Integrated Master in Chemical Engineering

Influence of the composition of a synthetic sludge on its dewaterability

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Abstract

Activated sludge dewatering has grown more necessary in order to decrease the volume of this waste. However, having a controlled experiment with an activated sludge remains difficult due to the living organisms that are keep changing characteristics. To overcome this problem a synthetic sludge was created to surrogate the real one. In this work the synthetic sludge has fresh yeast to simulate the individual bacteria, alginate to the extracellular material, MCC to filamentous microorganism and calcium to bridging ions.

To study the influence of each component in the dewatering process, filtration tests were performed. These tests were conducted by changing the concentration of each component. During the experiment of variation of the concentration of calcium, it was observed that this component made the aggregation in the flocs. Relatively to alginate it was observed that the water was less attached to the solids. For MCC it was observed that the backbone of the flocs was missing. Due to the absence of yeast the flocs were formed but the fouling was not observed.

Convective drying and desorption isotherms were used to better understand the moisture content inside some gels and in synthetic sludge. From the isotherms it was possible to observe that the calcium does not have a strong effect on the attachment of water in the sludge.

In this work it was possible to verity the behaviour and functionalities of each component of the synthetic sludge.

Keywords: Synthetic sludge, Dewatering, Filtration, Drying and Isotherms.

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Nomenclature and glossary

a_w – Activity of water

A(W) – Transfer area (m^2)

F_m – Evaporation mass flux ($g_{water}.s^{-1}.m^{-2}$)

m_s – Mass of dry solids (g_{solids})

P_a – Applied pressure (pa)

R_{fm} – Resistance of the filter medium (m^{-1})

RH_{eq} – Relative humidity

t - Time (s)

$V_{filtrate}$ – Volume of filtrate removed at the end of the filtration phase (m^3)

V – Volume of filtrate (m^3)

W – Ratio of the mass of solid deposited by volume of collected filtrate ($kg.m^{-3}$)

X_{eq} – moisture content at thermodynamic equilibrium ($g_{water}.g_{dry\ solid}^{-1}$)

X – Moisture content ($g_{water}.g_{dry\ solid}^{-1}$)

List of Initialism

SRF - Specific resistance of filtration

MCC - cellulose microcrystalline

YSC - Fresh yeast

TMEDA - propane-1, 3-diamine

Greek letters

μ - Liquid viscosity (pa.s)

Ω - Cross-sectional area (m)

1. Introduction

Wastewater treatment plants produce large amounts of waste activated sludge that has no use. Nowadays, this waste is one of the problems that confront us. Hence it is very important to increase the solids content and to decrease the volume of sludge by removing water. The mechanical dewatering, which is normally used, is not always sufficient to satisfy these objectives and thus another step is necessary [(1)].

The fact that there are two types of water inside an activated sludge further complicates this process. One can considerate: free water, which is not attached to the solids, and bound water, which its properties have been modified due to the presence of the solids [(2)].The bound water is the problem of the dewatering process because it is believed that free water can be removed by mechanical processes. Nowadays, it is important to study the behaviour of the water content inside an activated sludge to improve the process of dewatering. In laboratory scale, there are many studies in this area. However, studying an activated sludge remains problematic because living microorganisms are always modifying its characteristics. To overcome this problem, some studies were conducted in order to produce a synthetic sludge to surrogate the real one. This new sludge had to be well defined, stable and successfully represent the real activated sludge proprieties [(3)].

Activated sludge flocs are a mixture of microorganisms and inorganic particles aggregated and evolved by a polymeric matrix [(3)]. In the current work, the synthetic sludge used had fresh yeast (YSC) to simulate the bacteria, alginate for microbial extracellular polymers, calcium ions for the bridging cations and cellulose microcrystalline (MCC) to simulate the filamentous microorganisms that give the sludge a better resistance.

To study the mechanical dewatering, a filtration compression cell was used. This technique is applied under constant pressure and is constituted by two phases: filtration phase and expression phase. The filtration phase corresponds to the formation of a cake due to the accumulation of the solid particles on the surface of a filter medium. The expression phase corresponds to the removal of water by cake squeezing.

