differently to DLS, that measures the fluctuation of the intensity of scattered light as a function of time, the static light scattering is based on the time-averaged intensity of the scattered light.

The Zetasizer, ZNS, equipment, used in the previous size and zeta potential characterization, has also been to conduct the molecular weight measurements of the polymers. In order to guarantee accurate measurements it is important that the size of the particles to be measured is small enough to avoid the angular dependence of the scattering intensity, which leads to multiple scattering by the same particles, and by doing so, it can be assumed the Rayleigh scattering model, letting the angular disperse term $P_\theta$ to be equal to one, allowing then the use of the Rayleigh approximation for a single angle light scattering, the application of the Rayleigh equation, becoming the equation 3.6 [18] showed next.

$$\frac{KC}{R_\theta} = \left(\frac{1}{MW} + 2A_2C\right) P_\theta \tag{3.6}$$

Where:

- **$R_\theta$** is the Rayleigh ratio (ratio of scattered light to incident light of the sample);
- **$MW$** is the sample's molecular weight;
- **$A_2$** represents the second virial coefficient;
- **$C$** is the sample's concentration;
- **$P_\theta$** is the angular dependence of the sample scattering intensity, which in the case of Rayleigh scattering will assume the value of 1;
- **$K$** is the optical constant, which is obtained as shown in the next equation, (equation 3.7) [18];

$$K = \frac{2\pi^2}{\lambda_O^4 \, N_A} \left(n_0 \frac{dn}{dc}\right)^2 \tag{3.7}$$

Being:

- **$N_A$** is the Avogadro's constant;
- **$\lambda o$** is the laser wavelength;
- **$n_o$** is the solvent's refractive index;
- ***dn/dc*** is the differential refractive index increment, representing the change in the refractive index of the sample as a function of the polymer concentration.

The molecular weight measurements are normally performed using standards approach. This means that, in order to measure a sample's MW, it should be related to a "standard", that is a highly pure substance that has a well-known Rayleigh's ratio, and for which the scattering intensity will be first measured in order to compare and relate the measurements of the analyte's sample to be measured. In light scattering MW measurements, the most widely used standard is Toluene, which presents Rayleigh's ration suitably high to perform precise measurements for a good range of temperatures and wavelengths. Based on that approach [18], the next equation (equation 3.8) is used to calculate the Rayleigh ratio for a sample using toluene as standard.

$$R_\theta = \frac{I_A n_0^2}{I_T n_T^2} R_T \tag{3.8}$$

Where:

- $\boldsymbol{I_A}$ is the residual scattering intensity of the analyte;
- $\boldsymbol{I_T}$ the toluene scattering intensity;
- $\boldsymbol{n_o}$ is the solvent's refractive index;
- $\boldsymbol{n_T}$ the toluene refractive index;
- $\boldsymbol{R_T}$ is the Rayleigh ratio for toluene.

And so, taking into account that we will assume no angular dependence on the scattering intensity by the particles, supposing they are small enough to avoid multiple scattering behavior in the samples; supposing that in the Rayleigh theory the parameter $P_\theta$ assumes the value of one as a consequence, the intensity of the scattered light by a particle is to be proportional to the product of the weight-average molecular weight and the concentration of the particles in the sample. Thus, the Rayleigh equation will lead, when plotting the scattering intensity of the light as function of the sample concentration, to a graphic representation of a straight line, which intercepts the Y axis at zero concentration on an ordinate that represents the value of 1/MW that is given in Daltons.

Thus, the Zetasizer Nano measures the intensity of scattered light for the various concentrations (C) of the sample, at one angle ($P_\theta$), which is, then, compared with the scattering produced by the standard, in this case toluene, and the graphical representation (of the intensity of scattered light as function of the sample's polymer concentration) called Debye plot and it leads to the determination of the molecular weight and the second virial coefficient, $A_2$, which represents the interaction strength between the particles and the solvent. A typical Debye plot is shown in the next figure (Figure 3.5).

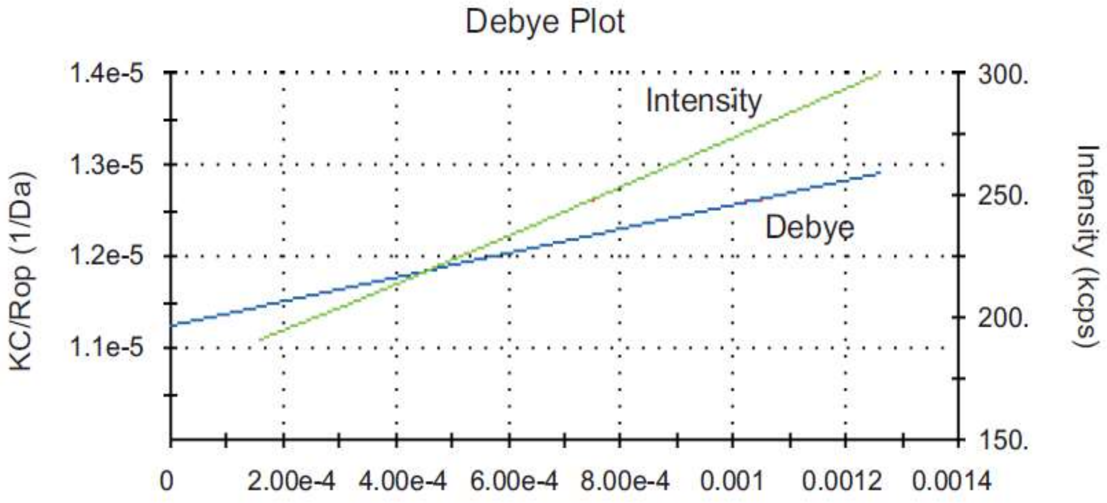


*Figure 3.5: Debye Plot [18]*

The Debye plot comprises two lines, as shown in the figure 3.5 [18]. The Debye line, in blue, from which the interception with the Y axis provides the 1/MW, and the green line, defined as intensity line, that gives information about the quality of the scattering measurements, mainly if the phenomena of multiple scattering is happening, which should be avoided.

The measurements of the molecular weight in the Zetasizer Nano were performed preparing first samples with appropriate concentrations, based on the previous size measurements for the same samples, from which the first range of concentration was defined, and preparing then a minimum of six samples with different concentrations within the range from 1% to 0.02% w/W. A table containing the concentrations used for each polymer will be shown in the appendix A, but those are normally the following: 1.0; 0.5; 0.2; 0.1; 0.05; 0.02, in percentage of weight of polymer by volumes of solution. The results for the tests showed that the concentration of 1%, and sometimes 0.5%, presented a behavior of possible multiple scattering, and so, later the 1% was cut and the 0.08% was added, as is shown in the tables presented in the appendix A. The flow diagram of the measurement process is shown next (Figure 3.6).

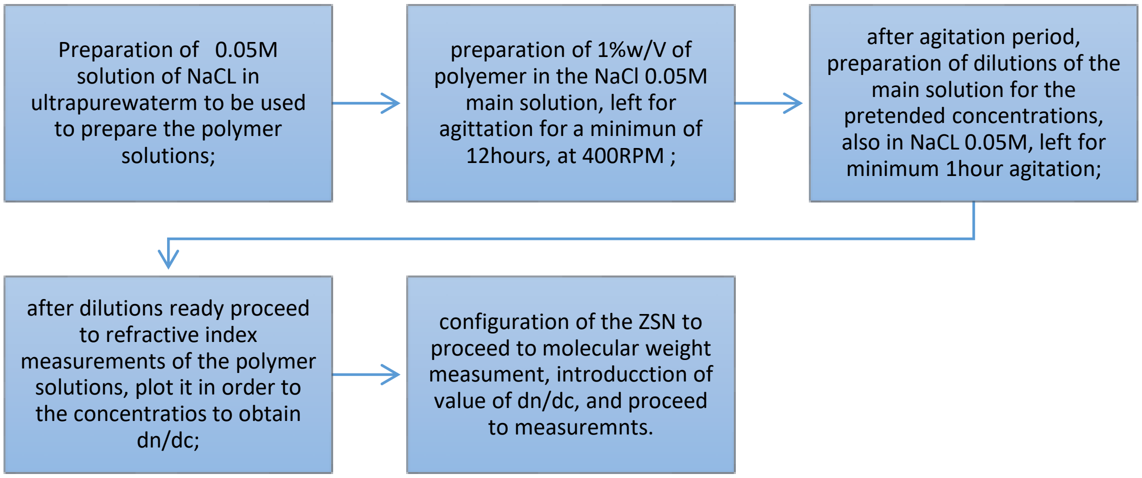


*Figure 3.6: Flow diagram for molecular weight measurements methodology adopted.*

To perform MW measurements the following order was followed:

- Standard measurement, in this case introduction of the toluene cuvette and measure;
- Introduction of a solvent pure cuvette to measure;
- Beginning of samples measurements, first the extreme concentrations, followed by the central and intermediate ones.

For all samples measurements, the filling of the measurement cell was made using a 5mL syringe coupled to a membrane filter of 0.45µm, in order to filtrate the solutions before perform the measurements. In addition, to low MW polymers the use of ultrasounds prior to measurements was not needed, but in case of medium to high molecular weight it was applied for two minutes before proceeding with the measurements.

### 3.5.4 Refractive index

To perform MW measurements, it is also necessary to know the differential increment for the refractive index as a function of the increasing range of concentrations of the sample's solution, which, as mentioned in the molecular weight Rayleigh theory, is an important parameter to be introduced in the ZSN software in order to calculate the sample's molecular weight. This was done by using the Atago RX-5000-CX Refractometer.

The Refractive Index (RI) was determined for each solution concentration, by first performing calibration with the solvent, solution of NaCl 0.05M, with fixed temperature of 25°C. After this step, the RI of the solutions, at the given temperature, was measured. RI was plotted as a function of the sample's concentration, which presented a linear behavior, from which the dn/dc value, slope of the straight line, was calculated. The RI results are shown in the appendix A.

## 3.6 LDS flocculation monitoring tests

After performing the decolorization trials using the standard procedure and the characterization of the polyelectrolyte's physical parameters that could most influence their performance as decolorization agents, it was decided to perform some trials, with the best decolorization agents, to try to follow continuously the flocculation process in carbonated sugar liquor, which was performed by Laser Diffraction Spectroscopy, For that end the Mastersizer 2000 by Malvern Instruments, Ltd (Figure 3.7). With adaptation of a thermal bath to allow to perform tests at temperature above the room temperature was used [13].

*Figure 3.7: System mounted for LDS monitoring of the flocculation process, comprising the Mastersizer and a water bath adapted to the system.*

By using laser diffraction spectroscopy (LDS) it is possible to obtain information about particle size and its distribution through measuring the scattering intensity as a function of the scattering angle and the wavelength of the light source [20]. This technique is able to measure particles and aggregates in a size range that goes from nanometers to few millimeters.

Briefly explaining, this characterization technic uses angular scattering patterns generated by a particle when it is illuminated by a light source, like a laser beam. Those angular patterns are then converted into intensity patterns by Fourier transforming, detected and processed as intensity flux pattern that will further be converted, using appropriated scattering theories, into a particle size distribution. LDS is suitable to give information about size, size distribution, shape and, in the case of the Mastersizer equipment used here, able to give those information in order to the time, what can give information about the evolution of the particles size and shape, allowing this way to monitor the flocculation kinetics [13].

The Mastersizer 2000 was used to evaluate the flocculation kinetics for four of the best performing polyelectrolytes used in decolorization of the carbonated sugar liquor, measuring the size distribution of the suspension along time, before the addition of the polymer for 30 minutes after polymer addition. Normally the polymer is allowed to react for a period of 15 minutes, in the decolorization process, but here is was intended to see what happens for longer periods of flocculation time. The results are presented in the next chapter and in the appendix C.

The monitoring trials were performed after preliminary tests in order to tune the best experimental conditions. First was tested with filtrated liquor, to try to detect the interaction of the polymer with the color compounds present in the liquor after submitting it to a filtration though a 1µm membrane. Although this was not successful due to the inappropriate laser obscuration. Then was tried to perform the tests with the carbonated liquor as it came, in a brix degree of around 65º, what was also not successful due to the very high obscuration of the laser and blue light in the Mastersizer system. After trying some dilutions, just enough to make achieve obscuration suitable to perform the tests it was decided to use a dilution of 1:4 of the original carbonated liquor in distillated water, which permit to have obscuration between 91% and 94% during the measurements, which is still a high obscuration, but it allowed the system could so perform the monitoring. The next diagram (figure3.8) shows the steps for followed while performing the LDS continuous monitoring of the flocculation for all the polymers tested.

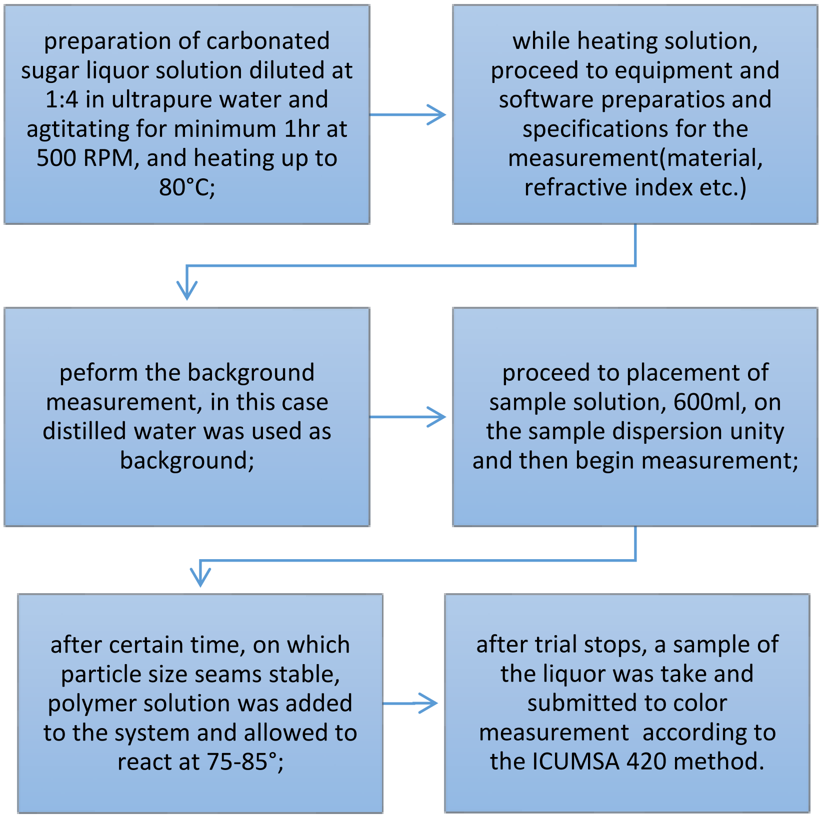


*Figure 3.8: Diagram representation of steps sequence for the LDS trials.*

For the trials the polymers solutions were prepared and dosed as done in the decolorization trials, described in the previous subsection, speed of the pumping system of the Mastersizer was set to 1400 RPM to avoid settling and the solution samples were kept in a 600ml beaker, and placed inside a jacket where hot water was circulating in order to keep the sample at temperatures between 75°C and 80°C, which is the temperature of the carbonatation process. The equipment has always been clean, lenses and tubes, before and after all trials. By agitating for a period of time before the data acquisition. The use of ultrasounds in the system has been avoided during trials, to prevent interfering with the decolorization process or aggregation of the calcium carbonate, present in the solution.

# Chapter 4. Results and discussion

In this chapter the results obtained in the study will be presented, being first shown the polymers characterization results, performed using the Zetasizer Nano, ZSN, comprising of the hydrodynamics diameter, zeta potential and molecular weight for the polyelectrolytes tested as color precipitants in this work. In the second part the decolorization achieved with each polymer in laboratorial tests are presented, keeping in mind that those results were performed according to the methods used in the sugar industry to measure the color of sugar solutions, which were presented in the previous chapter. A few tests to evaluate the change in the index value of the filtrated sugar liquor, the ratio between liquor color measured at pH 9 and the color at pH 4, were also performed and the results presented in the third part of this chapter. As final studies, the flocculation process online monitoring by using laser diffraction spectroscopy (LDS) is presented, as kinetic curves of the flocs size distribution during the flocculation process.

## 4.1 Polymer Characterization

One aspect to be observed, that should be of great importance for the present study, is the attempt to relate the performance of the polymers in the color removal process with its characteristics, namely the Molecular weight, hydrodynamics radius and the zeta potential(related to the polymer charge).

Those characteristics of the polyelectrolytes are known to be very important when studying flocculation. For that reason, the polymers used in the study were characterized by using the Zetasizer Nano ZSN equipment, according to the procedures presented in the previous chapter. The results obtained are summarized in table 4.1, where $D_z$ is the hydrodynamic diameter (the average-intensity weight average diameter), presenting three different measurements results, followed by the $D_z^{av.}$, which is the average of the three previous measurements; Z is the zeta-potential of the polymer solution, also presenting three values measured and the $Z^{av.}$, that is the average zeta-potential and the last column is the average molecular weight of the polymer, $MW^{av}$.

All procedures in the measurements were conducted with attention to avoid errors due to measurements procedures, namely contamination and manipulation of samples and testing cells. The solutions were all kept covered with parafilm, and filling of the cell was done by using syringes and a 0.45μm membrane filter, assuring always that no air bubbles were present in the measurement cells.

*Table 4-1: Polymer Characterization results.*

| Polymer | $D_z$ (nm) | $D_z^{av.}$ (nm) | Z (mV) | $Z^{av.}$ (mV) | $MW^{av.}$ (kDa) |
|---|---|---|---|---|---|
| **Amber 2001HMW** | 80,7 | 80,3 | 51,3 | 52,6 | 235,0 |
| | 80,6 | | 56,6 | | |
| | 79,7 | | 49,9 | | |
| **Amber 2002** | 75,1 | 74,7 | 49,3 | 51,2 | 158,0 |
| | 74,1 | | 48,2 | | |
| | 75,0 | | 56,1 | | |
| **Amber 2006** | 47,6 | 50,3 | 39,9 | 36,4 | 175,0 |
| | 48,5 | | 37,4 | | |
| | 54,7 | | 31,8 | | |
| **Amber 2008** | 37,3 | 36,8 | 49,1 | 48,0 | 138,0 |
| | 38,7 | | 42,1 | | |
| | 34,4 | | 52,7 | | |
| **Amber 2008HMW** | 36,3 | 35,8 | 73,2 | 72,0 | 120,0 |
| | 35,4 | | 68,1 | | |
| | 35,8 | | 74,7 | | |
| **Amber 2009** | 37,8 | 38,1 | 48,2 | 48,0 | 66,2 |
| | 38,4 | | 48,6 | | |
| | 38,0 | | 47,1 | | |
| **Amber 2013** | 46,1 | 45,3 | 20,8 | 20,1 | 160,0 |
| | 45,1 | | 20,6 | | |
| | 44,7 | | 18,9 | | |
| **Amber 2014** | 38,4 | 37,9 | 73,7 | 72,3 | 53,1 |
| | 37,9 | | 73,0 | | |
| | 37,3 | | 70,1 | | |
| **Amber MetQuat 6** | 44,4 | 44,4 | 40,5 | 52,6 | 152,0 |
| | 44,8 | | 45,8 | | |
| | 44,1 | | 42,1 | | |

In the appendix A, the graphs for size and zeta potential distributions and the molecular weight plots are presented.

For what can be observed in the results, the polyamines have the larger diameters (Amber 2001HMW, Amber 2006 and Amber 2002), and relatively higher molecular weight; all those results are obtained using a suitable concentration of the polymers in the solution, which was the most important, and also difficult, part of the characterization, finding out a proper range of concentrations to avoid polymer aggregation and to allow the equipment to perform good measurements.

For size and zeta potential the concentrations were of 0.1%, 0.05% and 0.02% w/w, being applied two minutes of ultrasound to samples before preceding to measurements. For the molecular weight, the range of concentrations used were from 1% to 0.02% w/w, but for most cases 1% was too high. In the end the most appropriated concentrations used in the trials were, for some cases beginning at 0.5%, and for all polymers the values of 0.2%, 0.1%, 0.05% and 0.02% were used. In some trials the 1% concentration was cutted off, and a new point added at 0.08%. For molecular weight measurements trials ultrasounds were just applied to the higher viscosity polymers, Amber 2001HMW, Amber 2006, and also Amber 2008HMW, the others the measurement achieved good results without needing ultrasound. The values for polymers Amber 2013 and 2014 were provided by Patricia Costa [21].

All the results met quality criteria in the Zetasizer software. As expected all the polymers presented a positive zeta-potential.

## 4.2 Standard decolorization tests results

The decolorization achieved in the laboratory decolorization trials by each polymer is here presented. These results are in offline laboratory flocculation tests in carbonated sugar liquor, provided by RAR Portugal, and proceeding along to the ICUMSA 420 method for color measurements of sugar solutions.

The decolorization was evaluated by comparing the color of the liquor submitted to the flocculation tests using the polymers, to the color presented in a carbonated liquor from the same batch of carbonatation, maintained at the same temperature for the same period of time, but without polymer addition, indicated in the results as blank. The results are presented taking into account the pH for the filtrated liquors, decolorized and blank, as required by the ICUMSA 420 method, this variable should be in the range of 7.00 ± 0,02, due to possible large changes in the color when pH of the solutions undergo significant variations. Decimal changes in the pH could imply changes of dozens ICUMSA units in the color. It should also be mentioned here that every trial for the same polymer was performed in a liquor from the same batch of carbonatation, to make a proper comparison between only carbonated liquor color and carbonated liquor using color precipitants agents.

An example of the plots of the ICUMSA color index for both, decolorized and blank liquor, is presented next (figure 4.1).

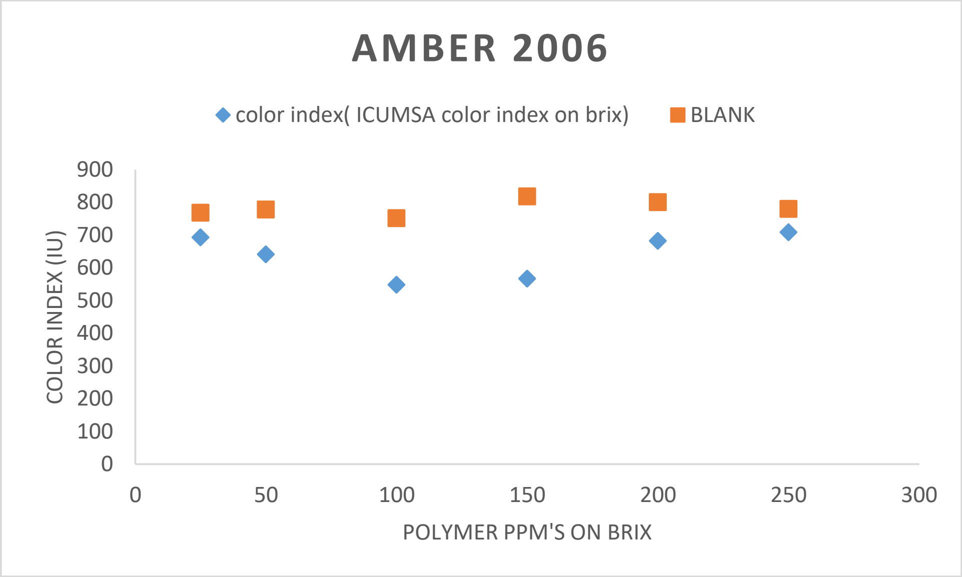


*Figure 4.1: Graphic representation of sugar liquor color (treated with polymer and blank) versus polymer dosage for tests with polymer Amber 2006.*

As shown in the plot above, the color index of the filtrated decolorized liquor has decreased to a certain amount as the dosage of the polymer increased, but at one point it goes up again, and this behavior has been presented in all trials results. Thus, we can conclude that the dosage of the polymer has a maximum, after which the color bodies return to the liquor, and in some cases it may even increase the color of the liquor [3], when flocculation stops being effective and the polymer can even contribute to redisperse the color agents by stabilizing them and contributing to keep them disperse in the liquor.

The following table presents all the decolorization performed by the polymer Amber 2006 (Table 4.2) showing that the pH of the liquor was always within the expected range. All measurements of color were performed complying to the ICUMSA 420 method, at temperature of 20°C and pH 7.00 ± 0.02, and filtrated through a 0.45µm membrane before absorbance measurements at 420 nm. The original pH of the carbonated liquor was in the range of 8.1 to 8.3, which is as expected at the second stage of carbonatation processes, being all the polymers active at this pH.

*Table 4-2: Decolorization performed by the polyamine Amber 2006.*

| pH (carbonated liquor) | pH blank. | Blank color (IU) | ppm's (polymer on Brix) | pH (decolorized) | Color (treated liquor ) (IU) | % Color Removed |
|---|---|---|---|---|---|---|
| 8,24 | 6,99 | 769 | 25 | 7,02 | 693 | 9,9 |
| 8,17 | 6,99 | 778 | 50 | 7,00 | 641 | 17,6 |
| 8,18 | 6,99 | 752 | 100 | 6,99 | 549 | 27,0 |
| 8,31 | 6,99 | 818 | 150 | 7,00 | 567 | 30,7 |
| 8,24 | 6,98 | 801 | 200 | 7,01 | 683 | 14,7 |
| 8,31 | 6,98 | 780 | 250 | 6,98 | 709 | 9,1 |

The complete tables of the results obtained in the decolorization tests will be presented in the Appendix B of this dissertation. Therefore the results of the decolorization trials performed are summarized in the next table (Table 4.3), presenting only the final decolorization percentage achieved for each polymer and for the different dosages. Another polyelectrolyte used was the Amber 2012, but its decolorization performance was not significant, so the results are not presented here but are also shown in the Appendix B.

*Table 4-3: Percentage of Decolorization per polymer and ppm dosage of polymer on Brix of the sugar liquor.*

| Polymer | 25 ppm (%) | 50 ppm (%) | 100 ppm (%) | 150 ppm (%) | 200 ppm (%) | 250 ppm (%) |
|---|---|---|---|---|---|---|
| **Amber 2001HMW** | 15,3 | 25,5 | 36,4 | 28,7 | 35,4 | 27,7 |
| **Amber 2002** | 11,6 | 18,4 | 25,6 | 14,0 | 1,6 | -6,2 |
| **Amber 2006** | 9,9 | 17,6 | 27,0 | 30,7 | 14,7 | 9,1 |
| **Amber 2008** | 15,7 | 20,1 | 31,7 | 23,9 | 14,7 | 11,9 |
| **Amber 2008HMW** | 14,4 | 20,5 | 12,9 | 8,2 | -2,3 | -10,5 |
| **Amber 2009** | 12,1 | 28,4 | 41,0 | 14,4 | 6,1 | -3,3 |
| **Amber 2010** | 3,6 | 19,8 | 21,7 | -8,6 | -7,9 | -12,6 |
| **Amber 2013** | 20,5 | 22,9 | 35,2 | 13,9 | 12,4 | -6,7 |
| **Amber 2014** | 9,2 | 23,8 | 13,7 | 7,9 | -11,2 | -15,8 |
| **Amber MetQuat 6** | 18,6 | 20,5 | 24,1 | 34,2 | 38,9 | 30,1 |

The complete results, including temperature and pH of flocculation, filtrated liquor pH at which color was measured and the respective ICUMSA color index are presented in the appendix B. the next picture (Figure 4.2) shows the filtrated liquor colors after carbonatation and after carbonatation using polymer Amber 2013 aid as color precipitant.

*Figure 4.2: the filtrated liquor blank (on the left) and treated with the polymer Amber 2013 100ppm (on the right).*

All polymers tested present good decolorization performance, having its optimal in the range of 50 up to 100 ppm, decolorization decreasing for dosages much higher than 100 ppm for most of the polymers, except for Amber 2001HMW and the novel polymer Amber MetQuat 6, that seemed to present good decolorization activity for higher dosages.

Next, the graphic representation presented (Figure 4.2) summarizes the final results achieved in the decolorization tests, presenting, for each dosage, the best performing polymer. Four of these polyelectrolytes have shown very good results in the tests, achieving, in the case of Amber 2009 at 100 ppm dosage, up to 41% decolorization when compared with the color of the filtrated liquor untreated with the polymer.

*Figure 4.3: Graphic representation of the by the best performing polymer at each dosage and respective percentage of decolorization achieved.*

At the dosages of 50 and 100 ppm the polymers Amber 2009, Amber 2013 and Amber 2001 HMW presented the highest percentages of decolorization. Thus, a few tests using a blend of these polymers were performed, to evaluate if in combination of two or three of them, they would present higher global decolorization.

Amber 2001HMW presents a high molecular weight and a large hydrodynamic diameter, but low polymer charge when comparing the MW and size of the other polymers, nevertheless, this polymer showed a good performance as color removal and flocculant. The polymers Amber 2013 showing a low charge and relatively high molecular weight showed very good decolorization performance at low dosages, 25-100 ppm, also from the flocculation monitoring presented a good result forming not much of large flocs, but resistant to breakage what can be understood as reason of its higher color removal performance. Amber 2009 is the polymer presenting lower molecular weight but shows an intermediate high charge, and low hydrodynamic diameter, showed very good decolorization action when used in dosages of 50 and 100 ppm, forming also small flocs but with good stability, from what can be seen from the continuous monitoring study. As for the novel polymer Amber MetQuat 6, this polymer presented intermediate characterization values, for molecular weight, size and charge, having good decolorization performance for a large range of polymer dosages.

The next table presents the decolorization achieved by using the blend of Amber 2001HMW, a polyamine, with Amber 2013, a poly (DADMAC), at three different dosages, 25, 50 and 100ppm, of each polymer.

*Table 4-4: Blend Amber 2013 & Amber 2001HMW decolorization performance.*

| ppm's (polymer concentration on Brix) | color index on brix (IU) | Blank Color (IU) | % Color Removed |
|---|---|---|---|
| 25+25 | 609 | 772 | 21,1 |
| 50+50 | 542 | 783 | 30,8 |
| 100+100 | 607 | 794 | 23,6 |

Comparing the values for using the polymers alone, Amber 2001HMW and Amber 2013, presented in table 4.3, and the ones obtained with the blend of the two polymers, no significant increase in decolorization is noticed. Moreover, when thinking about economic aspects is should not be suitable to use a blend in this case, but yet further studies should be performed, to understand if the polymers interfere with each other or if this output is due to the polymers targeting the same color compounds and thus competing with each other. Refining the polymer's dosage, should also be considered, especially studying the range below 50 ppm.

*Table 4-5: Blend Amber 2009 & Amber 2001HMW decolorization performance.*

| ppm's (polymer concentration on Brix) | color index on brix (IU) | Blank color (IU) | % Color Removed |
|---|---|---|---|
| 25+25 | 614 | 772 | 20,5 |
| 50+50 | 562 | 790 | 28,9 |
| 100+100 | 598 | 821 | 27,2 |

In table 4.5, the decolorization results reached by using the blend of Amber 2001HMW and Amber 2009 are shown. For the low dosage of 25 ppm, of each polymer, the mixture shows better results than using the polymers alone, comparing to table 4.3 results, but for higher dosage this does not happen. The fact that a low dosage leads to a color removal around 20% may be economically interesting.

Next, the result of testing a blend of the three polymers are presented in the following table (Table 4.6):

*Table 4-6: Blend using Amber 2013, 2009 & Amber 2001HMW decolorization performance.*

| ppm's (polymer concentration on Brix) | color index on brix (IU) | Blank Color (IU) | % Color Removed |
|---|---|---|---|
| 25+25+25 | 642 | 887 | 27,6 |
| 50+50+50 | 568 | 847 | 32,9 |
| 100+100+100 | 620 | 834 | 25,7 |

Again using a 25 ppm dosage, of each polymer, presents higher decolorization with the mixture than with the polymers alone. Also the 50 ppm dosage, of each one, shows higher decolorization than when using of the polymers alone.

The objective of testing these blends was to see if they improved the color removal, considering possible that the different polymers will present affinity to different color compounds in the solution, increasing, this way, the decolorization of the liquor in global.

The range around 25 ppm dosage should be better studied along with the economic aspects, to analyze the convenience or not of this methodology. Moreover, for this dosage, the decolorization achieved comes close to the best results achieved with the single polymers for a dosage of 100 ppm.

## 4.3 Determination of Index value

As said in the previous chapter, the Index Value is an important parameter to evaluate the types of colorants present in the liquor, related to the molecular mass of such color bodies. As an attempt to observe, using this parameter, if the color precipitants are removing more of the high or the lower molecular mass color components of the sugar liquor, a few trials were performed with the four best decolorization performing polymers. An example of the variation of the IV with polymer dosage is presented in the figure 4.3, in this case for the polymer Amber 2001HMW.

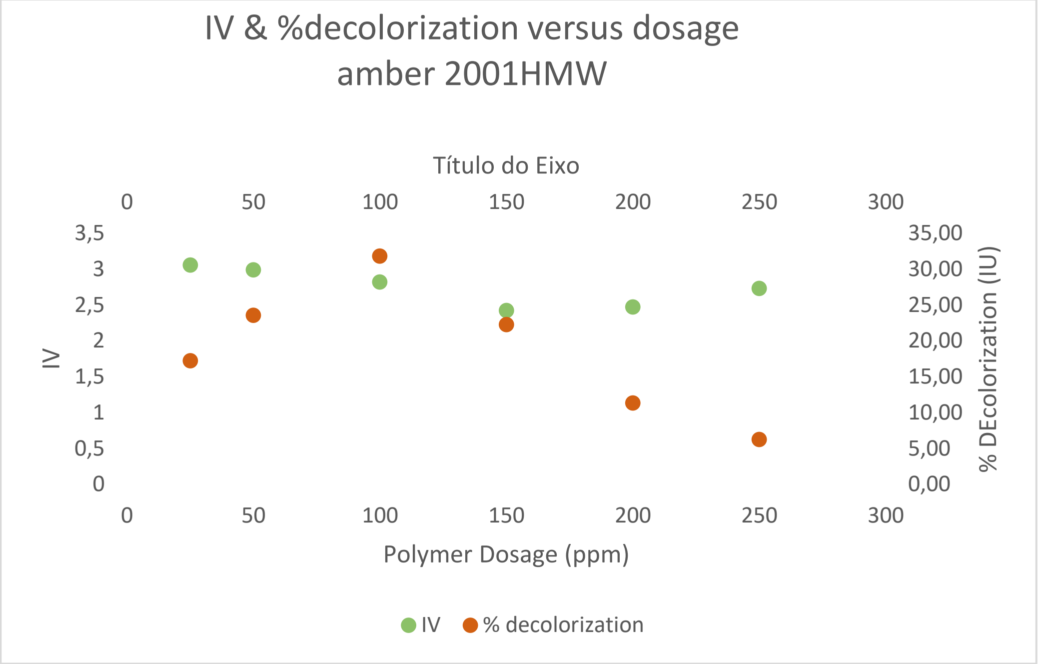


*Figure 4.4: Representation of Index Value and decolorization for filtrated liquor by decolorization with Amber2001 HMW.*

The IV for the filtrated sugar liquor after decolorization by the polymers is presented in the next table (Table 4.7). The index value of the carbonated liquor, before decolorization treatment with the polymers, was also measured being that the IV for the liquor used on the Amber 2001HMW tests was of 3,03, while the IV for the liquor used on trails with the other polymers was 2,89. The difference of those two IV is related to the origin of the liquor, which came from different carbonatation batches, as well as different raw sugar origins, as they were collected in different periods.

*Table 4-7: Index value (IV) for filtrated sugar liquor by ppm of polymer used.*

| Dosage (ppm) | Amber 2001HMW | Amber 2008 | Amber 2009 | MetQuat 6 |
|---|---|---|---|---|
| **Blank** | 3,03 | 2,89 | 2,89 | 2,89 |
| **25** | 3,06 | 2,99 | 3,19 | 3,10 |
| **50** | 2,99 | 3,01 | 3,14 | 3,04 |
| **100** | 2,82 | 3,05 | 3,28 | 3,26 |
| **150** | 2,43 | 3,14 | 2,93 | 3,36 |
| **200** | 2,47 | 2,94 | 2,71 | 3,12 |
| **250** | 2,73 | 2,78 | 2,90 | 2,95 |

The index value should be evaluated along with the decolorization performed by the polymers, and so, from the previous section, the decolorization was most effective till 150 ppm dosage for all polymers, except for Amber 2001HMW and MetQuat 6, that still showed good decolorization at higher dosage than 150 ppm (table4.3).

Looking at the results in table 4.7, the polymer Amber 2001HMW presented a reduction on the index value, along with the increase of the dosage, the same happening to the decolorization percentage up to 100 ppm (see Table 4.3). The opposite occurred for the polymers Amber 2008, Amber 2009 and the novel polymer MetQuat 6, for which no reduction on the IV was observed, instead of it, the IV increased, but for high dosages it decreased again, reaching values around that presented for the untreated liquor.

As mentioned by Bento [6, 7], high molecular weight color particles exhibit low Index Value, while low molecular weight color bodies show IV higher than five. It can be then understood that, if the index value of the overall solution reduces, higher IV colored compounds are being removed while if it grows lower values IV compounds are removed. So, here there is a possibility that the polymer Amber 2001HMW is removing low molecular weight colored compounds, while the others may remove better the higher molecular weight color bodies in the solution and thus the increase in the IV. In the case of Amber 2001HMW this agrees with the maximum decolorization within the range of 100-150 ppm.

This study alone is not enough to state surely if the polymers are removing better low or high molecular weight color compounds, thus a more profound study is required, using other analytical techniques, such as chromatographic and other techniques used by Bento [2, 6, 7].

## 4.4 Flocculation monitoring using LDS

In this section will be presented the results obtained by LDS (Laser Diffraction Spectroscopy) online monitoring of the flocculation process using some of the best performing polymers tested in the decolorization laboratorial trials. The results are presented as the kinetics plots of the flocculation process, showing the variation of the particles size indicator, d10, d50 and d90 for the suspension. The first one implying information about the evolution of the smaller particles, while the last one is related to the evolution of the large particles resulting from the flocculation process.

As mentioned earlier, in the previous chapter, those trials were performed using carbonated liquor, the same used in the decolorization trials, but here it had to be diluted in 1:5 in distilled water, in order to reduce the obscuration of the laser light in the Mastersizer 2000, allowing then the measurement of particle size and the size distribution in the colloidal suspension.

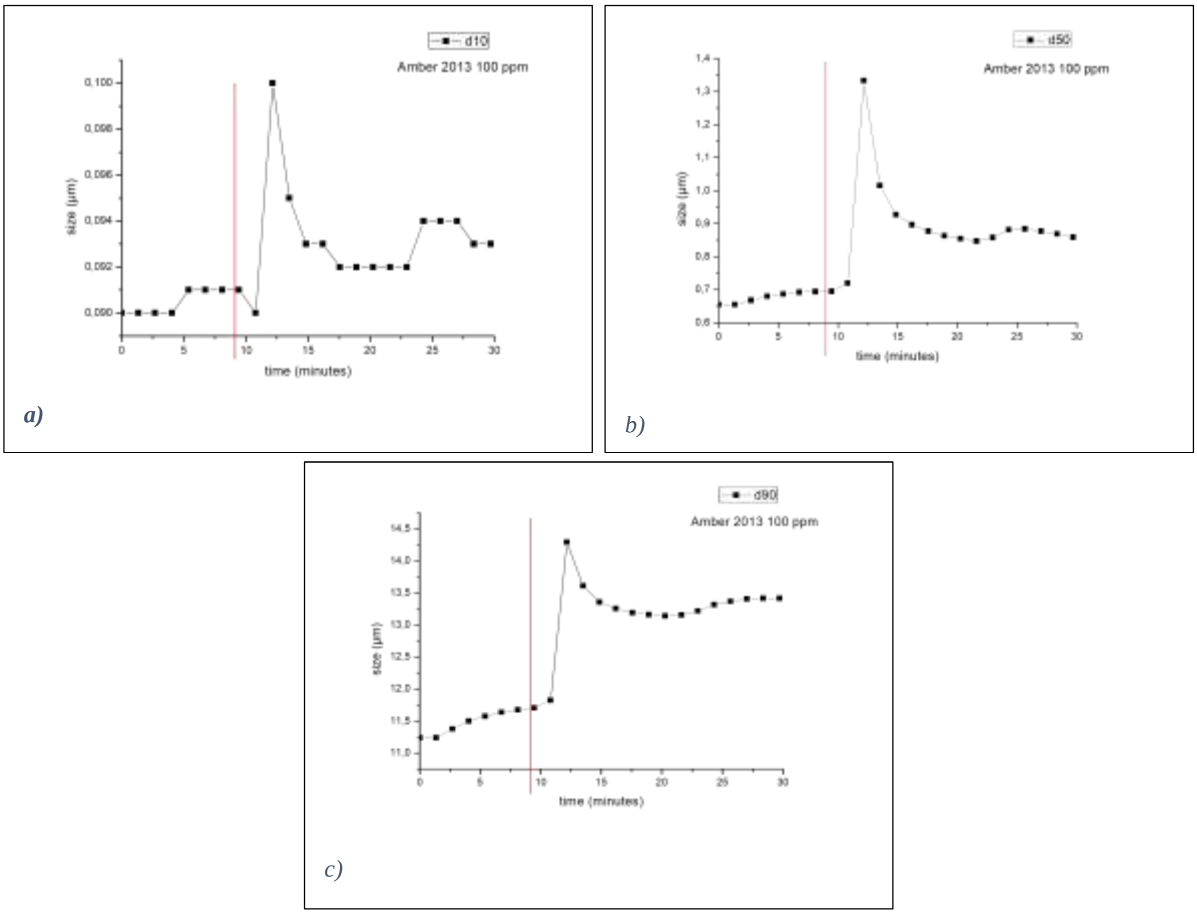
The next table (Table 4.8) presents the list of the polymers used in those trials, the dosage in ppm based on the degree of Brix of the sugar solution, the time for the monitoring and the decolorization percentage obtained at the end of the flocculation, being the decolorization based also on the color measured following the ICUMSA 420 analytical method [4].

*Table 4-8: List of polymers used in LDS tests, its dosage, time of flocculation and decolorization percentage at the end of trials.*

| Polymer | Dosage ( ppm on brix) | Time (min.) | Decolorization % |
|---|---|---|---|
| Amber 2013 | 100 | 30 | 24,9 |
| Amber 2001HMW | 100 | 15 | 20,2 |
| Amber 2001HMW | 100 | 30 | 18,4 |
| Amber 2001HMW | 200 | 30 | 16,6 |
| Amber MetQuat6 | 100 | 30 | 16,8 |
| Amber 2008 | 100 | 30 | 17,2 |
| Amber 2009 | 100 | 30 | 24,3 |
| Blend Amber 2001HMW+2009 | 100+100 | 30 | 30,2 |
| Blend Amber2013 + 2001HMW | 110+100 | 30 | 30,9 |
| Blend Amber2013 +2009+ 2001HMW | 50+50+50 | 30 | 24,7 |
| Blend Amber2013 +2009+ 2001HMW | 100+100+100 | 30 | 29,2 |

For the Amber 2001HMW at 100 ppm dosage, the color of the filtrated liquor was measured after fifteen and thirty minutes of the polymer addition to the liquor, to evaluate if significant difference is shown in the color of filtrated liquor, following the ICUMSA 420 method.

The kinetic curve for the flocculation in the diluted carbonated sugar liquor, using the different polymers and for 30 minutes of monitoring will be shown next. The kinetic curves are presented for the three size indicators, d10, d50 and d90.



a)

b)

c)

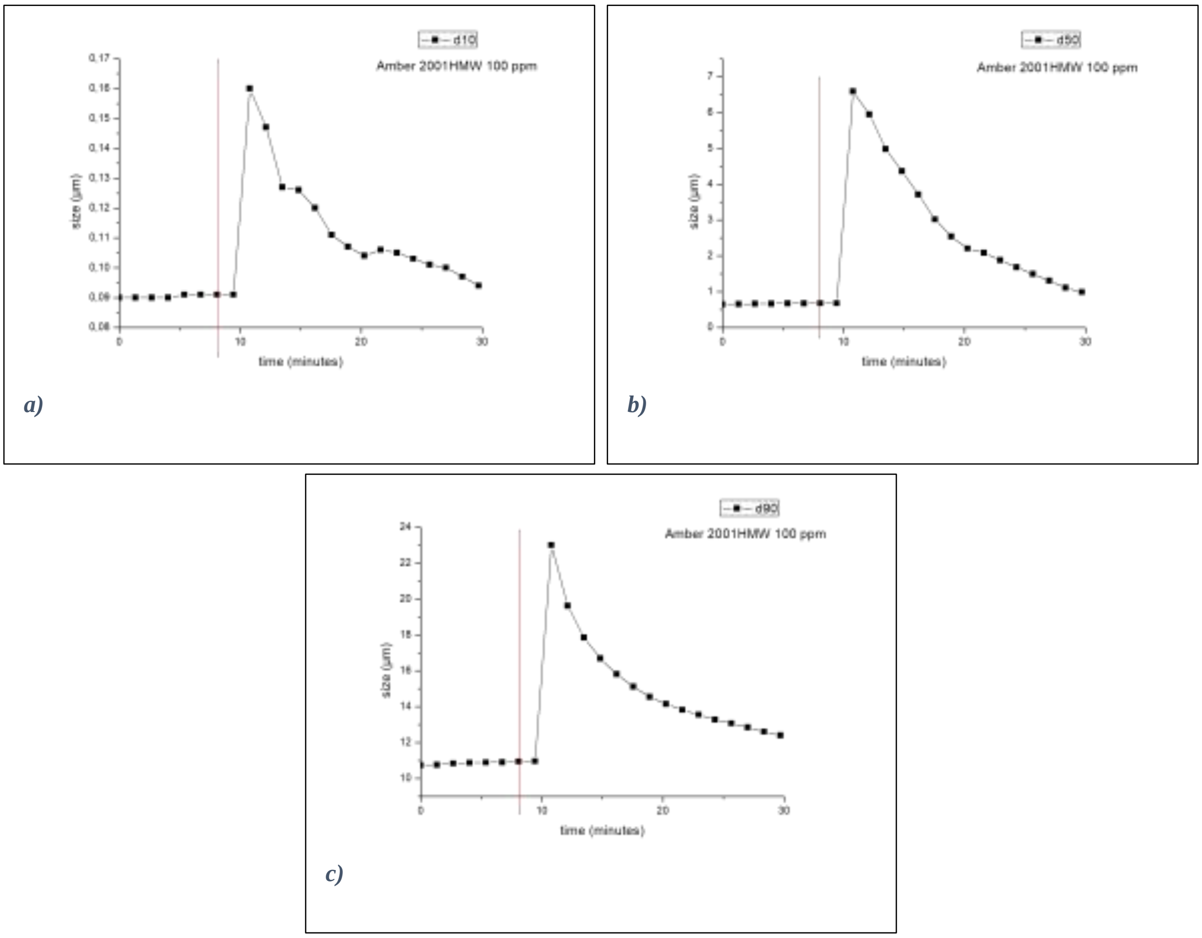
*Figure 4.5: Flocculation kinetics for carbonated sugar liquor using Amber 2013 at 100ppm dosage: a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

The red lines in the graphics represent the point where the polymer was added to the system, after what it can be seen that the size has a step increase, short time after the polymer addition. Even if the polymer was added careful and slowly to the system, it induces immediately formation of flocs, which are bigger at beginning. As time goes the size reduces, reaching a stabilization value, this happens for all the polymers tested, and can be understood as result of the hydrodynamics of the system. As time passes, flocs break and reconfirm, forming smaller ones. The time and speed of agitation are the parameters which have a significant influence in the flocculation process. At the end of 30 minutes the size parameters d10, d50 and d90, for all the polymers tested, show always larger particles than before the addition of the polymer, confirming that flocculation occurred, even if this increase is more pronounced for some of the polymers (Amber 2013, MetQuat 6 and Amber 2009).