Moreover, to better understand the water content inside a synthetic sludge, two different techniques were used: desorption isotherms and convective drying. Desorption isotherms allows one to describe the changes of the moisture content within the sample in relation to the thermodynamic activity of the water, at a fixed

temperature. On the other hand, convective drying is used to eliminate water from a solid material by evaporation [4]. During evaporation the rate of water depends on the type of bonds between water and the solids particles. While observing a drying curve, it is possible to observe different types of attachments of the water with the solid.

In the present work, it was proposed to conduct a study of the behavior of each component of a synthetic sludge to understand which one could influence more the dewatering process. To achieve that, different compositions of synthetic sludge were produced and posteriorly filtrated. Tests of drying and isotherms were carried out to estimate the bonding strength of the water within the solid matrix. Two different types of gels were tested to better understand the gel effect on the synthetic sludge.

2. State of art

Nowadays, the environmental problems have been increasing on the world agenda. The wastewater treatment has been improved over the years in order to have better efficiency at the lowest possible cost. This work aims to study one of the problems of a wastewater treatment, the waste activated sludge. It is important to decrease the volume of this waste. To do so, mechanical dewatering is normally used however this is not sufficient, another steps are usually needed. Several studies of the activated sludge have been made to try to understand why it is so difficult to dewater this kind of sludge. Normally, the distribution of the water content inside the sludge is considered to be the better approach to this issue.

2.1. Water classification

Generally two types of water are considered inside of an activated sludge: Bound water and free water. Free water is considered to be the one not influenced by the solids particles and the bound water is the one witch proprieties can be changed due to the presence of the solid. Another kind of classification of water was made and so the water was divided in four categories:

- Free water: water non-associated with solid particles and including void water not affected by capillary forces.
- Interstitial water: water trapped inside crevices and interstitial spaces of flocs and organisms.
- Surface (or vicinal) water: water held on the surface of solids particles by adsorption an adhesion.
- Bound (or hydration) water.

Furthermore, it was found that this classification does not fully consider the impact of polymeric matrix which constitutes activated sludge. A large quantity of water is trapped inside the polymeric network, and so this water needed to be considered as well. A new classification was introduced; it was made in order to cover surface bound water, osmotic water as well as the water trapped within the polymeric network. It was named “water holding”. However, this classification does not consider the intracellular water that has not been well defined yet.

Nevertheless, it is quite difficult to have a clear picture of the water distribution within activated sludge. So, a few studies with different methods, have been tried to quantify these two types of water [(2).]

2.1.1. Drying tests

A drying curve describes the evolution of the evaporation flux versus the mean moisture content. Here, the quantity of bound water can be estimated. This test appears to be questionable by recent studies that describe the formation of a crust and cracks in the surface and within the sludge, respectively. This can disturb the analysis of the drying curve, and proves the inadequacy of using the drying test for water classification proposes [(2)].

2.1.2. Dilatometric test

The differentiation of the bound and free water in this method resides in the fact that these two types of water, freeze at different temperatures. The free water can be determined by observing the expansion of a given sludge sample, due to the solidification of free water into ice. Then, the bound water content can be calculated by the difference between all quantity of water (determined by drying at 105° C during 24h) and the free water. However, various studies show that some parameters such as gas bubbles liberated from the sludge, freezing temperature and solids concentration, can disturb the frozen water measurements [(2)].

2.1.3. DTA and DSC tests

These methods have the same principles as the dilatometric, where bound water does not freeze at a temperature below the threshold temperature. The DTA test, measures the difference between a study sample and a thermally inert sample in relation to imposed temperatures. A graph of the difference of these temperatures versus several fixed temperatures shows increasing and decreasing peaks, characteristic of endothermic and exothermic transformation, respectively. Considering the area of peaks and the heat of the water freezing it is possible to convert the temperature data into mass of unfrozen water, with the middle step of calculation of the amount of heat required for transformation.