The figure 4.5 presented before refers to the polymer Amber 2013, at 100 ppm on brix dosage, and for what can be seen after 30 minutes of test monitoring the final size shown in the parameters d10, d50 and d90 is bigger than in the begin, and after this time color measured shows a good decolorization in the filtrated liquor (Table 4.8). This polymer presents an relatively high molecular weight and low charge(table 4.1), and from the kinetic curve seems like the flocs formed are not so much bigger but compact enough to be noticed even after the 30 minutes of monitoring.

Tests with higher dosage, 200 and 300 ppm, for this polymer were performed but as the results does not show significant differences comparing to the 100 ppm dosage, and the color removal is lower, the graphics will be presented in the appendix C.

Following will be presented the graphics for Amber 2001HMW (Figure 4.6), a high molecular weight polyamine, for a dosage of 100 ppm on brix of the sugar solution. Test was conducted at the same conditions and specifications as the previous trial with Amber 2013.



*a)*

*b)*

*c)*

*Figure 4.6: Flocculation kinetics for carbonated sugar liquor using Amber 2001HMW, at 100ppm dosage: a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

Comparing to the previous polymer, Amber 2013, this polyelectrolyte presents larger hydrodynamic diameter, as well as higher molecular weight and zeta potential (see table 4.1

previous section), and for what can be seen in the plots the size of flocs formed initially after polymer addition are larger as expected. The larger initial flocs might be related to possible bridging flocculation with calcium carbonated bonded to color bodies, which later undergoes breakage e reorganization. Thus, in the end, since breakage may be more pronounced for this polymer due to its higher molecular weight, the final flocs size decreases a lot, the final values being similar or smaller than the ones obtained with Amber 2013, also decolorization is higher with Amber 2013.

A trial for Amber 2001HMW at 200 ppm dosage was also performed, and the resulting kinetic curve is plotted next, as decolorization is yet good at this dosage, this test aimed to evaluate if the final size was also affected (Figure 4.7).

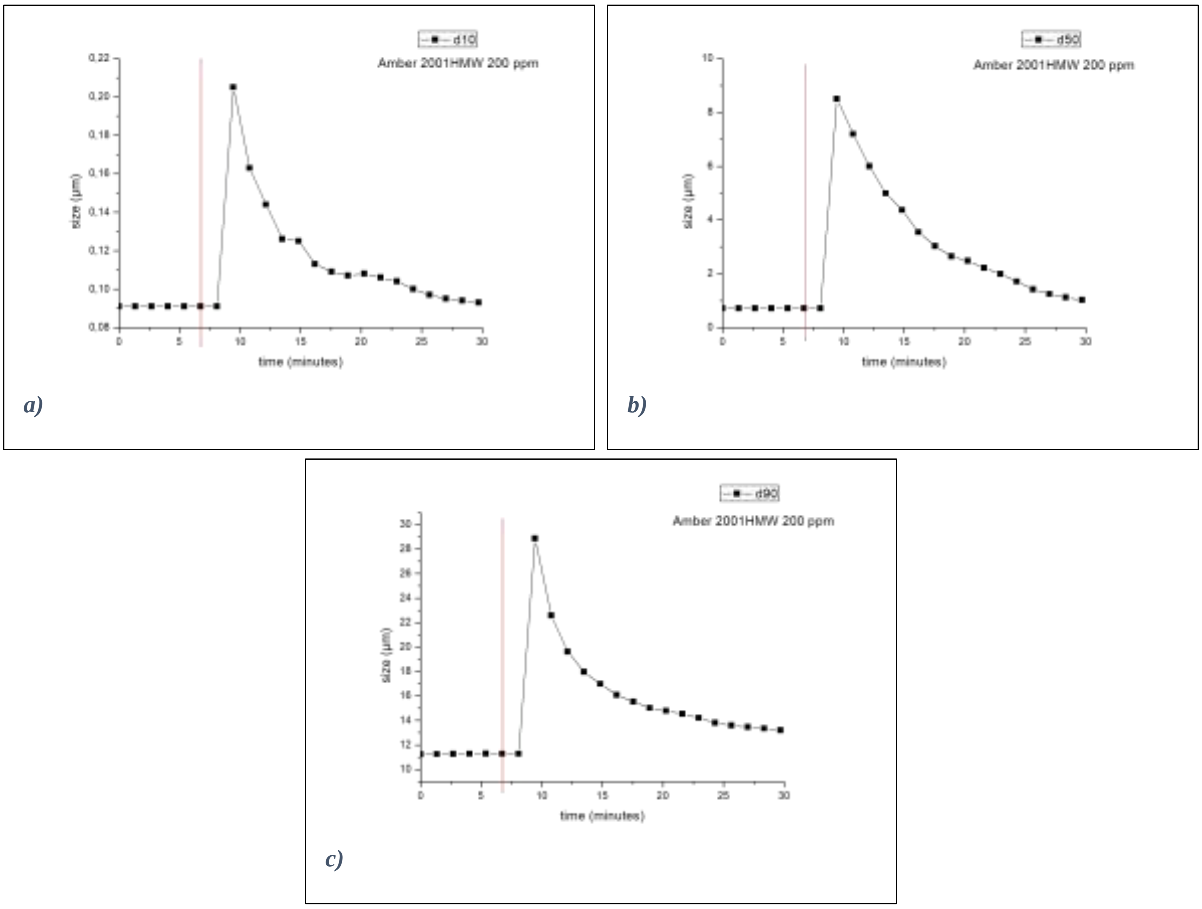


*Figure 4.7: Flocculation kinetics for carbonated sugar liquor using Amber 2001HMW, at 200ppm dosage: a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

Those results are similar to the ones obtained for the100 ppm dosage of the same polymer, even if the color removal is slightly lower. The flocs at the beginning of flocculation are slightly larger with this dosage, but after the thirty minutes of flocculation the sizes are similar (probably breakage was more pronounced and thus the slightly lower color removal).

For the polymer Amber 2001HMW more tests were performed, using dosages of 300, 400 500 and 600 ppm, and longer time of flocculation

Above 300 ppm color removal was ineffective, and flocculation kinetic curves did not show appreciable differences (see appendix C).

Next the result for the flocculation kinetics using the novel polymer, Amber MetQuat6, is presented (Figure 4.8). The flocculation was proceeded in the same conditions as for the previous polymers.

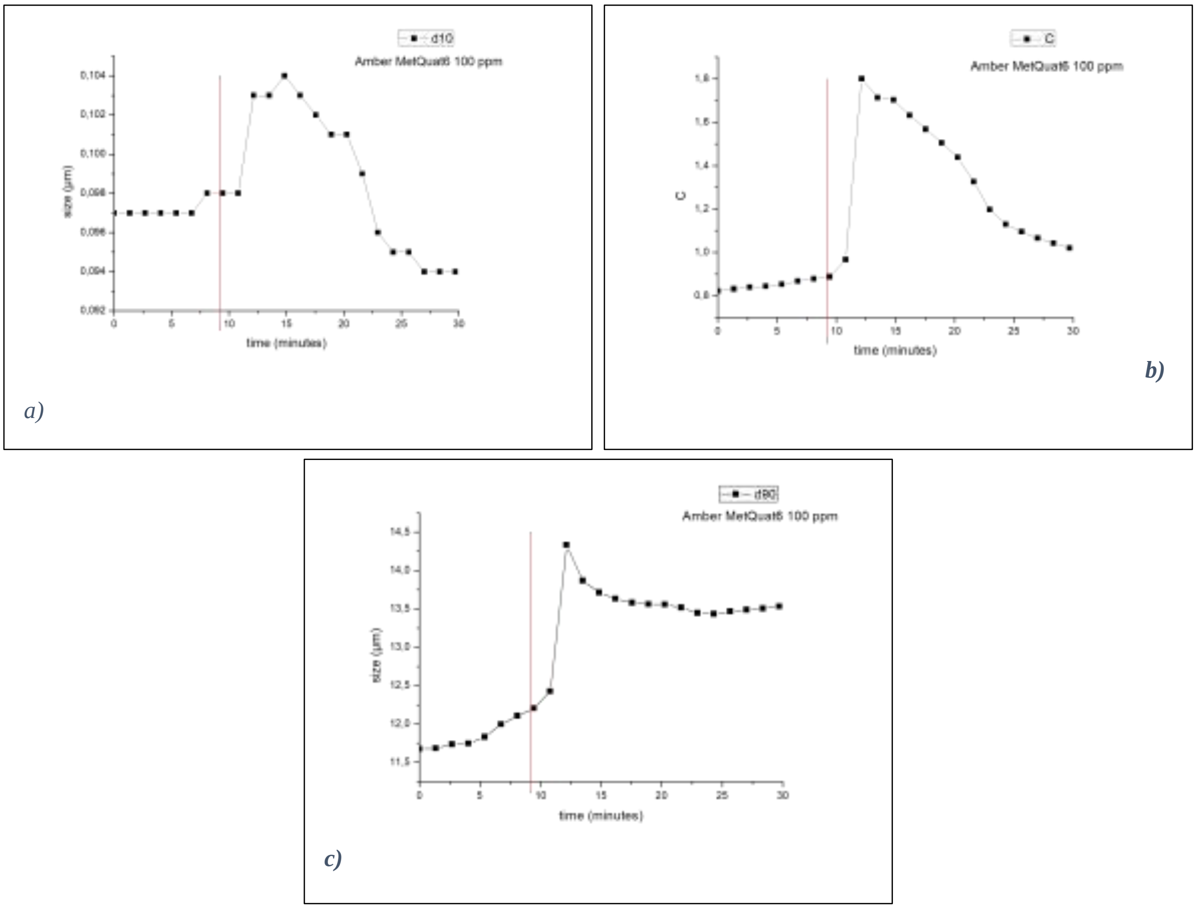


*Figure 4.8: Flocculation kinetics for carbonated sugar liquor using Amber MetQuat6 at 100 ppm dosage: a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

The polymer Amber MetQuat 6 presents significant shifting in the particle size, for all parameter monitored, that is indicative of higher flocculation, especially evident when looking at the kinetics of d90 evolution, as well as appreciable decolorization for the time of the test. Apparently the initial step increase is not as large as for Amber 2001HMW, but it stabilizes for a much higher value of d90. In the offline trials for decolorization this polymer showed good decolorization activity also at different dosages higher than 100 ppm.

Similar to Amber 2013 this polymer has a lower molecular weight, and a higher charge than Amber 2013, and thus the flocs obtained must be more compact and not so exposed to breakage.

In the following graphic, (Figure 4.9), the kinetic curve for the poly (DADMAC) Amber 2008 is presented for 100 ppm dosage and the same flocculation conditions as for the previous polymers.

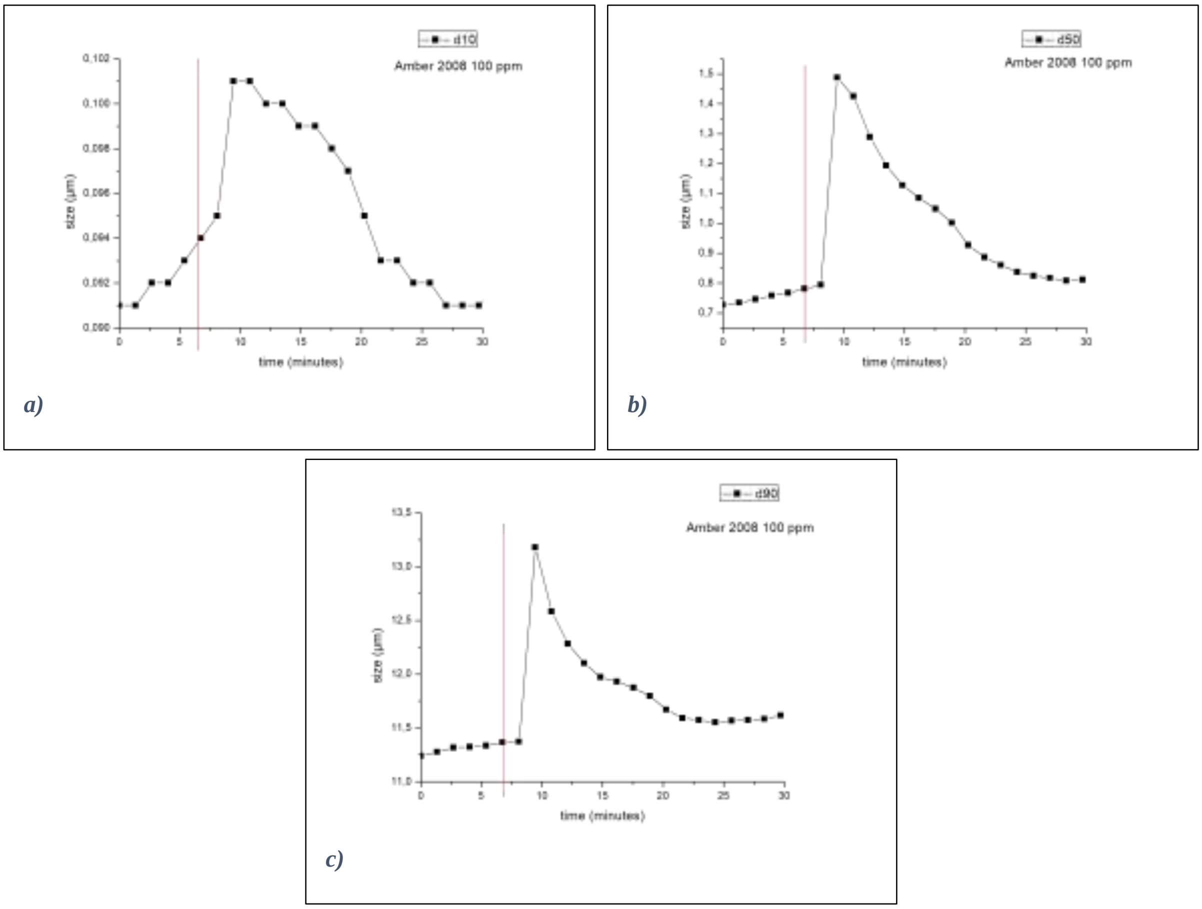
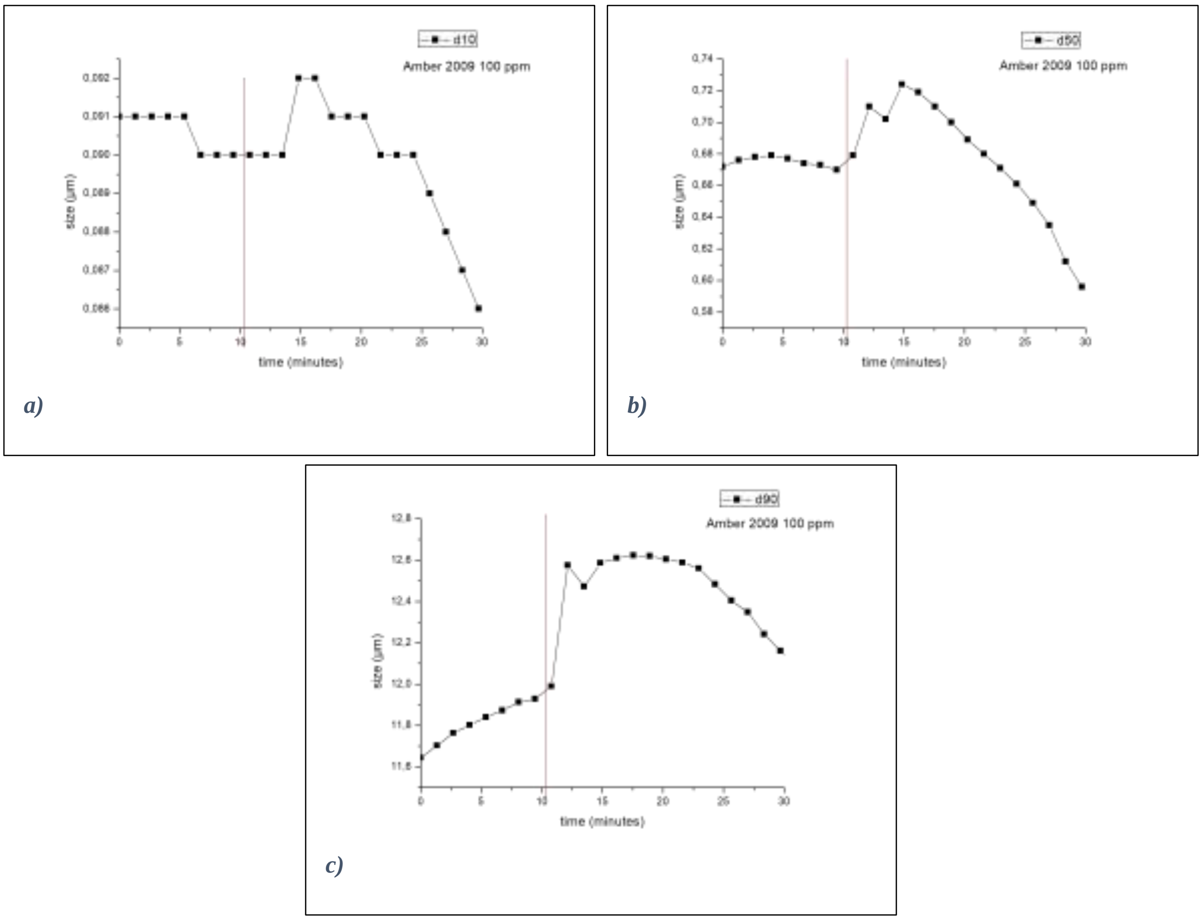


*Figure 4.9 Flocculation kinetics for carbonated sugar liquor using Amber 2008 at 100 ppm dosage: a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

This polymer presented good decolorization activity in the offline decolorization laboratory tests for the time of fifteen minutes, but for thirty minutes it is not as good result as the previous one, the color removal activity decreasing with time of flocculation. In fact the size values presented in the kinetic curves after 30 minutes of flocculation are not so significantly different from the initial ones, which agrees with the low decolorization achieved for 30 minutes. The behavior of this polymer and the polymers characterization is not clear.

In the next graphic set(Figure 4.10), the curves for Amber 2009, a poly(DADMAC), are shown. This is one of the best polymers tested for the dosage of 100 ppm, according to the results showed before, table 4.3 of this chapter and table 4.8. The kinetic flocculation curves shown in Figure 4.9 present an atypical behavior, comparing to the other polymers used, showing that for d10 and d50 after twenty minutes of the test those values are smaller than in the beginning of the test, where no polymer was added. This may result from some inhomogeneity of the initial liquor, comprising sucrose, color compounds and calcium carbonate crystals, which were later redispersed. Still flocculation obvious when looking at the d90 evolution, which agrees with higher decolorization obtained with this polymer.

Even if flocculation may be difficult with this polymer due to its lower molecular weight, considering the polymer charge the flocs obtained must be compact and resistant to breakage, which agrees with the higher decolorization percentage.



*a)*

*b)*

*c)*

*Figure 4.10: Flocculation kinetics for carbonated sugar liquor using Amber 2009 at 100 ppm dosage: a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

After presenting the individual polymers kinetic tests, the next step is to present the graphic results when blends of two and three of the previous polymers were used, to compare the kinetic curves and size indicators obtained.

The first combination was a blend of 100 ppm of Amber 2001HMW polyamine with 100 ppm of Amber 2013, poly (DADMAC). From the IV tests, it is seems that those polymers may target different color bodies, what supposedly will increase decolorization, still it does not imply a decolorization performance equal to the sum of that achieved by each polymer individually. The kinetic curves are shown if figure 4.11:

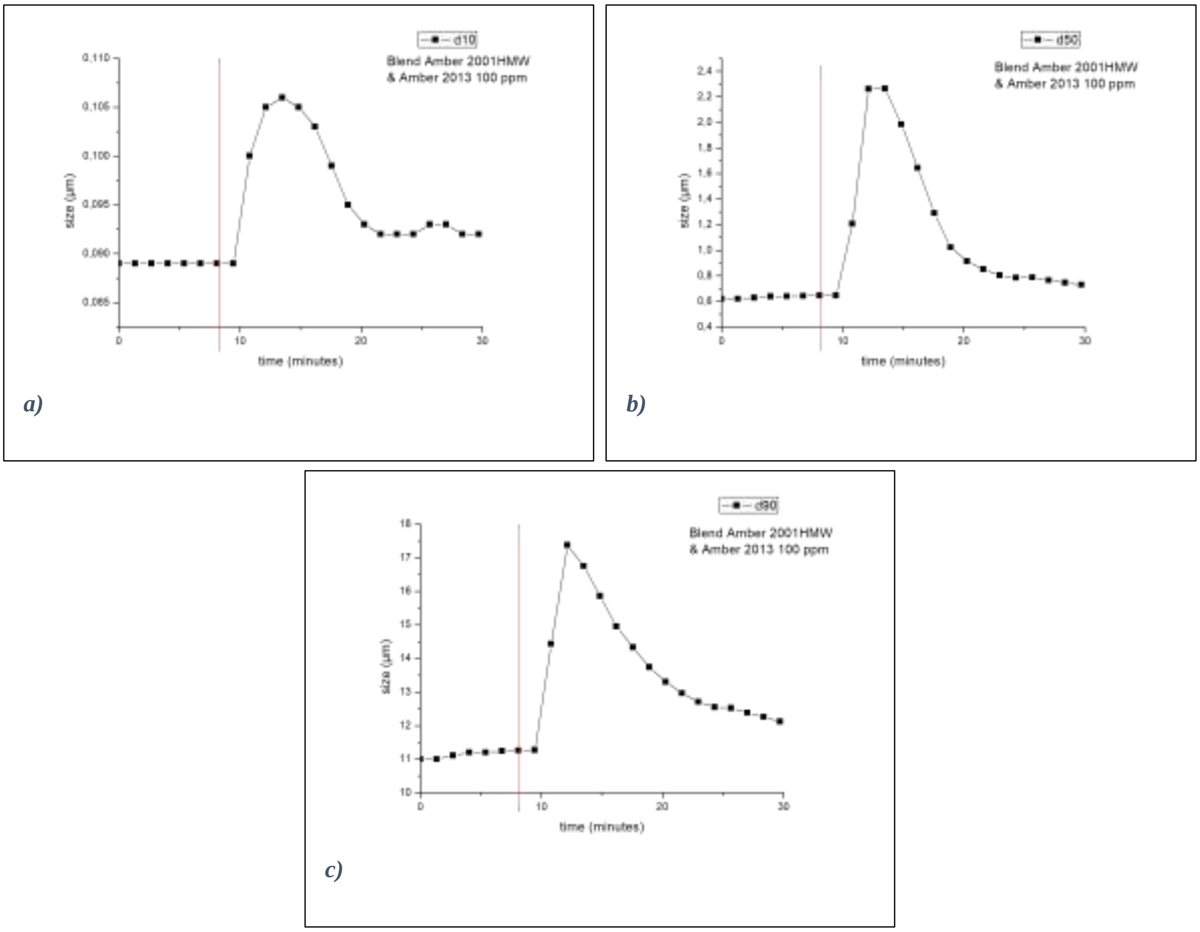


*Figure 4.11: Flocculation kinetics for carbonated sugar liquor using the blending Amber 2001 HMW & Amber 2013 at 100 ppm dosage of each polymer: a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

Comparing to the graphics presented before for the individual polymers at 100 ppm (Figures 4.5 and 4.6), the values of D50 and D90, obtained with blend are between those for Amber 2013 and Amber 2001HMW, what is here interpreted as that both polymers are active as color precipitation agents. The final color removed is in the order of 30%, which is a good value, higher than the polymers alone, but also not equal to the sum of the decolorization achieved individually. The fact that, in total, the sum of the concentrations of the two polymers has increased twice the value used previously with the individual polymers, may have enhanced flocculation.

A similar test was then performed for another blend, using this time another poly (DADMAC), Amber 2009, and again Amber 2001HMW, both at a 100 ppm dosage referred to the content of sucrose in the solution. The results are shown in the next graphic, figure 4.12:

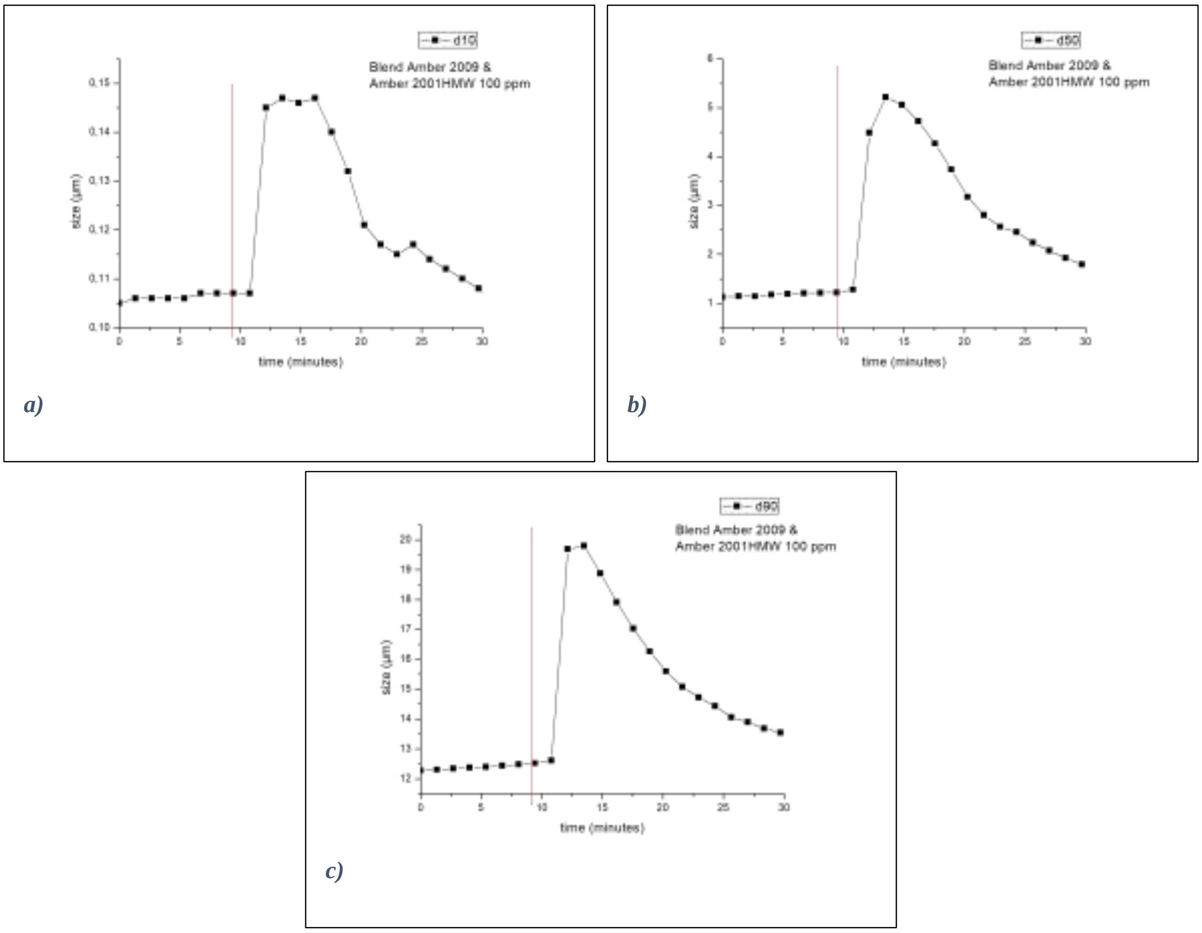


*Figure 4.12: Flocculation kinetics for carbonated sugar liquor using Amber 2009 and Amber 2001HMW, both at 100ppm: a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

Here it can be observed again that the size parameters are similar to that for the blend with Amber 2013. However, it seems that flocculation is not yet fully stabilized, aggregation still going on after 20 minutes. Also the values of d10, d50 and d90 at the begin of flocculation are in the range between those for the flocculation using the two polymers individually. Finally decolorization percentage is also in the order of 30%, higher than when suing the polymers individually, suggesting that the two polymers are active as color precipitants in the flocculation process. The combination of a low and a higher molecular weight polymer may beeffective in color removing.

Finally, the blending of the three polymers, Amber 2001HMW, Amber 2013 and Amber 2009 was tested, this time for lower dosages, 50 and 100 ppm based on the brix degree of the filtrated solutions.

First the kinetic curve for using 50 ppm of each polymer in the blend is presented in the figure 4.13, the test having been carried out in the same conditions as in all the others before.

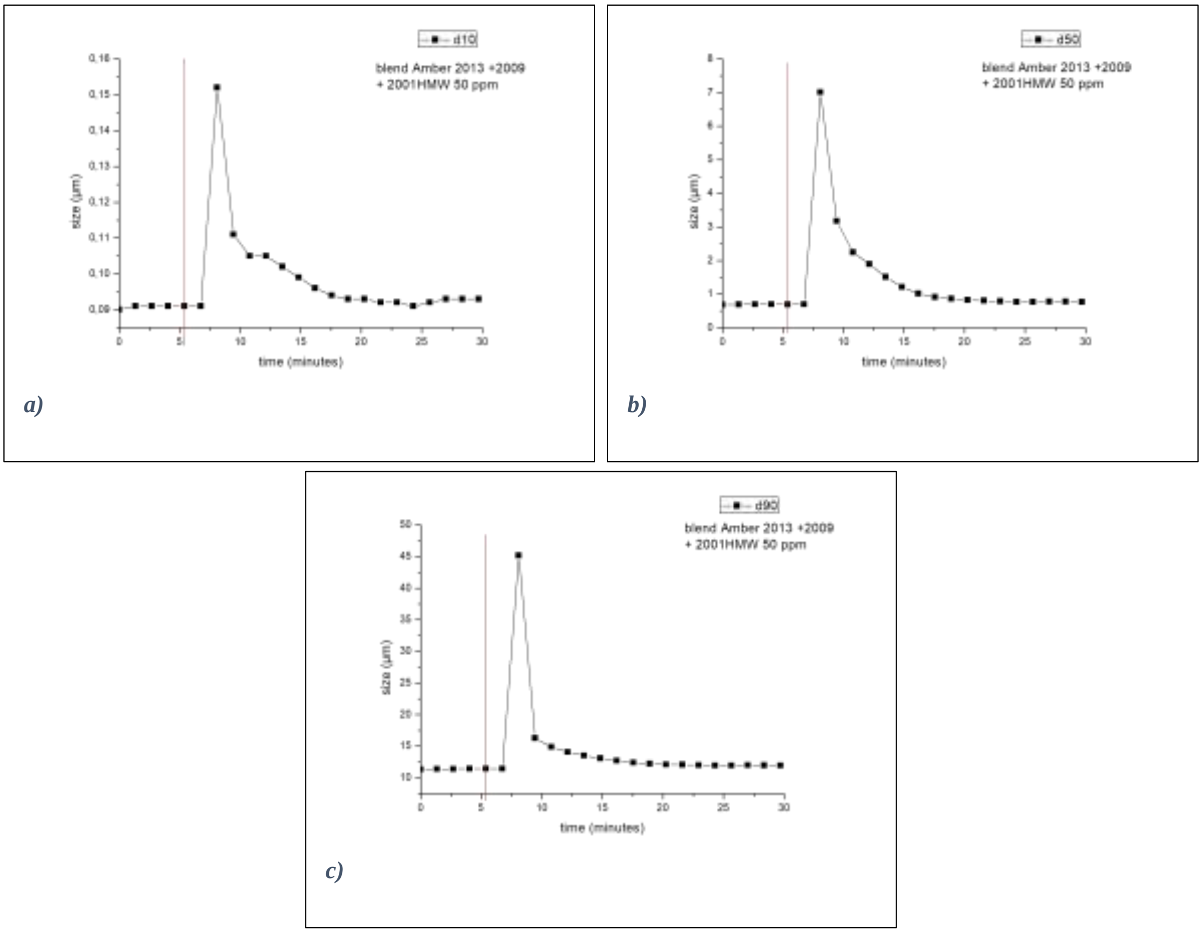


*Figure 4.13: Flocculation kinetics for carbonated sugar liquor using Amber 2009, Amber 2013 and Amber 2001HMW, at 50 ppm each one, a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

Looking at the graphic representations, what first calls the attention is that the size parameters d10, d50 and d90 values all go up to a sharp pic, more like a pulse, decreasing more quickly to what seems a more stable size. The d90 shows a much higher pulse after addition of polymer than in the previous tests, but decreases in the next point to a value in the range of the trials with two polymers blends, below 20µm. The pulse intensity is related to the addition of the three polymers blend but the following points are between the values for Amber 2001HMW and the two poly(DADMAC), confirming the activity of the polymers used. The final decolorization was in the order of 24% after 30 minutes of the test, lower than when using the two polymers blends.

The nest graphics, figure 4.14, presents the resulting kinetic curve for the flocculation using the blend of the same three polymers, Amber 2001HMW, 2013 and 2009, again but this time using higher dosage, 100ppm of each polymer.

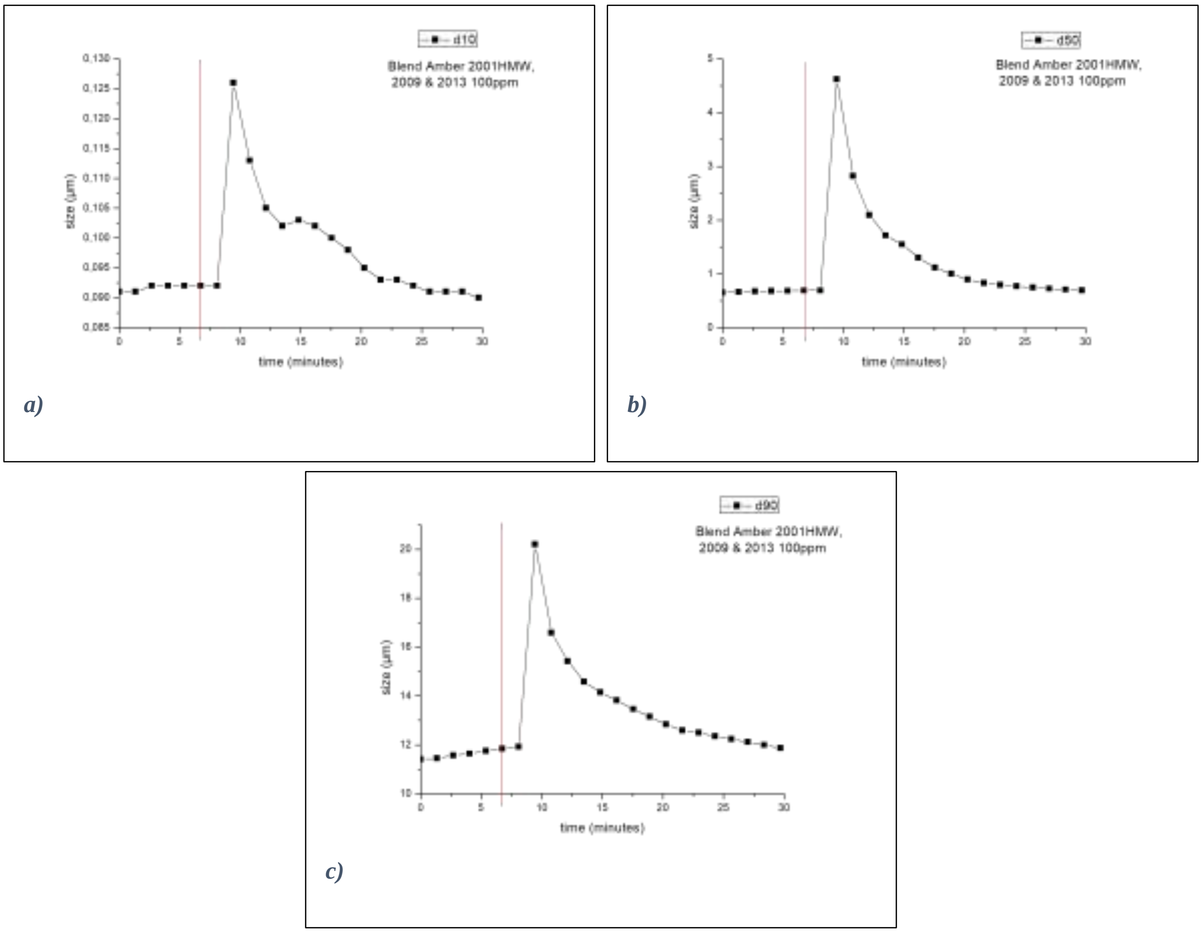


*Figure 4.14: Flocculation kinetics for carbonated sugar liquor using Amber 2009, Amber 2013 and Amber 2001HMW, at dosage of 100ppm each polymer, a) d10, b) d50 and c) d90. The bar line corresponds to the addition of polymer.*

The kinetic curve presented above are similar to that presented in the figure 4.12, but the shape is a little different, showing slower decreasing in the size values. Also in the d90 curve the larger pic presented before at around 40µm does not appear, it is here more smooth, decreasing more slowly to a stable value which maybe attribute to an overall higher concentration of the polymers blend. Values for the final diameters are slightly higher than that of the poly

(DADMAC)’s alone, but below the values presented for Amber 2001HMW individually. The d90 value is slightly higher in this case than when a lower concentration was used, suggesting that 50 ppm of each polymer maybe too low concentration for effective flocculation. In fact, the decolorization achieved here, after 30 minutes was in the order of 29%, higher than when using only 50 ppm of each polymer.

Overall analyzing the results of the polymers blends it may be interesting to use blends of two complementary polymers, while the three polymers blends do not appear very effective. Also, in general, it seems possible to conclude, from the results in this section, that for decolorization to be effective it is not necessary to produce very large flocs. The results shown that decolorization is more effective with not too large, but more compact flocs not so much affected by the breakage.

# Chapter 5. Conclusions and future works

## 5.1 Conclusions

The present study had as main objective to evaluate the performance of cationic polymers as color removal agents in the sugar refining process, and to try establish correlations between performance and the polymers characteristics, namely, molecular weight, zeta potential and hydrodynamics radius.

After a tentative to understand and correlate the results, regarding polymers characteristics, their performance as color removal and also the continuously monitoring of the flocculation process induced by those polymers in sugar carbonated liquor, the following conclusions were reached:

- Regarding the color removal, all the polymers showed activity, being some of them able to perform good color removal, up to 41% over carbonated liquor color, being the polyamine Amber 2001HMW, the poly(DADMAC)'s Amber 2013 and Amber 2009 and the novel polymer Amber MetQuat 6 the the ones showing the better decolorization performance;
- The dosage most effectives were between 25 and 100 ppm on brix of solution, used in the second stage of carbonatation process conditions, temperature around 80ºC and pH 8-8,5 and after 15 minutes of flocculation it was possible to reach higher color removal in the tests performed;
- For what could be observed about the changings in the Index Value of the solutions after decolorization using the polymers, the Polyamine showed a reduction in the value of IV, while the poly(DADMAC) increased the IV, as well as the MetQuat 6, based on this it is possible infer that the Amber 2001HMW removes more high IV colorants from the liquor, while the DADMAC's and MetQuat remove lower IV colorants;
- After testing some blends of polymers to perform decolorization, in dosages of 50 and 100 ppm of each polymer. It showed higher decolorization than using one polymer alone, 50 ppm of Amber 2001HMW with 50 ppm Amber 2009 or Amber 2013 showed good color removal action in the liquor. By the IV tests performed for the polymers the poly(DADMAC) and polyamines seem to have different affinities with the different types of colorants;

- Relating the polymer’s characteristics and color removal performance, it showed that best performing polymers are characterized by having a high molecular weight with a moderate polymer charge, and polymers having a medium molecular weight that present higher polymer charge;
- The online monitoring of the flocculation process using LDS, with a stirring speed of 1200 rpm, showed evidence of flocculation activity of the polymers. Observing the kinetics of the flocculation, after 10 minutes of flocculation the flocs breakage and reflocculation are predominant, and after 15 minutes flocs breakage went on increasing and, with this, color molecules seam to return to the liquid, as the liquor showed higher ICUMSA color index. This strategy allowed to perform a better understanding of the polymer action, enlightening some parameters to be improved in the process;
- The total color removal promoted by the addition of the polymer was in the range of 30-41% in the carbonated sugar liquor, with dosage of polymers between 50 and 100 ppm on brix of liquor;
- Some major factors affecting the color removal in the carbonated liquor were identified as the pH, time of reaction of the flocculants with the solution, besides stirring speed, polymer molecular weight and charge;
- Poly(DADMAC) seems to perform good decolorization for all the polymer tested(different molecular weight polymers).

## 5.2 Future works

After the present study and observations along it, some points should be further addressed, which can have a deeper impact in the technology in the future, to know:

- Perform deeper study with high molecular weight polyamines having high-moderated charge for the polymer, and medium molecular weight poly(DADMAC) that present medium to high polymer charges;
- The dosage of those polymers should be tested and screened from 25 to 100 ppms on brix dosage, and blending could be tested in range of 10-50 ppm dosage of each polymer;
- From the IV information obtained in this study maybe the blending of polyamines and poly(DADMAC) could be an interesting solution, and promote higher decolorization but, yet, economic impact should be evaluated;

- Testing slower stirring speeds and in the time interval of 10 to 15 minutes in the flocculation monitoring process, to see if any improvement in decolorization can be achieved;
- An economic study to screen the polymers used, their color removal activity, and the impact on the saving in secondary decolorization processes, as well as to estipulate the most appropriated dosage relating decolorization activity and economical cost should be performed;
- The LDS technic can be used to enlighten some factors of the process, so further study on the flocculation kinetics should be performed in the carbonated liquor, to try to understand better the flocculation mechanisms involved in relation with the polymers characteristics. For that a better control of the system refining temperature, agitation and dilution will be important, or better yet, to find a way to perform simultaneously a carbonatation flocculation monitoring, to understand the influence of the carbonatation along the flocculation promoted by the polymers, where agitation would be promoted by gas bubbling in the system, what can reduce flocs breakage, even if some other monitoring technique rather than LDS would have to be used;
- Understand better the relation between the characteristics of the flocs obtained and the performance influence in the subsequent operations in the refining process.

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# Appendix

# Appendix A. Polymer Characterization

## A.1 Size distribution by intensity for the polyelectrolytes

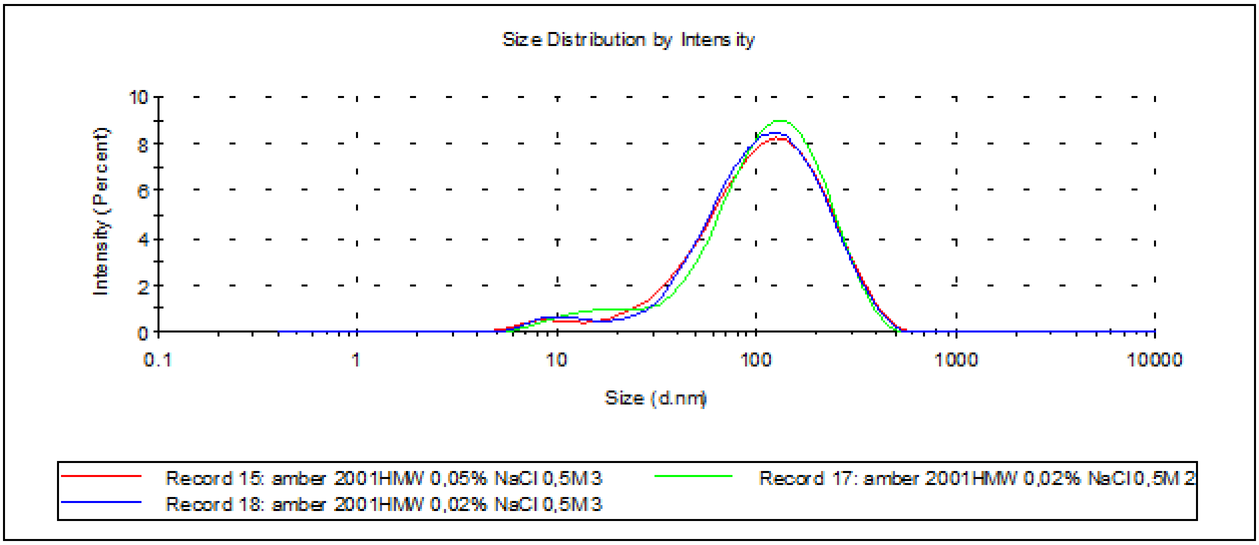


*Figure A.1: Size distribution by intensity for polymer Amber 2001 HMW at 0,02 and 0,05% w/V*