On the other hand, DSC measures the variation of the heat absorbed or released by a sample, placed in a controlled atmosphere exposed to a temperature scanning. Any transformation in the sample induced by the evolution of temperature

can be observed and described by thermal direct analysis. So, if the bound water does not freeze at a temperature below, the heat released during the DSC test is proportional to the free water amount. The bound water can be determined by the difference between the total water amount and free water amount (The first one can be calculated by drying the sample 24 h at 105° C). Nevertheless, this method is not well adapted because the sample uniformity cannot be guaranteed and the sludge normally contains large particles that are not in conformity to the samples used in this method, which are usually small. Yet, the choice of a threshold temperature can be really complex and difficult [(2)].

2.1.4. Centrifugal Settling tests

This method assumes that a sample centrifuged under an infinitive rotational speed tends towards an equilibrium height (h_∞) which corresponds to sediment composed by dry solid and bound water. The bound water per mass of drying solid (ϕ_w) can be derived from a mass balance:

$$\phi_w = \left(\frac{\rho_s - \rho_w}{\rho_{s1} - \rho_w}\frac{h_\infty}{h_0} - 1\right)\frac{\rho_w}{\rho_s} \quad (1)$$

The big problem in this method remains in hardness to estimate h_∞ [(2)].

2.1.5. Filtration tests

In this test the moisture content of the sludge is measured, after vacuum filtration. It is assumed that the water that remains on the cake after filtration is bound water. Other studies observed a constant period of the cake drying that normally corresponds to free water. This approach brings out some doubts about this test [(2)].

2.1.6. Expression tests

This technique defines the bound water as the final moisture content of the sludge expressed under a very high constant pressure (normally around 31 MPa). Other studies have showed that the bound water estimated for this method is different from the bound water estimated by drying. It is possible to say that this

method is not well defined in bound water classification but it can be a good method to evaluate the upper limits of any conventional mechanical dewatering device.

2.1.7. Sorption isotherms

With this technique, from the isotherm curve analysis (moisture content versus thermodynamic activity of water), it is possible to differentiate three types of water attachment (monolayer, multilayer and Capillary water). The free water content can be determined at a_w=1 but it is not a very accurate estimation. Indeed it is considered that this technique is more adapted for the characterization of bound water. Regarding the durability of the tests, and knowing that the activated sludge proprieties change over time, it is possible to say that this method is not well adapted for the study of sludge [(2)].

After reading all this methods, the biological proprieties of an activated sludge appear to be a problem in experimental characterization of the water content.

2.2. Synthetic sludge

The creation of a synthetic sludge was necessary because of the constant changing of the characteristics of the activated sludge. As it is known, an activated sludge is a complex mixture of various constituents and shows a wide variation in its physical, chemical and biological proprieties. The biggest problem in the study of this sludge is, undoubtly, the biological content. The living microorganisms are always changing proprieties, making it inapplicable to carry out the controlled experiments. To overcome this problem a synthetic sludge was created to surrogate the real one. This synthetic sludge was constituted by polystyrene particles with the size of bacteria to simulate the individual bacteria, alginate to simulate extracellular material and calcium ions to bridging cations [(5)].

After comparing physical and chemical proprieties in the two sludge, synthetic and activated sludge, one component that gives the flocs consistency was missing. This component was the filamentous microorganisms that provide activated sludge a backbone. Cellulose fibers with different diameter were chosen to simulate this component. Three types were chosen: microgranular, medium fibrous and long

fibrous. Then, after preliminary experiments, medium fibrous was chosen to be used in the rest of the experiments [3].

In the same assumptions a new formulation was made, changing the sulphate polystyrene latex particles to fresh yeast [6]. Another study used the same formulation with alginate, fresh yeast, microcrystalline cellulose and calcium chloride but here added another ion, potassium [7].

This new formulation did not contain the proteins and the lipids that are two important gelling agents, present in activated sludge, which are responsible for the bad dewatering. Bovine Serum Albumine and stearic acid were added in a new formulation to simulate the proteins and lipids, respectively [8].

All these studies have been made to try to reach a formula more similar in terms of physical and chemical proprieties and the level of consistency of the flocs, just to do a better study of the dewaterability problems of the activated sludge.