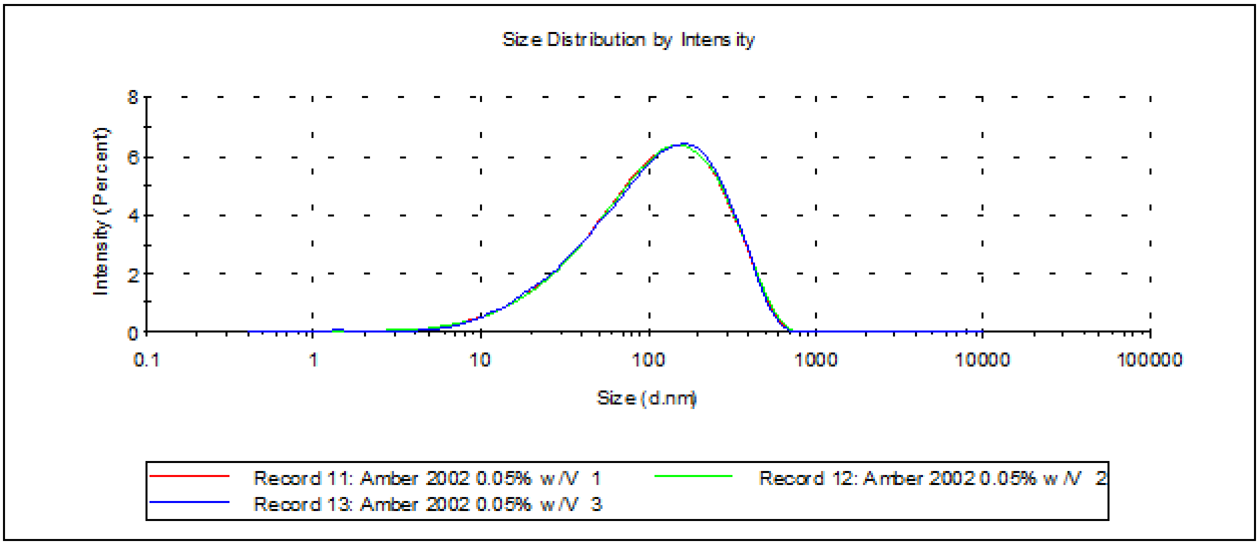


*Figure A.2: Size distribution by intensity for polymer Amber 2002 at 0,05% w/V*

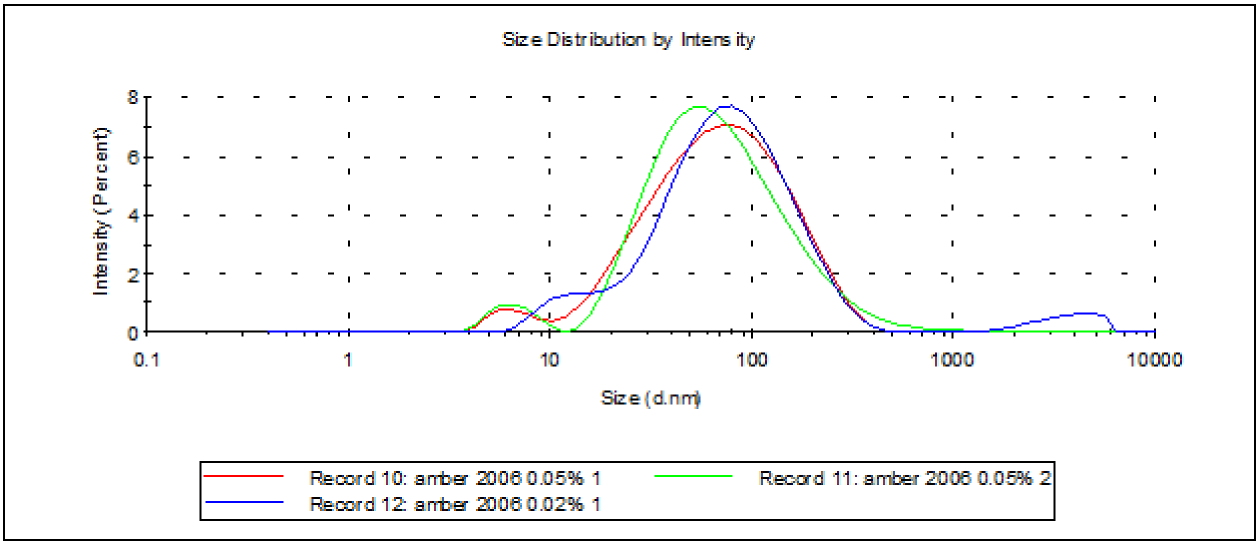


*Figure A.3: Size distribution by intensity for polymer Amber 2006 at 0,02 and 0,05% w/V*

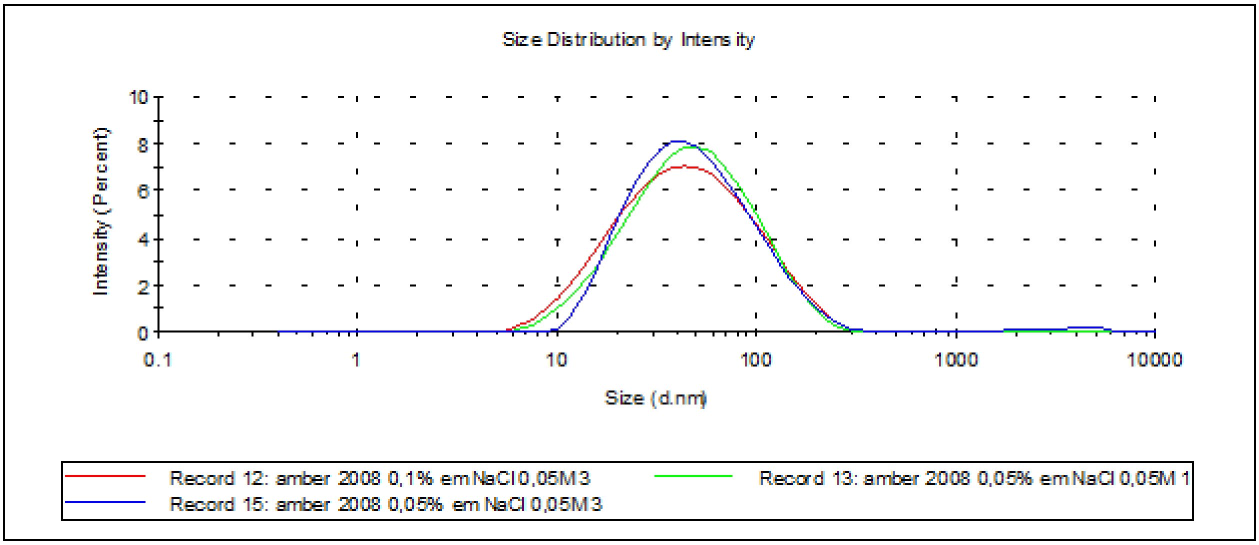


*Figure A.4: Size distribution by intensity for polymer Amber 2008 at 0,05% w/V.*

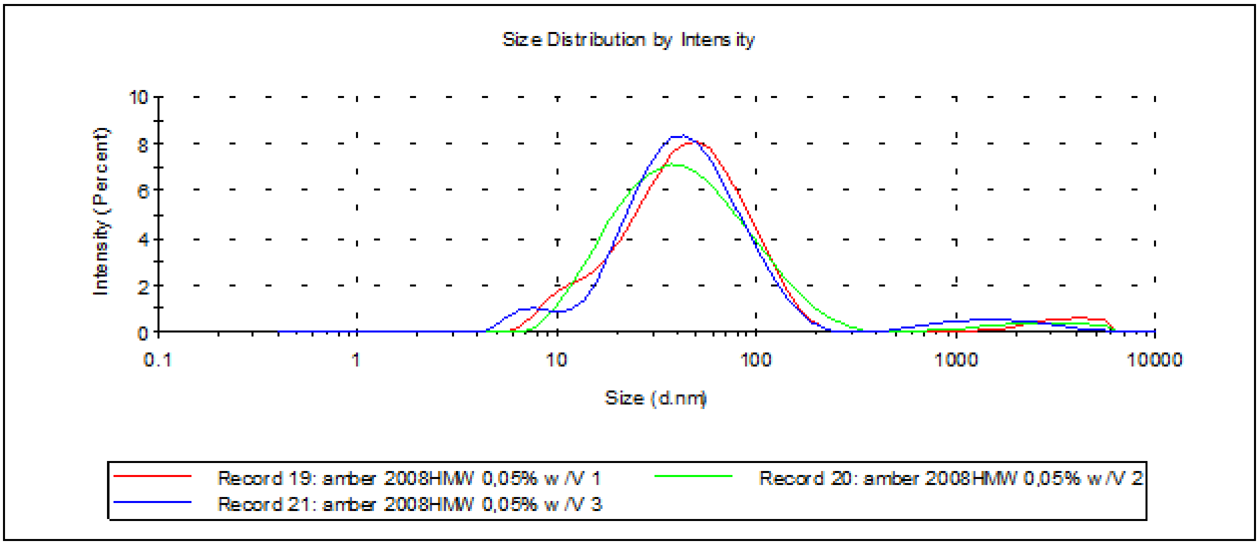


*Figure A.5: Size distribution by intensity for polymer Amber 2008HMW at 0,05% w/V.*

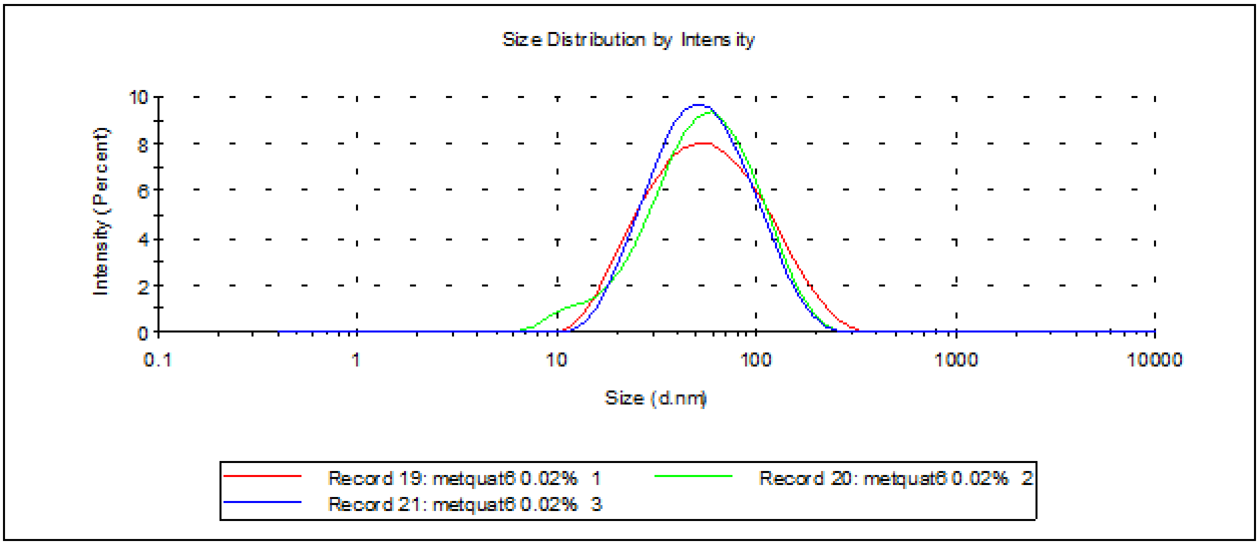


*Figure A.6: Size distribution by intensity for polymer Amber MetQuat 6 at 0,02% w/V.*

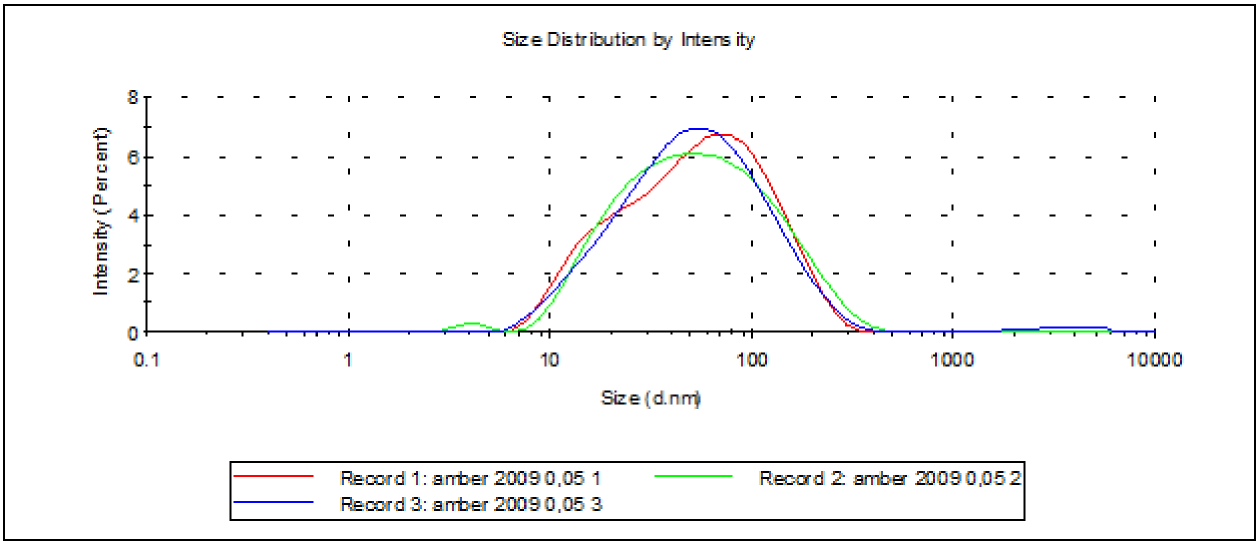


*Figure A.7: Size distribution by intensity for polymer Amber 2009 at 0,05% w/V*

## A.2 Zeta potential graphics

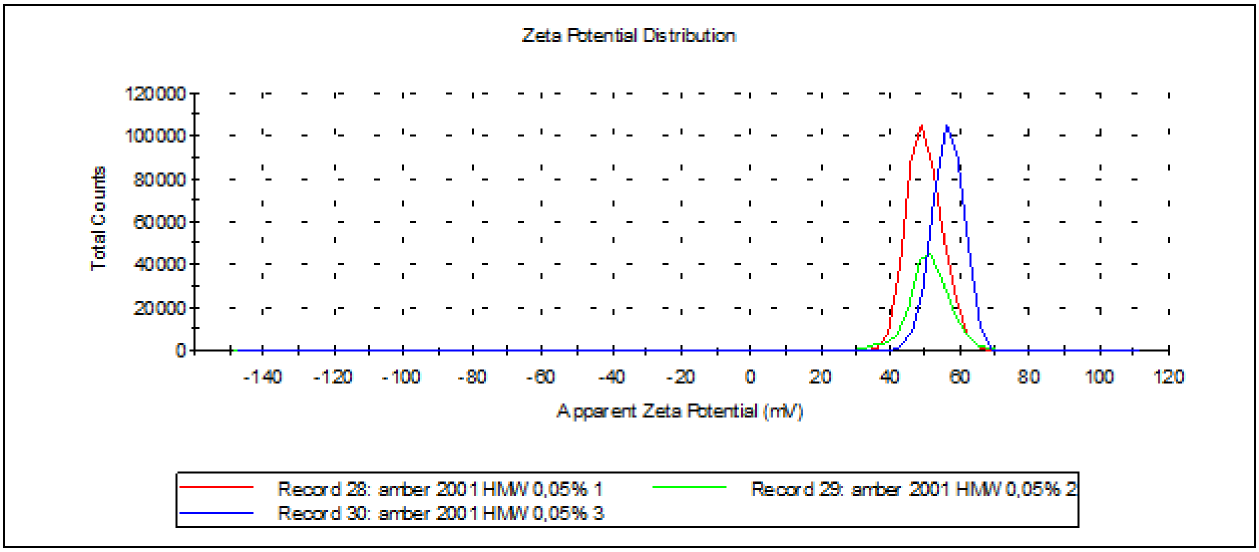


*Figure A.8: Zeta potential graphics for Amber 2001HMW.*

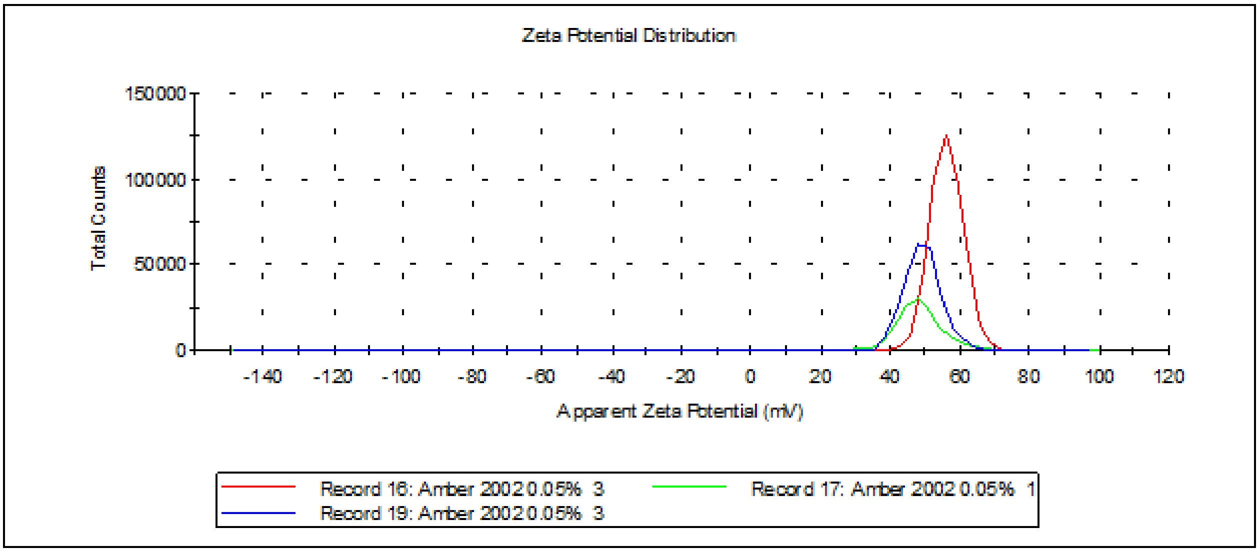


*Figure A.9: Zeta potential graphics for Amber 2002.*

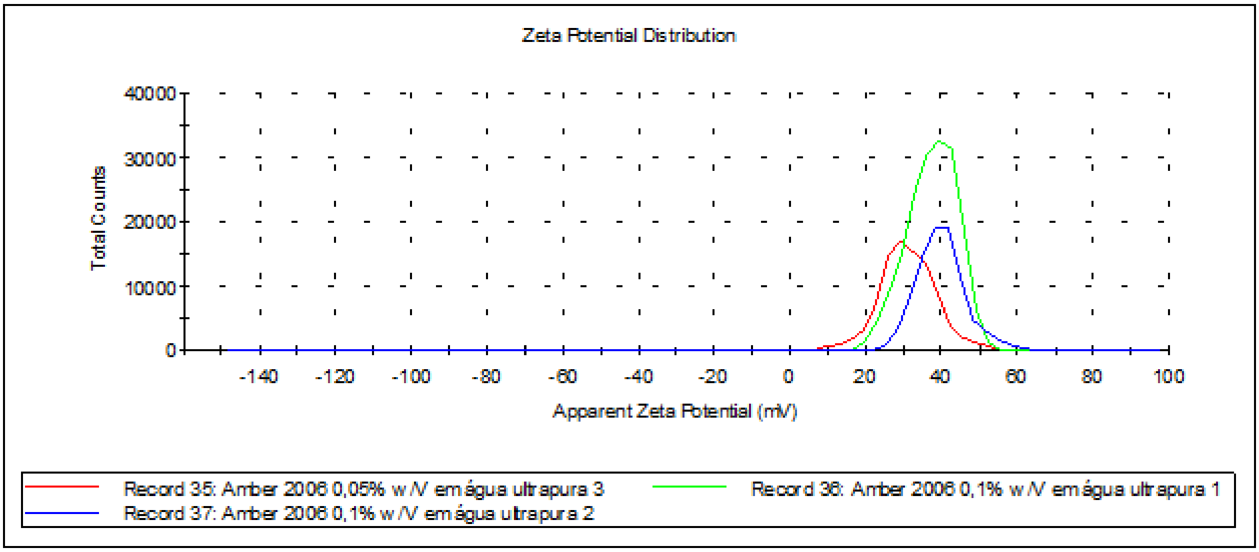


*Figure A.10: Zeta potential graphics for Amber 2006.*

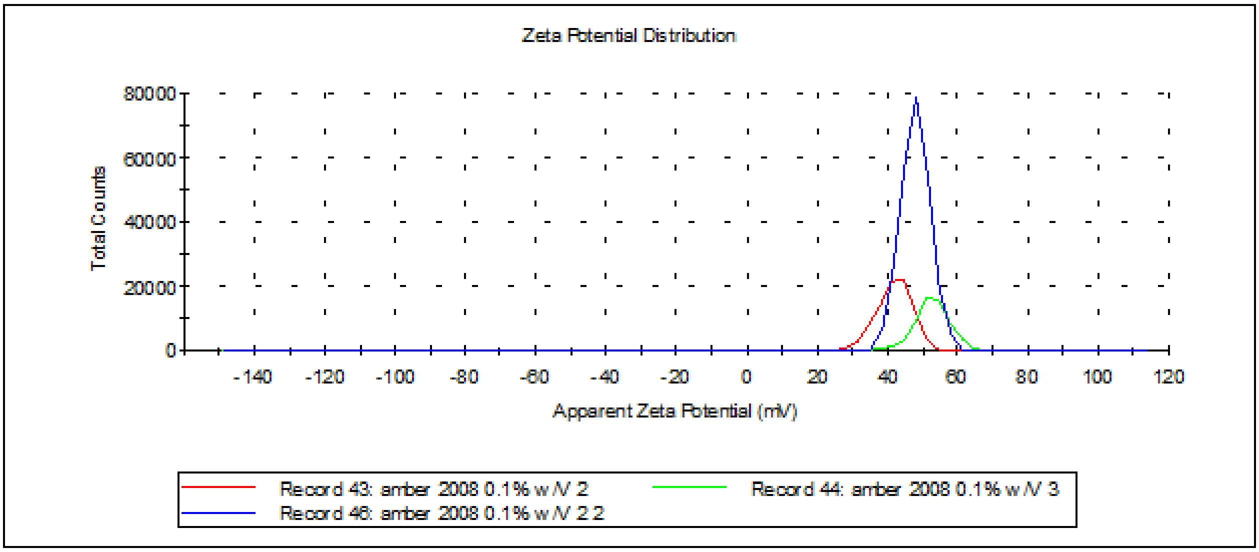


*Figure A.11: Zeta potential graphics for Amber 2008.*

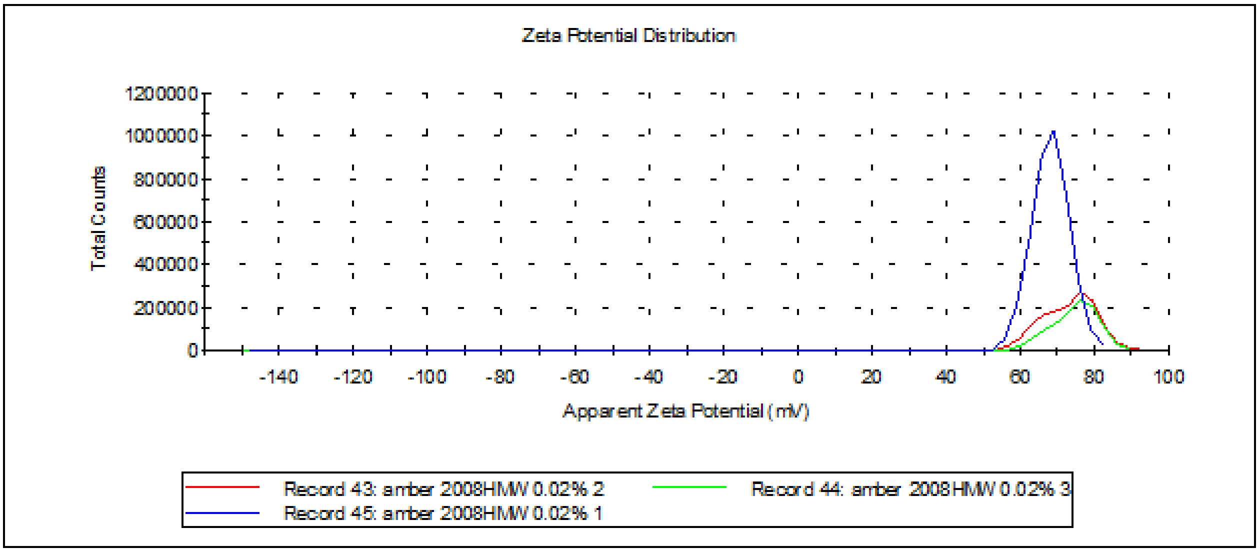


*Figure A.12: Zeta potential graphics for Amber 2008HMW*

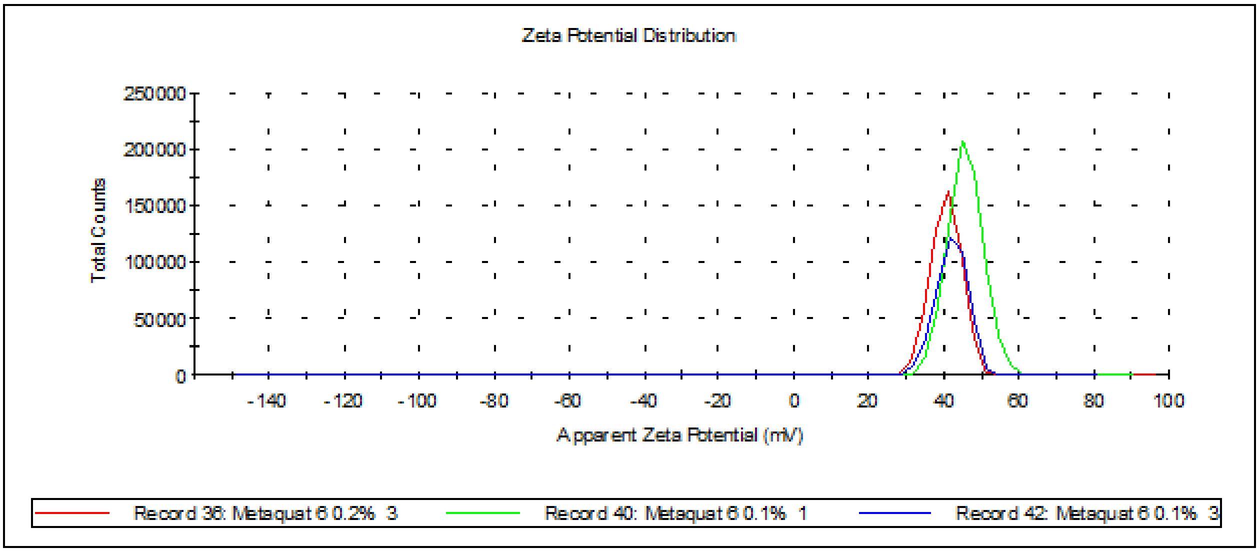


*Figure A.13: Zeta potential graphics for Amber MetQuat 6.*

## A.3 Molecular Weight Debye plots for the polymers

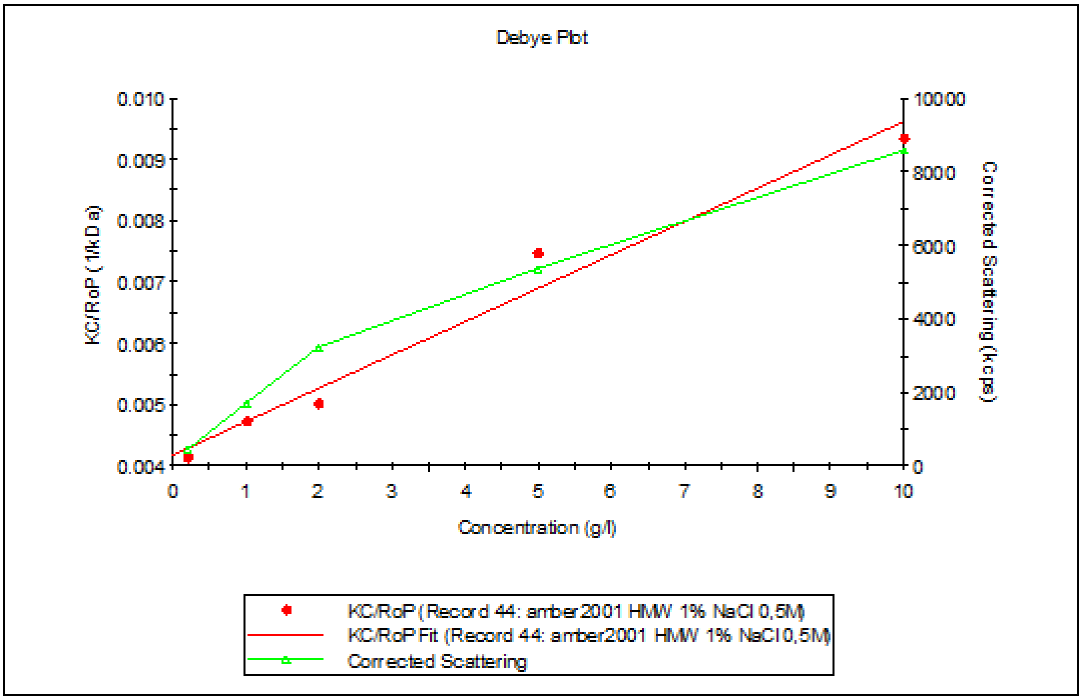


*Figure A.14: Debye plot for Amber 2001HMW 1.*

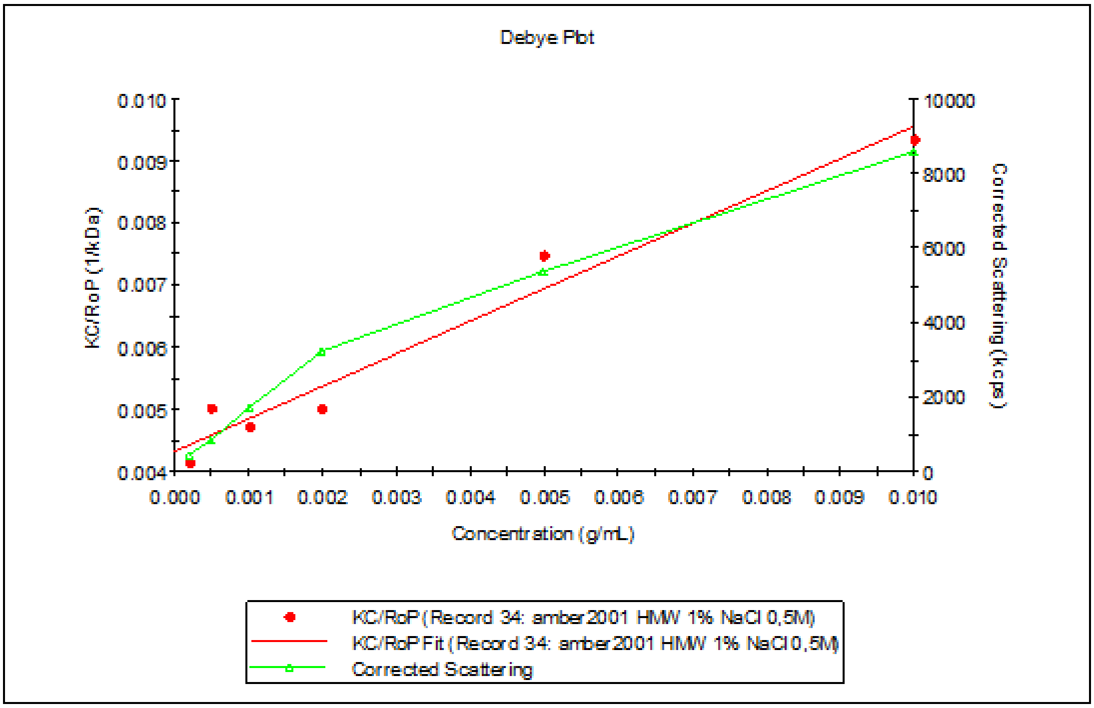


*Figure A.15: Debye plot for Amber 2001HMW 2.*

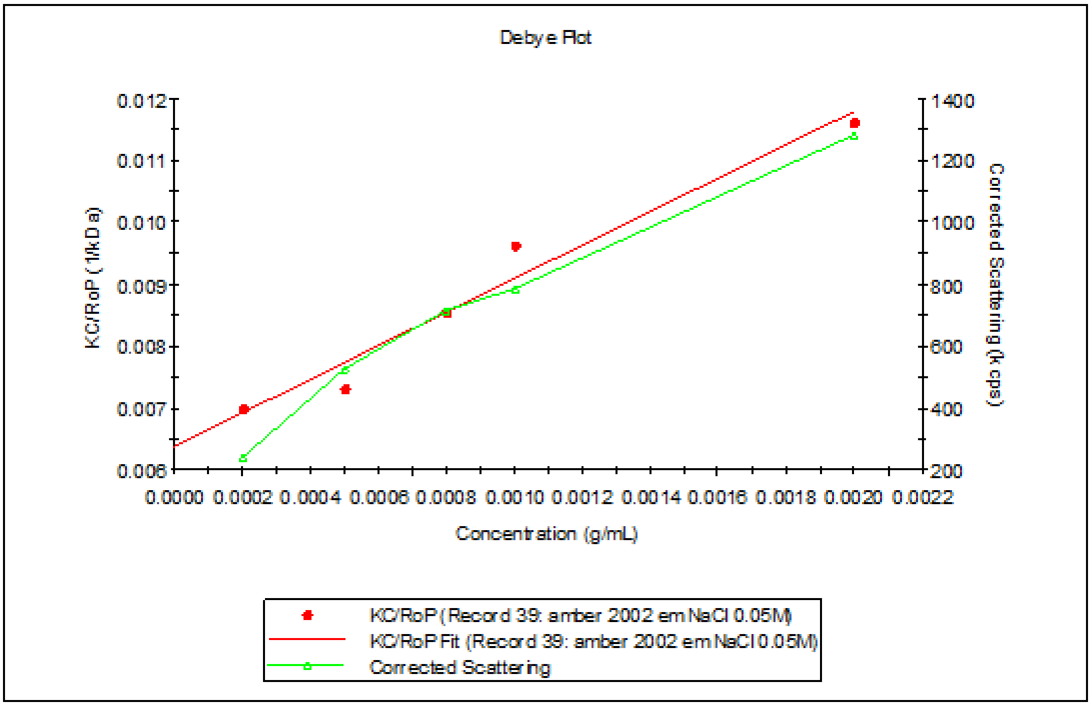


*Figure A.16: Debye plot for Amber 2002.1.*

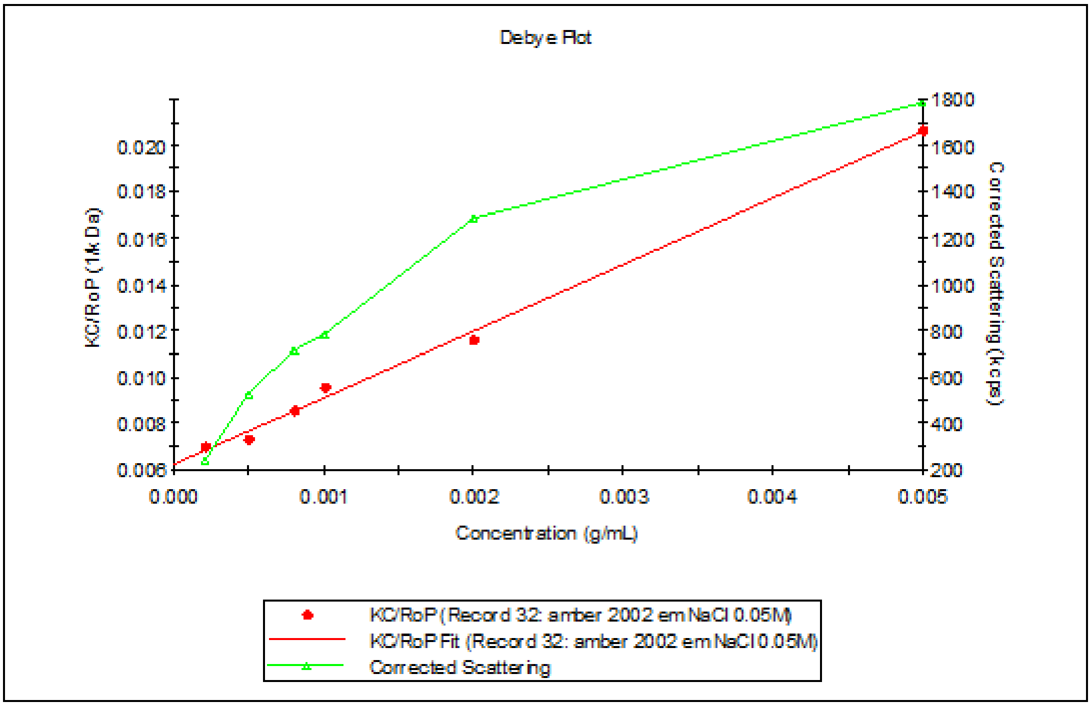


*Figure A.17: Debye plot for Amber 2002.2.*

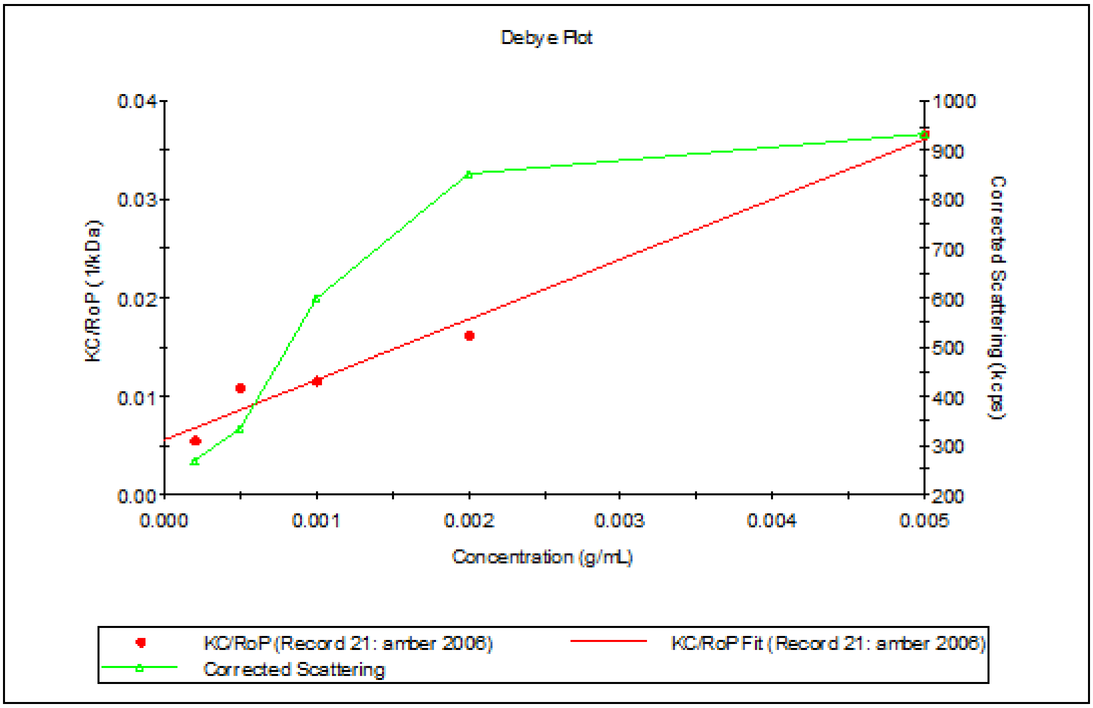


*Figure A.18: Debye plot for Amber 2006.1.*

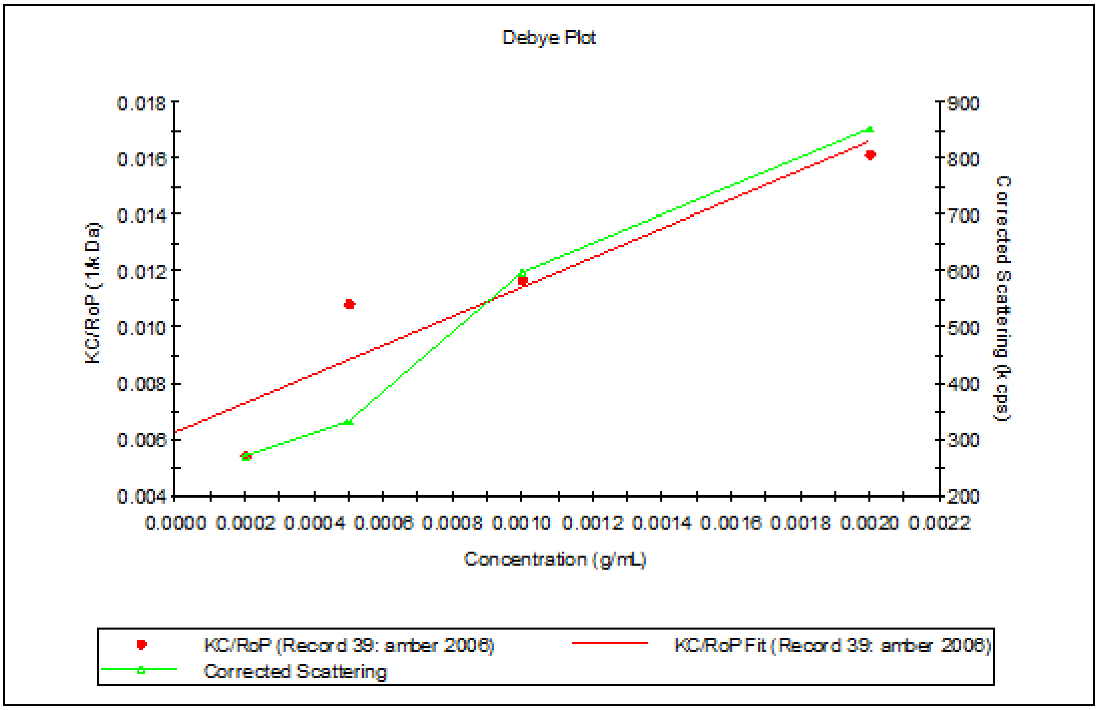


*Figure A.19: Debye plot for Amber 2006.2.*

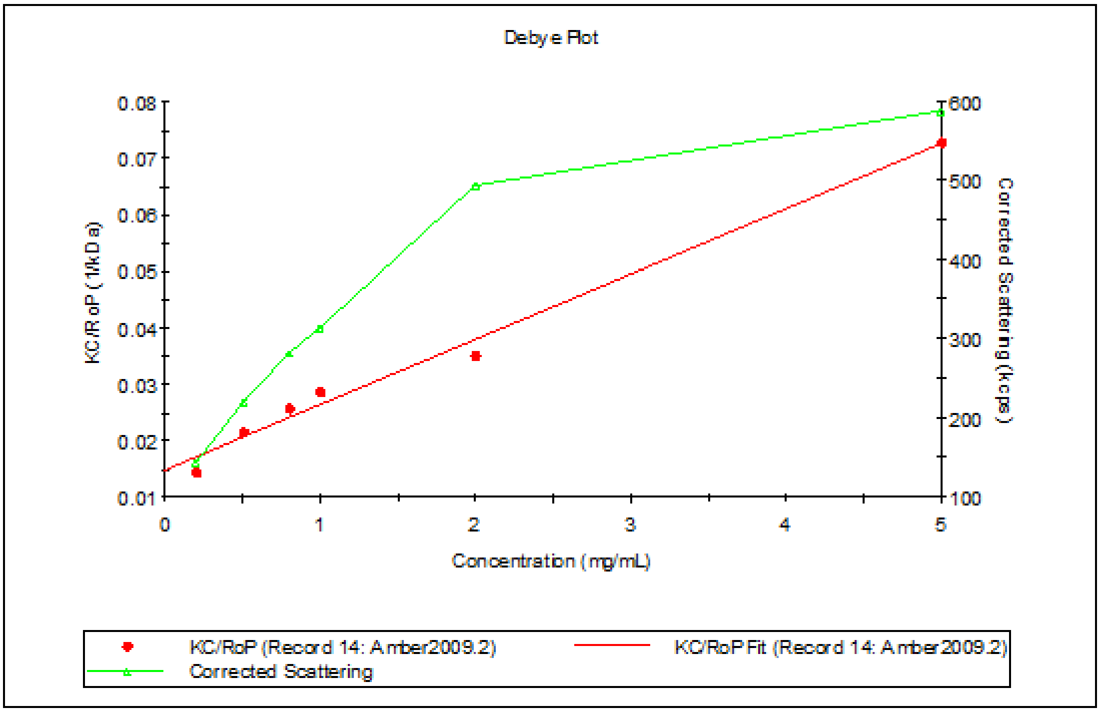


*Figure A.20: Debye plot for Amber 2009.1.*

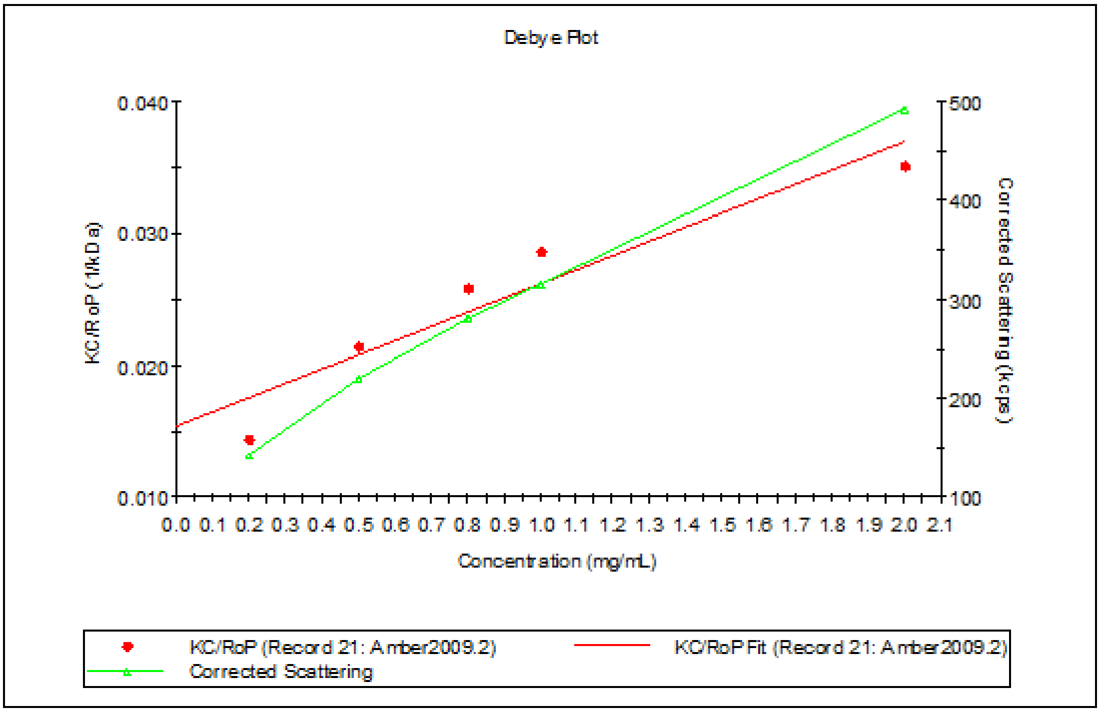


*Figure A.21: Debye plot for Amber 2009.2.*

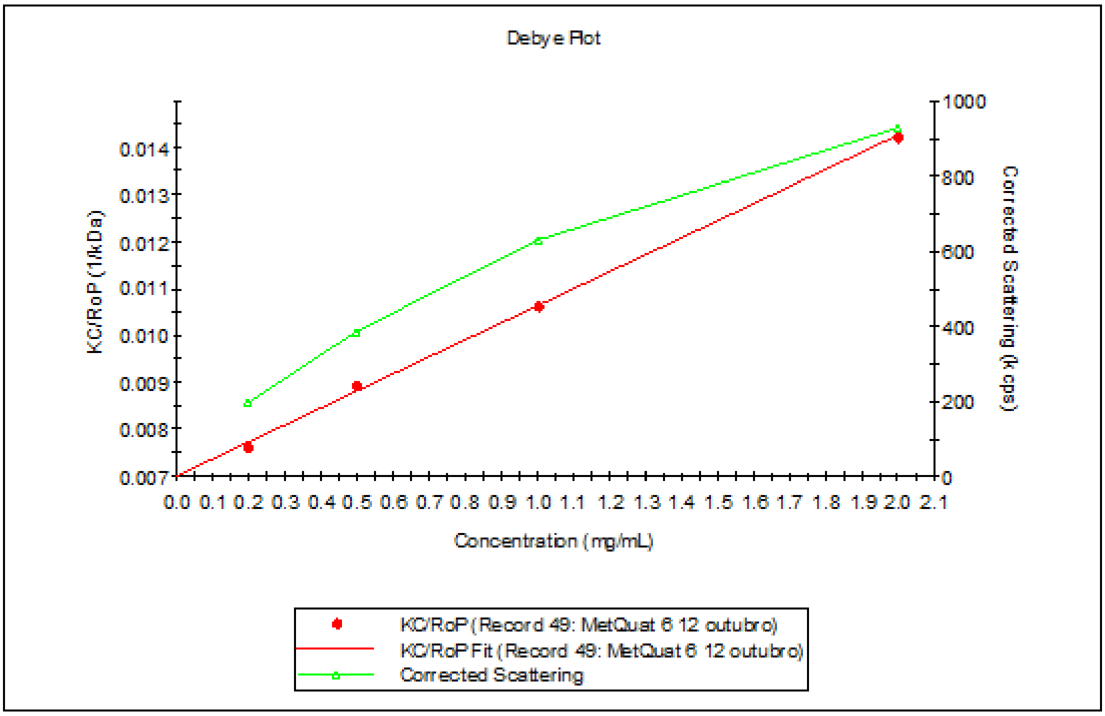


*Figure A.22: Debye plot for Amber MetQuat 6 1.*

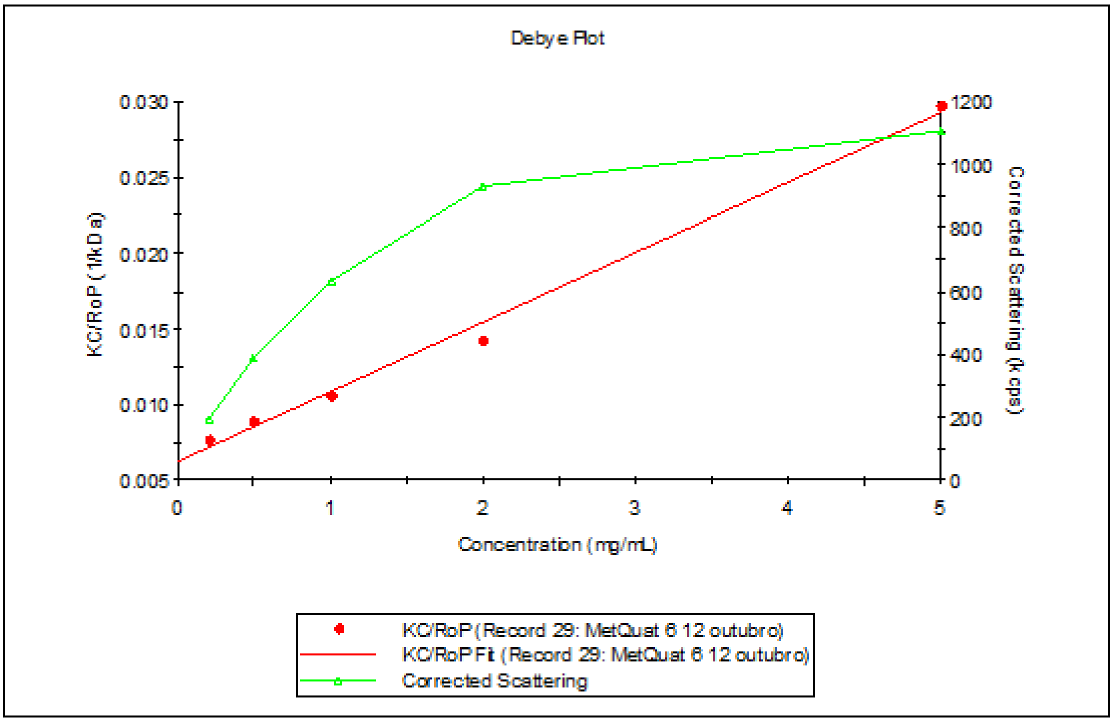


*Figure A.23: Debye plot for Amber MetQuat 6 2.*

# Appendix B. Decolorization tests results

## Tables and graphics of laboratorial decolorization tests results.

*Table B-1: Decolorization results using Amber 2001HMW*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| **76,2-78** | 8,18 | 6,99 | 25 | 643 | 761 | 15,51 |
| **76,1-78,5** | 8,19 | 7,00 | 50 | 664 | 894 | 25,54 |
| **76-78,4** | 8,16 | 7,00 | 100 | 570 | 896 | 36,38 |
| **75,8-77** | 8,25 | 6,99 | 150 | 571 | 801 | 28,71 |
| **76-78,6** | 8,24 | 7,00 | 200 | 512 | 793 | 35,44 |
| **75,8-77,2** | 8,20 | 7,02 | 250 | 552 | 763 | 27,65 |

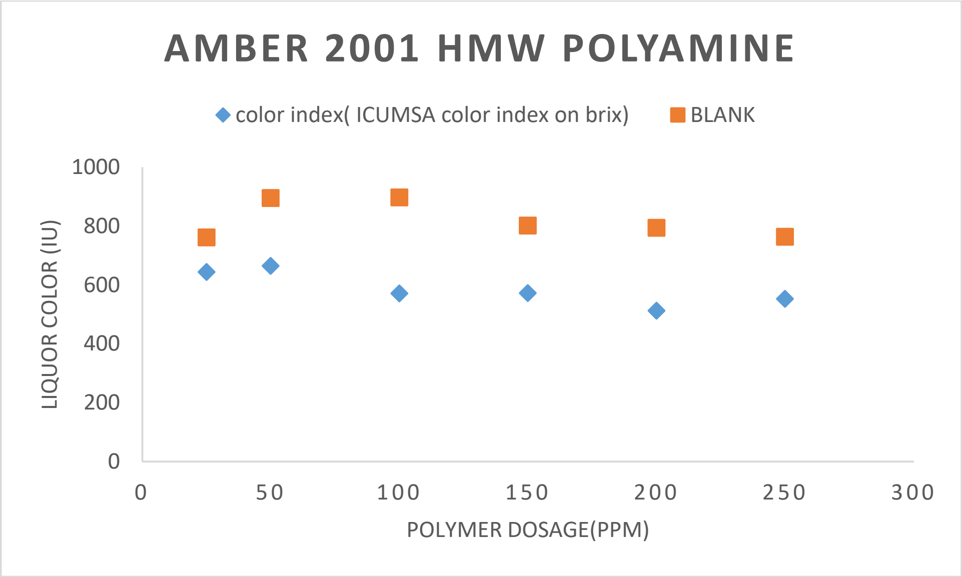


*Figure B.1: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2001HMW*

*Table B-2: Decolorization results for Amber 2002*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| **77,9-79** | 7,80 | 6,94 | 25 | 622 | 902 | 11,64 |
| **77,8-80,1** | 7,86 | 6,99 | 50 | 728 | 849 | 18,37 |
| **78,8-80,4** | 7,97 | 7,03 | 100 | 657 | 883 | 25,59 |
| **78,9-80,2** | 8,31 | 6,98 | 150 | 631 | 734 | 14,03 |
| **78-80,6** | 8,22 | 7,03 | 200 | 734 | 746 | 1,61 |
| **78-79,7** | 8,17 | 7,01 | 250 | 784 | 738 | -6,23 |

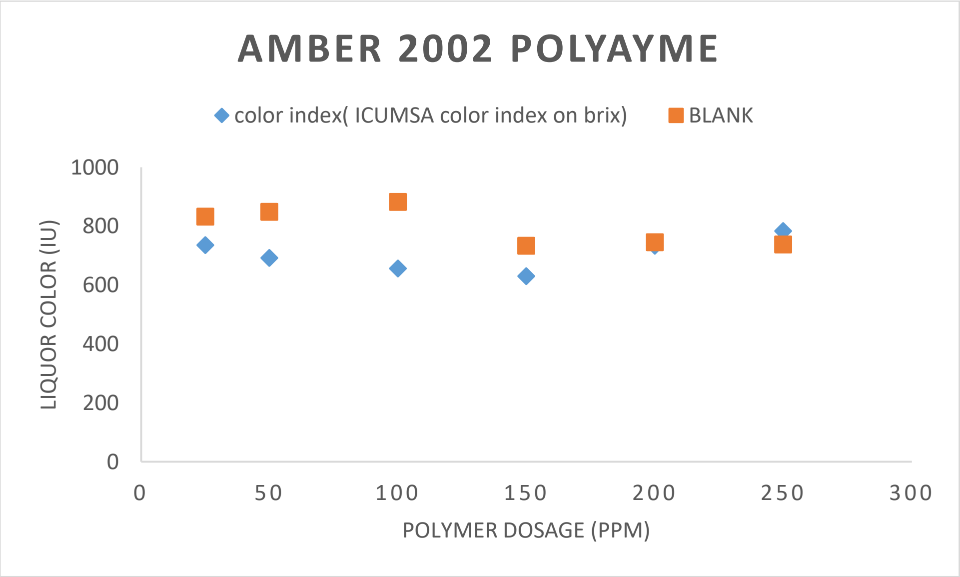


*Figure B.2: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2002*

*Table B-3: Decolorization results for Amber 2006*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| **77,2-79,2** | 8,24 | 7,02 | 25 | 693 | 768 | 9,77 |