3. Experimental

3.1. Gels

3.1.1. Chemical gel

Four solutions are needed for this gel in the proportion that shows in the next table.

Table 1 – Concentration and proportion of gel components.

Component	Concentration (mol.L^{-1})	Proportion (mL)
Acrylamide	4	5
Bis-acrylamide	0.02	5
$K_2S_2O_8$	0.18	1
TMEDA	0.3	1

Within a goblet these proportions were mixed together. After 15 to 30 min, and once the polymerization has happened, the gel is ready to use.

3.1.2. Physical gel

For this gel, two compounds are needed: Poly (vinyl alcohol) (PVA) and Borax. A 50 mL of a solution of PVA at 4% is prepared in bain-marie. The temperature has to increase to 90 º C until dissolution happens. After, 12 mL of a solution of 4 % of borax is added. In a further step posteriorly is necessary to be fast, to mixture the two solutions and then take the gel.

3.2. Synthetic sludge

A solution of sodium alginate 10 g/L has been prepared. When the solution was completely homogeneous an amount of MCC, YSC and water was added. To promote the bonding between the alginate and the solid particles, the solution was mixed by a magnet stirrer during two hours. Afterwards, a solution of calcium chloride 0.05 M was added and the solution was stirred at 500 rpm for 3 min.

In the following table it is possible to observe the proportion, the dry mass and the amount that each component has in synthetic sludge.

Table 2 - Composition of the synthetic sludge.

Component	Proportion (%)	Dry mass (g)	Amount (ml)
Alginate (10 g.L^{-1})	10	3.7	370
YSC	27	10	
MCC	61.5	22.8	
Water			452
Calcium (0,05 M)	1.5	0.55	278
		Total	1000

To study the influence each component had in the solution, the concentration of the compounds was changed. The next figure shows the different percentages that were used.

Table 3 - Percentage used of each component.

Component	%			
Calcium	0	0.5	1	3
MCC	0	20	40	-
Alginate	0	2.5	7.5	-
YSC	0	-	-	-

3.3. Filtration

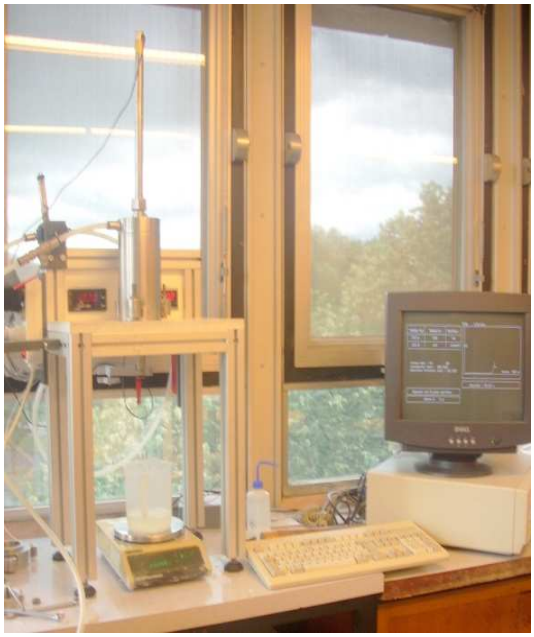

Figure 1 - Filtration compression cell device

This apparatus is constituted by a deep cylindrical stainless steel chamber with an internal diameter of 0.07m and a perforated disk collocated in the bottom of the cylinder that supports the filter medium. The paper filter used in the experiment was Whitman 541. Then a piston was added to the apparatus and pressure is fixed. For this current job the pressure used was 4 bar. A weight machine is connected to a computer that made the acquisition of the mass of water over the time.

3.4. Isotherms

Figure 2 - Desorption isotherms equipment

The samples (synthetic sludge, gels, MCC slurry) were placed in containers where the relative humidity was fixed due to saturated solutions of different types of salts. The containers were set inside a chamber under controlled temperature. In this case when the thermodynamic equilibrium was reached the experiment could be stopped and the samples were dried under 105 ºC over 24h. This equilibrium is reached when the difference between two measurements over two days was 5 mg.