| **77,7-79,1** | 8,17 | 7,00 | 50 | 641 | 778 | 17,61 |
| **76,8-79,2** | 8,18 | 6,99 | 100 | 549 | 752 | 26,99 |
| **77,1-80,6** | 8,31 | 7,00 | 150 | 602 | 797 | 24,47 |
| **76,7-79,4** | 8,24 | 7,01 | 200 | 683 | 801 | 14,73 |
| **77,1-79** | 8,31 | 6,98 | 250 | 709 | 780 | 9,10 |

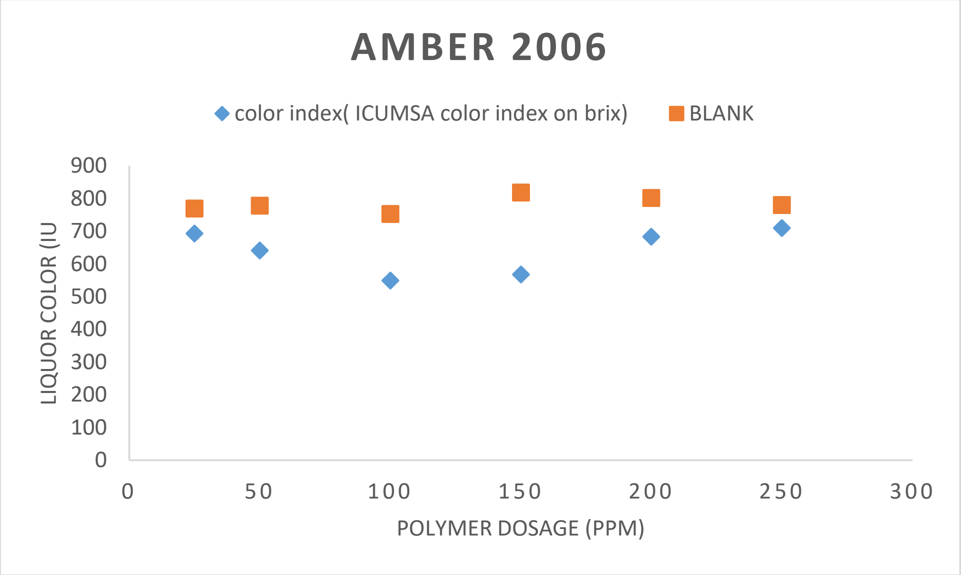


*Figure B.3: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2006*

*Table B-4: Decolorization results for Amber 2008*

| **T. flocculation (°C)** | **pH initial** | **pH adjusted** | **polymer dosage (ppm)** | **color ICUMSA (IU)** | **Blank ICUMSA (IU)** | **% color removed** |
|---|---|---|---|---|---|---|
| 77 | 7,80 | 7,01 | 25 | 638 | 757 | 15,72 |
| 77,5 | 7,86 | 7,02 | 50 | 682 | 781 | 20,10 |
| 78 | 7,97 | 7,01 | 100 | 538 | 787 | 31,73 |
| 78,2 | 8,31 | 6,99 | 150 | 610 | 802 | 23,94 |
| 77,4 | 8,22 | 7,01 | 200 | 681 | 798 | 14,66 |
| 75,4-79,8 | 8,17 | 7,00 | 250 | 750 | 851 | 11,87 |

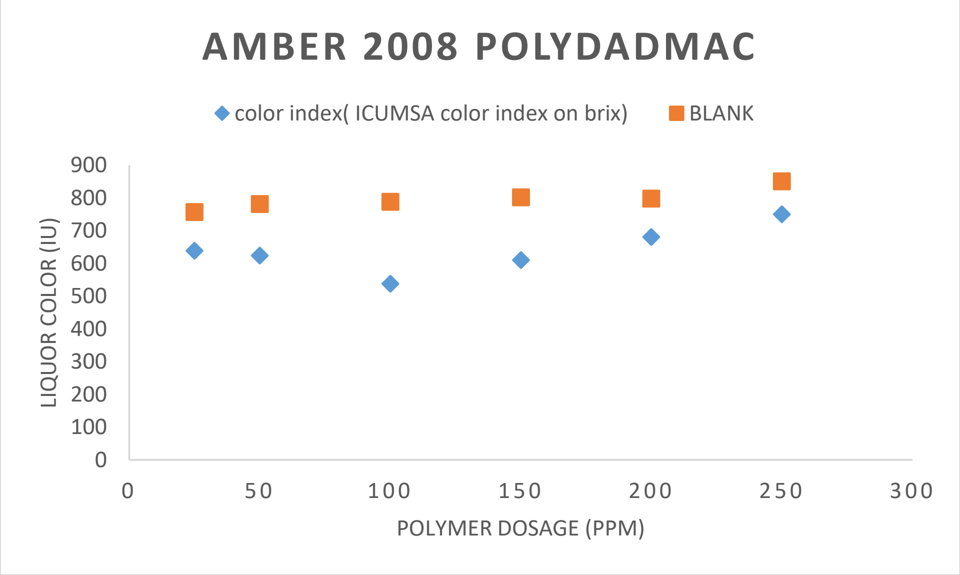


*Figure B.4: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2008.*

*Table B-5: Decolorization results for Amber 2008HMW*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | color ICUMSA (IU) |
|---|---|---|---|---|---|---|
| 76-79,6 | 7,80 | 6,94 | 25 | 667 | 779 | 14,38 |
| 77-80,2 | 7,86 | 6,99 | 50 | 696 | 875 | 20,46 |
| 76-80,1 | 7,97 | 7,03 | 100 | 771 | 885 | 12,88 |
| 77-79,2 | 8,31 | 6,98 | 150 | 820 | 893 | 8,17 |
| 76-79,6 | 8,22 | 7,03 | 200 | 923 | 902 | -2,33 |
| 78-79,1 | 8,17 | 7,01 | 250 | 968 | 876 | -10,50 |

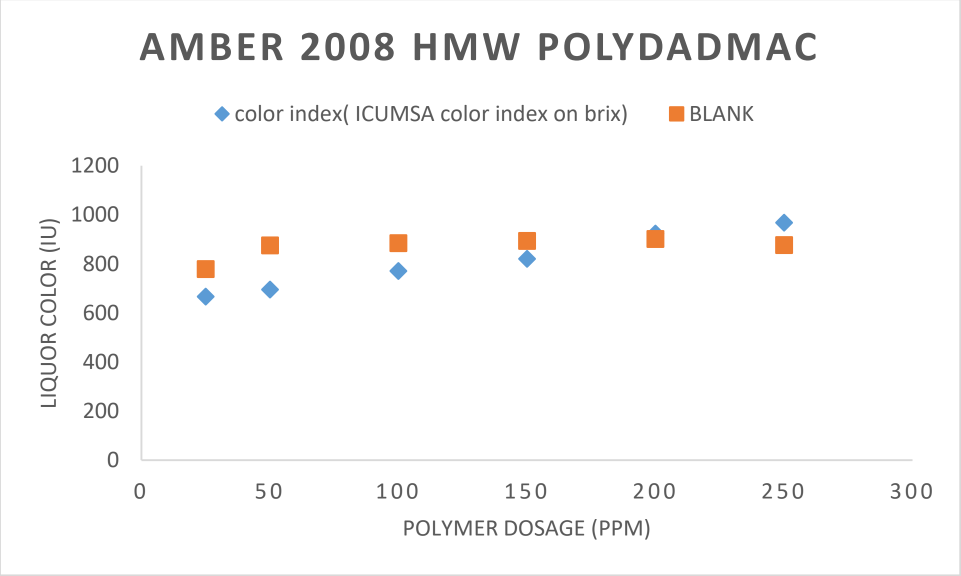


*Figure B.5: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2008HMW.*

*Table B-6: Decolorization results for Amber 2010*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| 77-79.6 | 8,31 | 7,01 | 25 | 721 | 748 | 3,61 |
| 77-80,1 | 8,22 | 7,02 | 50 | 593 | 739 | 19,76 |
| 77-78 | 8,23 | 7,00 | 100 | 589 | 752 | 21,68 |
| 76-79 | 8,19 | 7,00 | 150 | 870 | 801 | -8,61 |
| 78-79 | 8,22 | 7,00 | 200 | 846 | 784 | -7,91 |
| 77-79,1 | 8,17 | 7,03 | 250 | 878 | 780 | -12,56 |

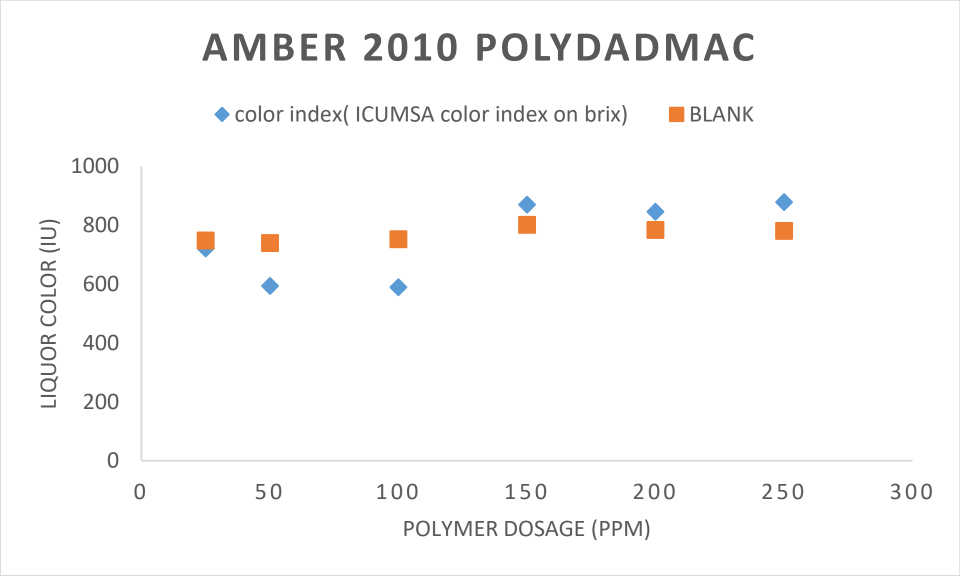


*Figure B.6: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2010.*

*Table B-7: Decolorization results for Amber 2009*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| 76-77 | 8,27 | 6,91 | 25 | 586 | 667 | 12,14 |
| 76-78 | 8,26 | 7,01 | 50 | 518 | 723 | 28,35 |
| 76,5-77,9 | 8,23 | 7,02 | 100 | 477 | 809 | 41,04 |
| 76-77 | 8,25 | 6,99 | 150 | 659 | 770 | 14,42 |
| 76-78,2 | 8,22 | 7,00 | 200 | 734 | 782 | 6,14 |
| 76-78,5 | 8,27 | 6,99 | 250 | 722 | 699 | -3,29 |

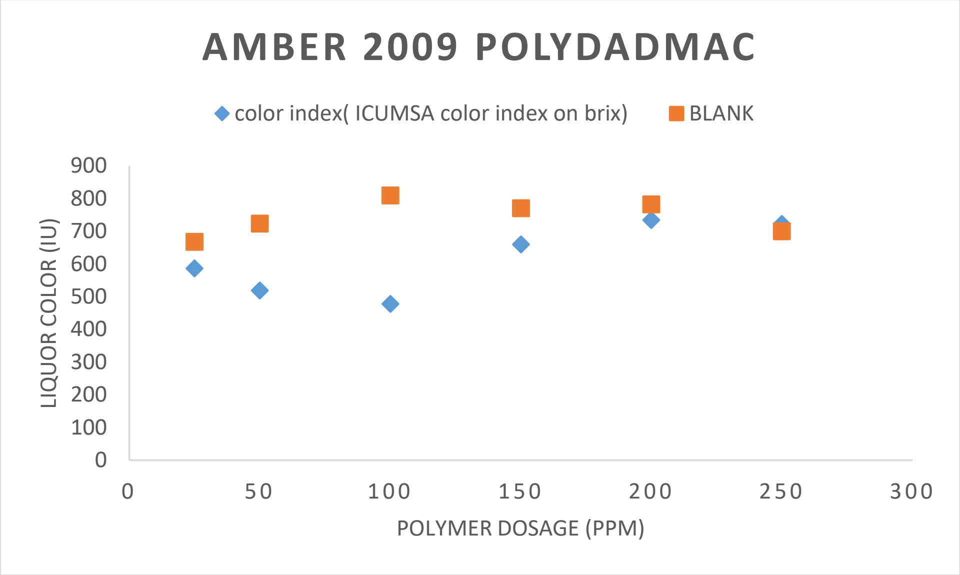


*Figure B.7: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2009*

*Table B-8: Decolorization results for Amber 2013*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| 75,4-77,8 | 8,23 | 7,00 | 25 | 674 | 848 | 20,52 |
| 76-78 | 8,29 | 7,01 | 50 | 600 | 778 | 22,88 |
| 76-77,8 | 8,30 | 7,01 | 100 | 518 | 799 | 35,17 |
| 75,6-78,5 | 8,31 | 6,98 | 150 | 599 | 630 | 13,94 |
| 76,5-79 | 8,31 | 7,00 | 200 | 545 | 645 | 12,40 |
| 76-78,7 | 8,34 | 6,99 | 250 | 734 | 631 | -6,69 |