3.5. Drying

This is a closed system in which humid air circulates by one ventilator. A heat resistance fixes the temperature of the air and a steam generator, connected at the installation by a control valve, fixes the relative humidity. The software made in the laboratory, allows the regulation of the operating conditions and the acquisition of the weight of the sample over time. The sample is exposed to three constant parameters (temperature, relative humidity and air velocity). For the current work the conditions are: T=55 ºC, H=15% and v_{air}=1 m/s.

Figure 3 - Convective drying device

4. Results and discussion

4.1. Filtration tests

This filtration is well described by the t/V versus V plot. It is possible to distinguish the two phases: filtration and expression. The filtration phase is characterized by the linear part. The other part of the curve corresponds to the expression phase. The specific resistance to filtration (SRF) describes the ability of forming a cake to let the water go through and is possible to calculate by using the slope of the linear part according to the following equation [9]:

$$\frac{t}{V} = \frac{\mu \cdot SRF \cdot W}{2P_a \cdot \Omega^2} V + \frac{\mu \cdot R_{fm}}{P_a \cdot \Omega} \quad (2)$$

To study the dewaterability of each component, different sludge with different percentage of each component were tested.

4.1.1 Variation of the concentration of calcium

As was explained above, the calcium forms the bridges between the extracellular materials themselves, and between the extracellular material and the bacteria. So calcium is an important component to the formation of the flocs, because without this connection the flocs do not exist.

- **0 % calcium**

With the absence of calcium, there is not the formation of the aggregates of the particles. As it is possible to verify in the picture, the solids are concentrated on the bottom of the jar and do not have aggregates. Some particles are suspended all over the solution.

Plotting the experimental values, the t/V versus V curve could be constructed.

Figure 4 - Synthetic sludge with 0% of calcium

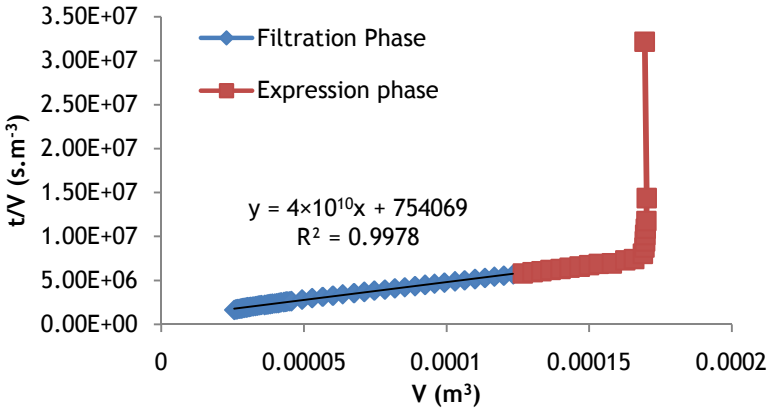

Figure 5 - Dewatering curve for the sludge with 0 % of calcium

It is possible to distinguish the two phases: Filtration phase and expression phase. As referred before, the filtration phase is linear, and with its parameters it is possible to calculate the SRF.

From the linear adjusting of the linear phase the SRF is equal to 6.53×10^{12} $m.kg^{-1}$. It was also possible to calculate the volume of filtrate that was equal to $1.23 \times 10^{-4} m^3$.

- **0.5, 1 and 1.5 % of calcium.**

In these percentages, a layer of solids, which the water could not pass through, was formed and the filtration did not happen as normal. After several hours (see appendix C) there was not any cake and all the water and suspended solids were inside the chamber. Only a small quantity of water was able to pass.

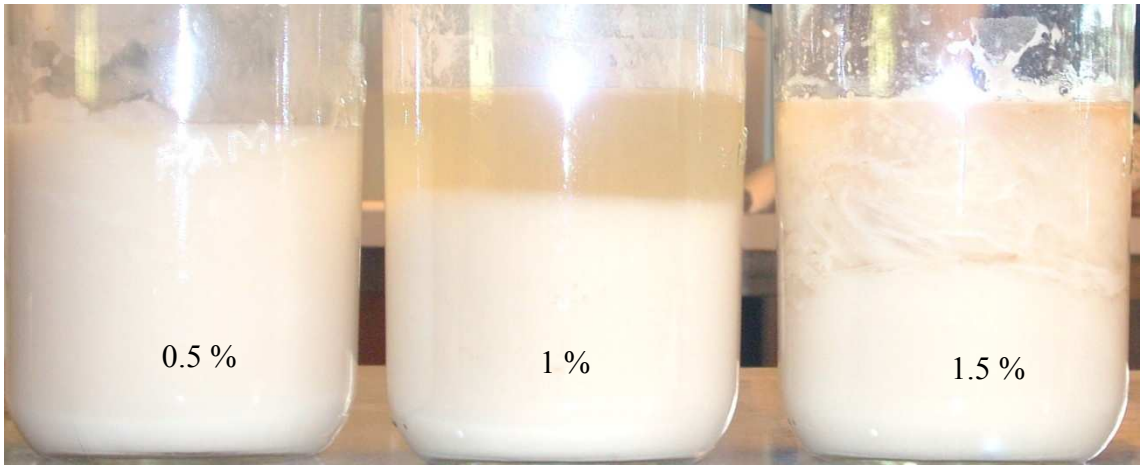

Figure 6 - Synthetic sludge with 0.5, 1 and 1.5 % calcium

Figure 7 - Layer of solids

This figure shows the layer that was formed in the filtration of these three percentages. Normally, if a filtration follows its normal course, a cake with a thickness of five millimeter approximately is formed. This layer of solids normally has one millimeter of thickness even with more time of filtration. This may be happening because of the formation of fouling [10]. This phenomenon is an accumulation of unwanted material in solids surfaces, in this case in a filter. Another filter was tested in order to verify if this phenomenon happen due to the characteristics of the filter used. In this filter fouling was formed as well.

- **3.0 % of Calcium**

With this percentage, strong and well defined flocs were formed. The water was just surrounding the solids, there were no suspended solids, and the filtration was really fast, as it is possible to check by the following figure.

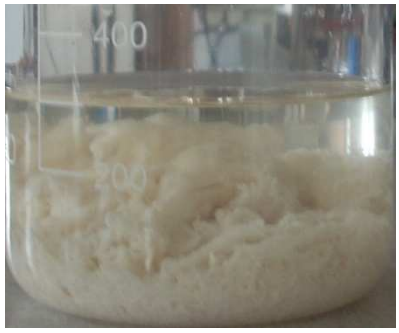

Figure 8 - Synthetic sludge with 3 % of calcium

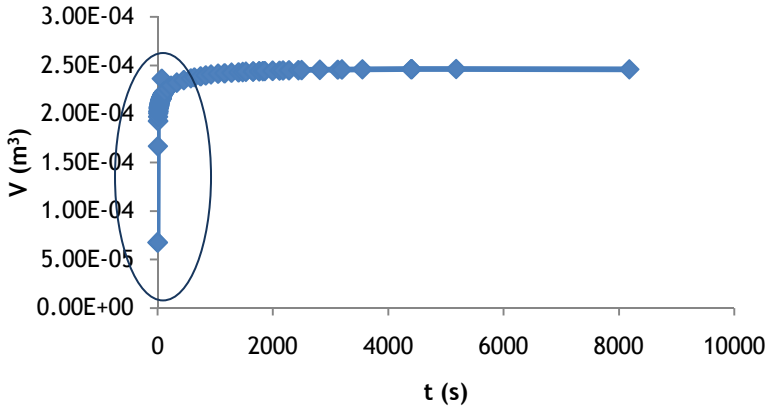

Figure 9- Evolution of the mass of water over the time.

After trying to found a linear fitting for the filtration phase, the founded value for the correlation factor was 0.9883.