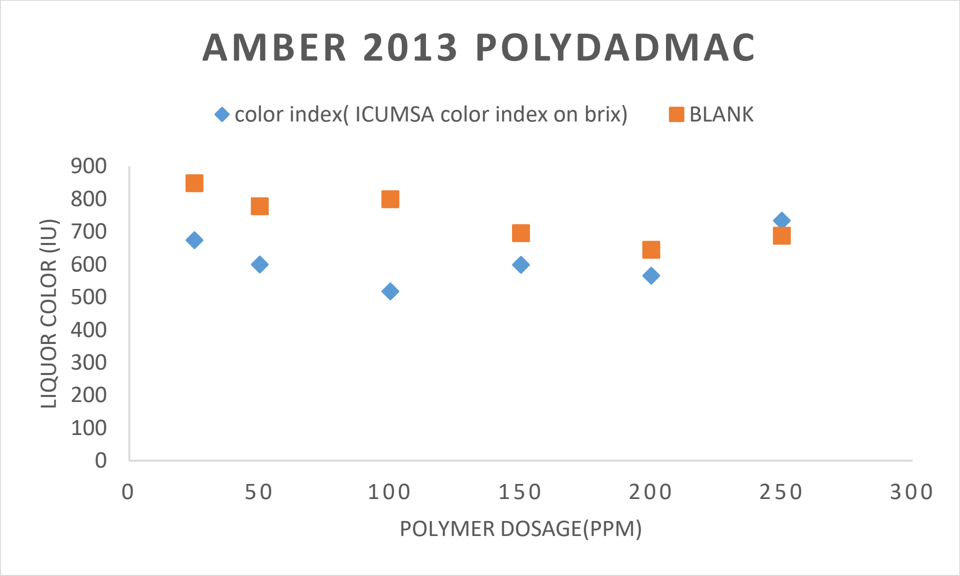


*Figure B.8: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2013*

*Table B-9: Decolorization results for Amber 2014*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| 76,9-78 | 8,37 | 7,00 | 25 | 562 | 619 | 9,21 |
| 76,1-78,4 | 8,37 | 7,00 | 50 | 468 | 614 | 23,78 |
| 76-78,2 | 8,32 | 6,99 | 100 | 547 | 634 | 13,72 |
| 75,9-77,9 | 8,38 | 7,01 | 150 | 604 | 656 | 7,93 |
| 76-77,9 | 8,41 | 7,02 | 200 | 724 | 651 | -11,21 |
| 76,1-78,7 | 8,35 | 6,99 | 250 | 778 | 672 | -15,77 |

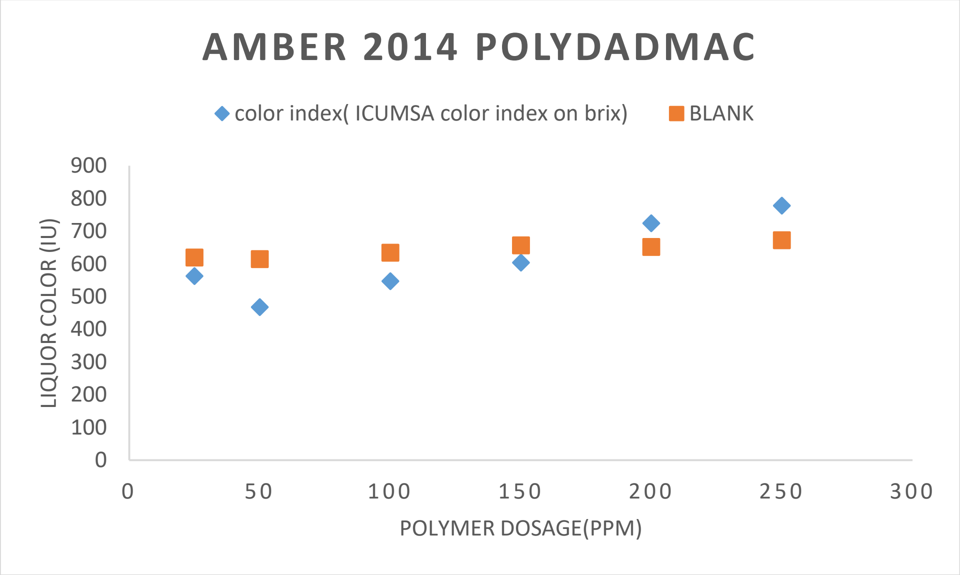


*Figure B.9: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber 2014.*

*Table B-10: Decolorization results for Amber MetQuat 6*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| 76-77,8 | 8,20 | 7,02 | 25 | 595 | 731 | 18,60 |
| 75,8-78,1 | 8,19 | 7,00 | 50 | 674 | 848 | 20,52 |
| 76-77,8 | 8,24 | 7,02 | 100 | 610 | 804 | 24,13 |
| 76-78 | 8,15 | 7,02 | 150 | 505 | 767 | 34,16 |
| 76,2-78,9 | 8,20 | 7,02 | 200 | 497 | 823 | 39,61 |
| 76-78,4 | 8,23 | 6,99 | 250 | 554 | 793 | 30,14 |

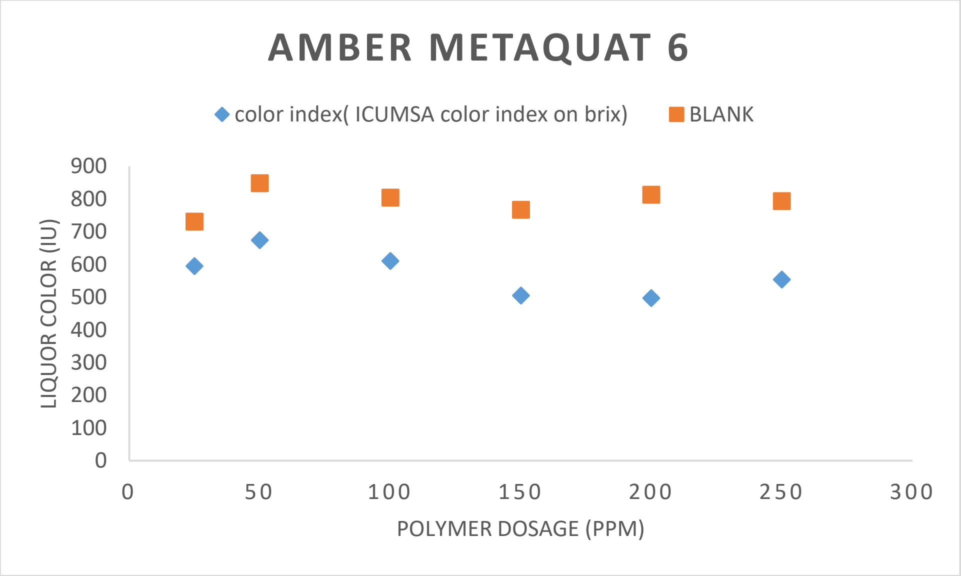


*Figure B.10: Graphic representation of color (IU) of the liquor, treated and untreated with the polymer, versus polymer dosage for the test using Amber MetQuat 6.*

*Table B-11: Decolorization results using Blend Amber 2009 & Amber 2001HMW*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| 78-80 | 8,32 | 7,00 | 25 | 614 | 772 | |
| 78-79 | 8,39 | 7,00 | 50 | 562 | 790 | 28,86 |
| 78-80 | 8,30 | 6,99 | 100 | 598 | 821 | 27,16 |

*Table B-12: Decolorization results using Blend Amber 2013 & Amber 2001HMW*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| 78-80 | 8,27 | 7,01 | 25 | 609 | 772 | 21,11 |
| 78-79 | 8,31 | 7,00 | 50 | 542 | 783 | 30,78 |
| 78-80 | 8,29 | 7,00 | 100 | 607 | 794 | 23,55 |

*Table B-13: Decolorization results using Blend Amber 2013, Amber 2009 & Amber 2001HMW*

| T. flocculation (°C) | pH initial | pH adjusted | polymer dosage (ppm) | color ICUMSA (IU) | Blank ICUMSA (IU) | % color removed |
|---|---|---|---|---|---|---|
| 78-80 | 8,20 | 7,00 | 25 | 642 | 887 | 27,62 |
| 77-79 | 8,26 | 7,00 | 50 | 568 | 847 | 32,94 |
| 76-79 | 8,31 | 7,00 | 100 | 620 | 834 | 25,66 |

# Appendix C. Flocculation monitoring additional tests.

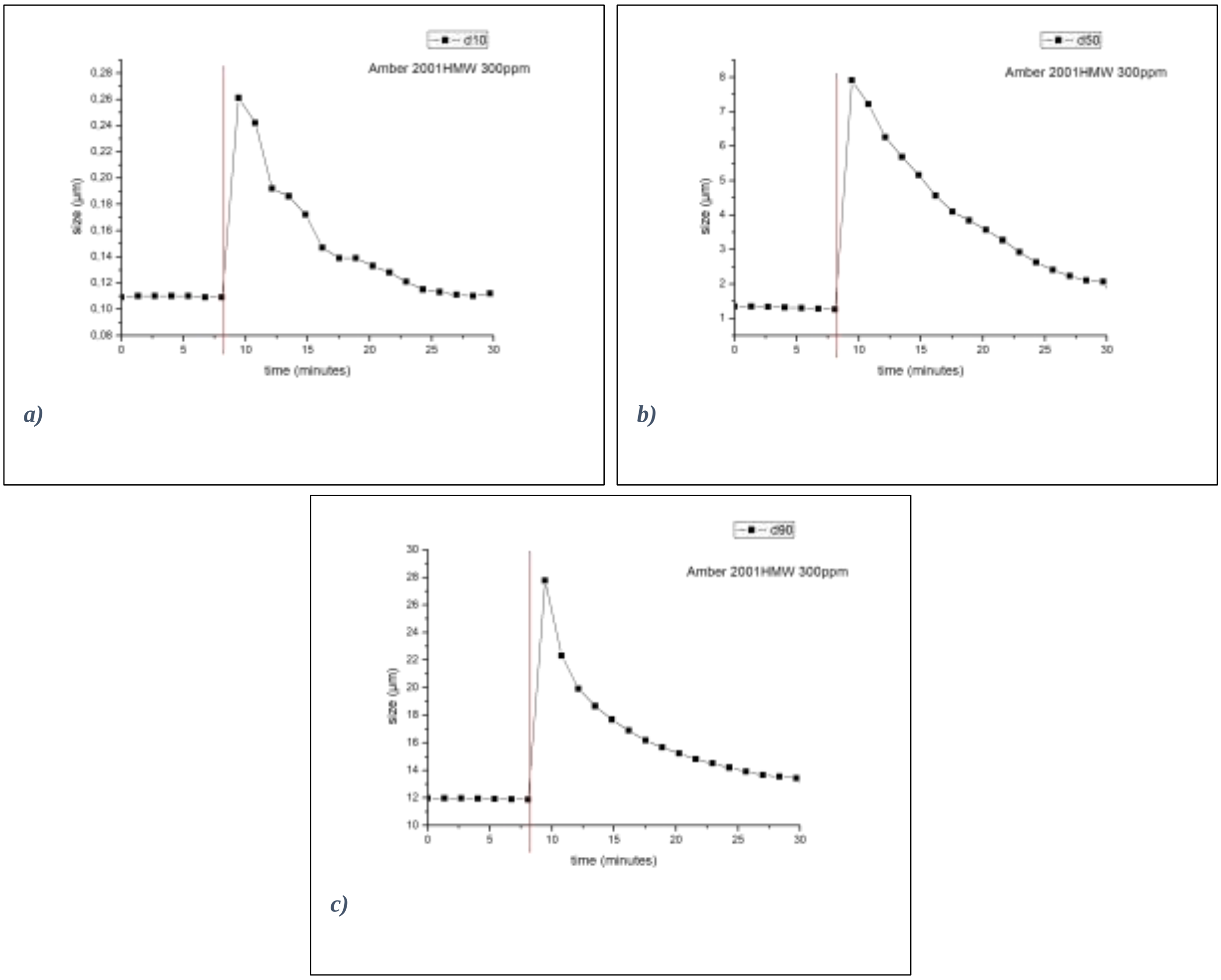
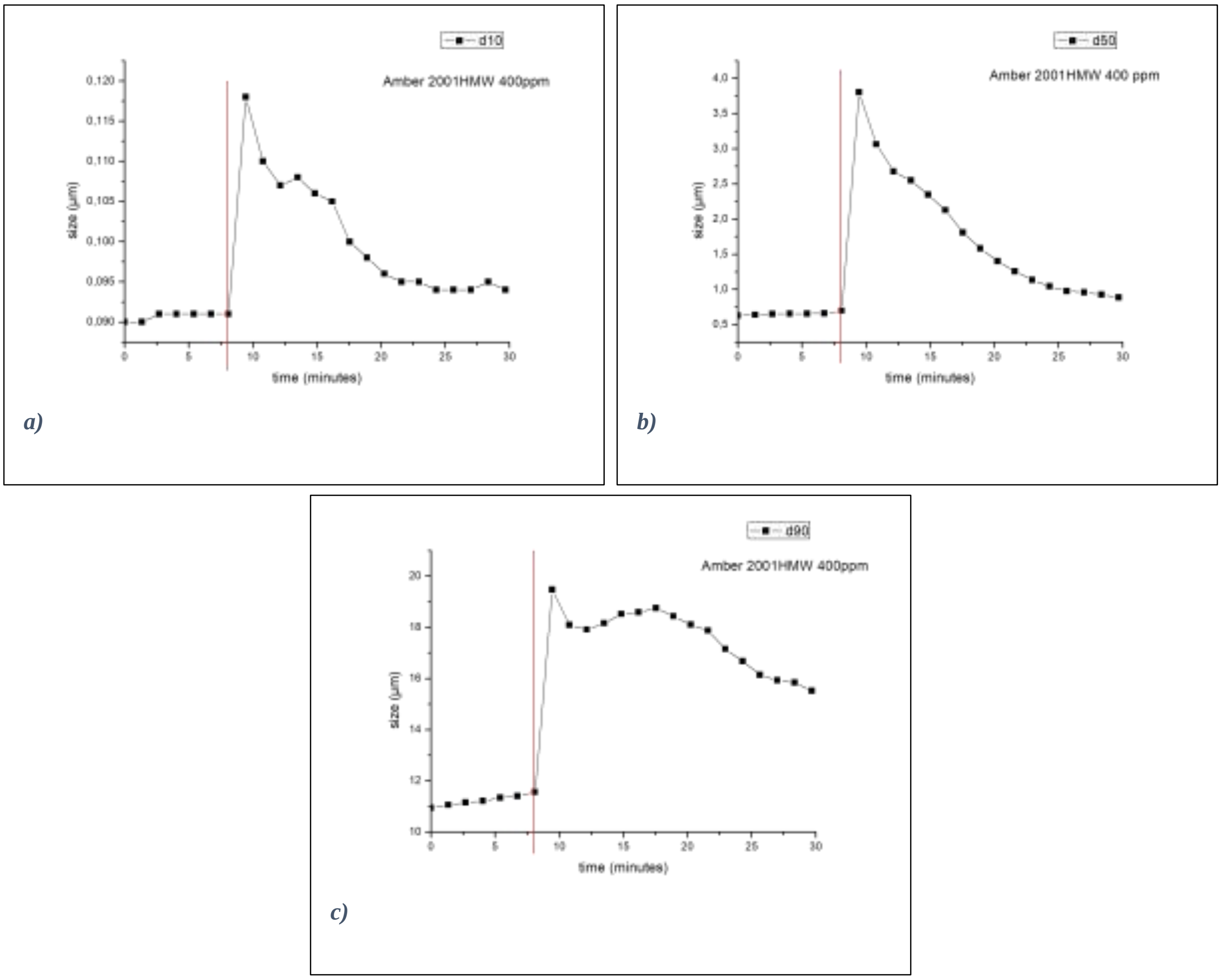


*Figure C.1: Plot for flocculation kinetics using Amber2001HMWat 300 ppm, a) = d10, b) = d50 e c) = d90*



***a)***

***b)***

***c)***

*Figure C.2: Plot for flocculation kinetics using Amber2001HMWat 400 ppm, a) = d10, b) = d50 e c) = d90.*

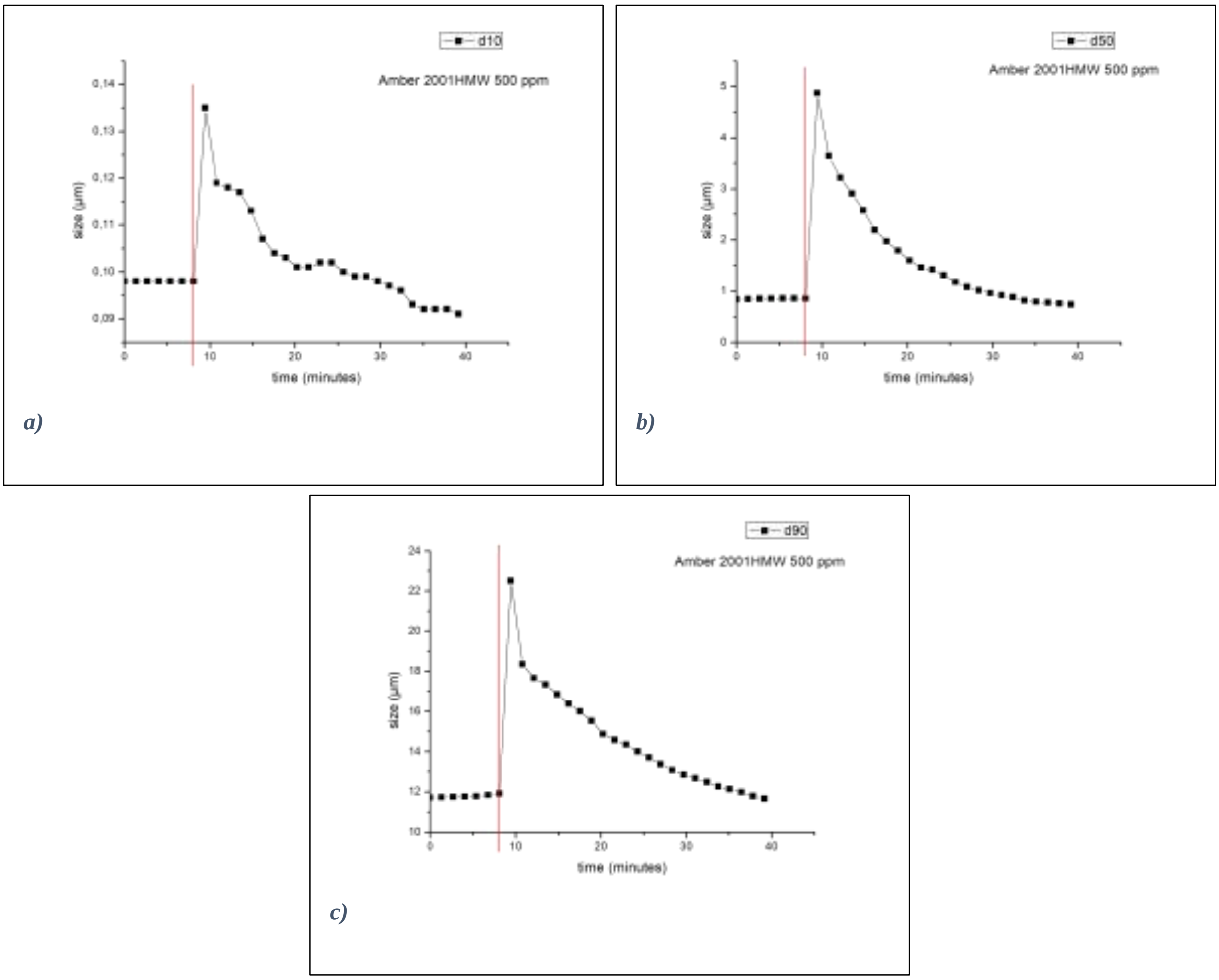


*Figure C.3: Plot for flocculation kinetics using Amber2001HMWat 500 ppm, a) = d10, b) = d50 e c) = d90.*

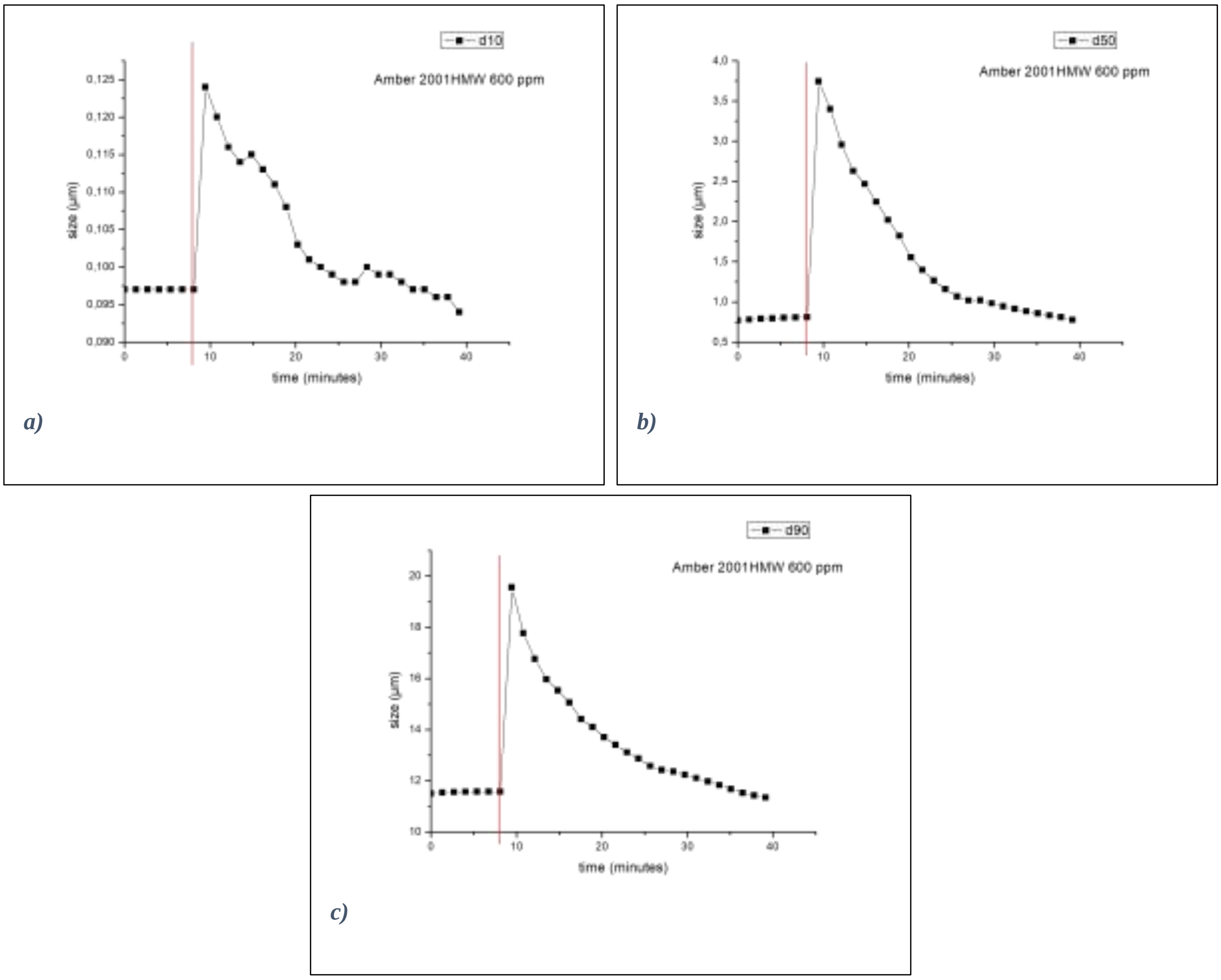


*Figure C.4: Plot for flocculation kinetics using Amber2001HMWat 600 ppm, a) = d10, b) = d50 e c) = d90.*