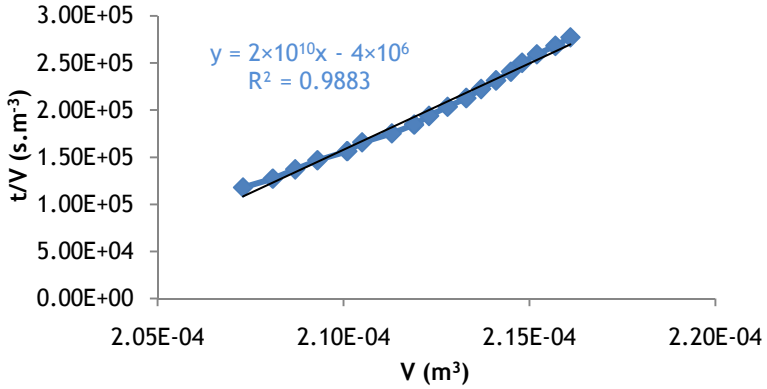

Figure 10 - Adjustment of the filtration phase

For this sample, the SRF was 5.43 × 10^{12} m.kg^{-1} and the volume of filtrate estimated was 2.16 × 10^{-4} m^3. These values, especially the value of SRF, cannot be takes into good account since the low adjustment of the curve.

Comparing all the samples, the variation of calcium has a high influence on the synthetic sludge. The increasing of attachment inside the sludge is observed with the increasing of calcium content. This is explained by the function of calcium in the sludge, a bridging ion. The increasing of calcium increases the link capacity of the sludge, and turns more aggregated.

4.1.2 Variation of the alginate content

Such as it was mentioned above, the alginate simulates the extracellular material in the sludge. In the presence of calcium, a calcium-alginate gel is formed.

- **0% of alginate**

Without alginate, the matrix cannot be formed. So, even with the presence of calcium, there is not extracellular material to bridge with other components and so, the flocs are not formed. As it is possible to observe in the picture, like calcium, non aggregated particles are on the bottom of the jar. This happens because of the non-existence of the gelatinous matrix.

Figure 11 - Synthetic sludge with 0 % of alginate

By plotting the experimental results it is possible to distinguish the filtration phase from the expression phase. The adjustment of the curve has a good correlation factor hence it is possible to say that the curve is well adjusted to a linear curve.

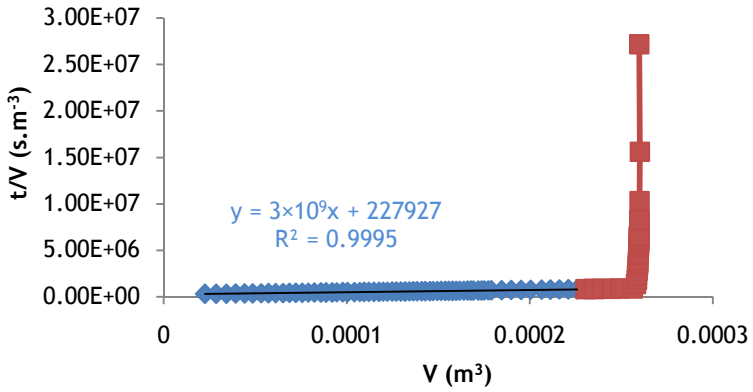

Figure 12 - Dewatering curve for the sludge with 0 % of alginate

The SRF and the volume of filtrate are, respectively, 1.22×10^{14} $m.kg^{-1}$ and $2.26 \times 10^{-4} m^3$.

- **2.5 % of alginate**

From this concentration it is possible to observe more solids, both in the bottom and suspended in the solution. The filtration of this took more time than the usual. When the program was stopped, it was possible to see that a cake was formed but the solution was not totally filtrated.

Figure 13 - Synthetic sludge with 0 and 2.5 % of alginate

- **7.5 % of calcium and 3 % of calcium.**

In this experiment, in order to compare the values, a concentration of 3 % of calcium was used. The consistensy and the appearance of the flocs were very similar with the sludge containing 3 % of calcium. Thus from the appearance of the two curves, of the mass of water over the time, were compared.

Figure 14 - Synthetic sludge with 7.5 % of alginate and 3 % of calcium

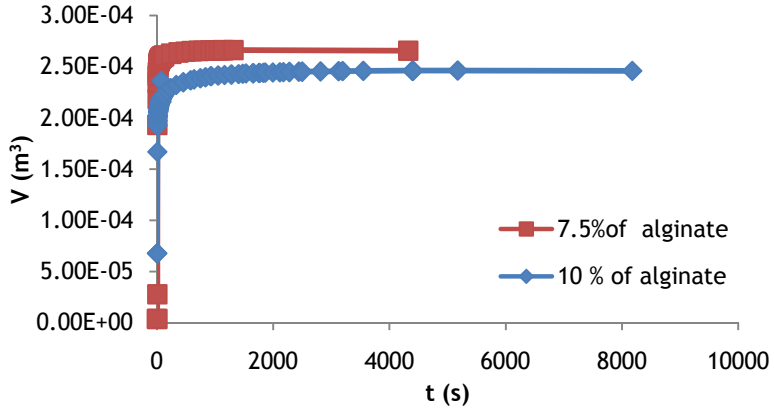

Figure 15 - Evolution of the mass of water over the time

Analyzing the two curves it is possible to state that the concentration of alginate influences the connection between the water and the solids. The increase of alginate increases this connection. From 7.5 % of alginate, the water that is surrounding and not linked to the solids is bigger than for 10 %.

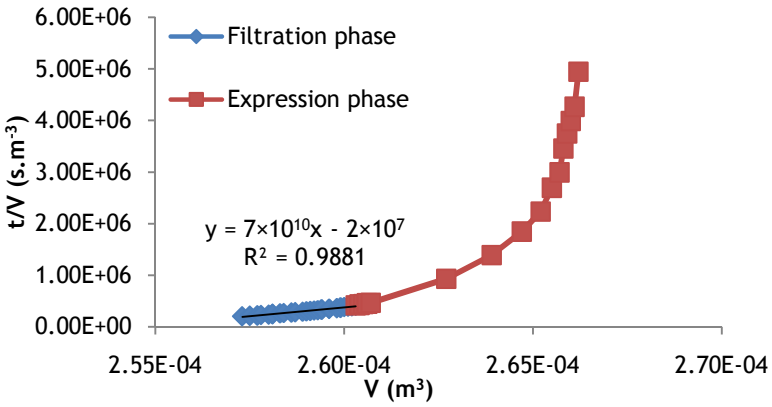

Figure 16 - Dewatering curve of a synthetic sludge with 7.5% of alginate and 3% of calcium

For this sludge the values of SRF and volume of filtrate are, respectively, 2.23 × 10^{13} and 2.60 × 10^{-4}. But also that, the sludge with 3% of calcium and 10 % of alginate, have a low correlation factor.

4.1.3 Variation of the concentration of MCC

The MCC simulates the filamentous microorganisms that provide a backbone to the sludge. Without this component the flocs can still be formed but they are weaker and less compacted.

- **0% of MCC**

In this experiment all the solution passed through the filter. No cake or even a layer was formed. This is explained by the fact that the MCC particles provide a backbone to the sludge and without it, the structure of the sludge is weaker and the particles smaller.

- **20 % and 40 % of MCC**

In these two concentrations a similar behavior to the one 0.5, 1 and 1.5 % of calcium concentration was observed. A formation of a layer of solids was observed and the sample was not filtrated. This can be explained too due to the formation of fouling.

As it was mentioned before, the MCC was the backbone of the sludge and if some weaker flocs are mixed, this link maybe broken. So, using the solution of lower percentage (20%) of MCC and then if during 30 min with a medium speed maybe will cause the break of the link. Despite the mixing on the beginning there was more water leaving the filtration chamber, again a layer was formed and the filtration did not happen.

4.1.4. Absence of fresh yeast

For this component only one test was conducted, in order to check the impact in the sludge. In the studies of activated sludge it is impossible to remove this component is not viable because it is not possible to change the quantity of this component in the sludge. A solution with 0 % of YSC was tested and filtrated.

Figure 17 - Synthetic sludge with 0 % of MCC

Seeing these results it is possible to confirm that the fouling that appears in the solutions was formed by the yeast in contact with another material of the sludge. Looking at the sludge it is possible to say that the flocs were formed. The only difference in this sample was the colour.

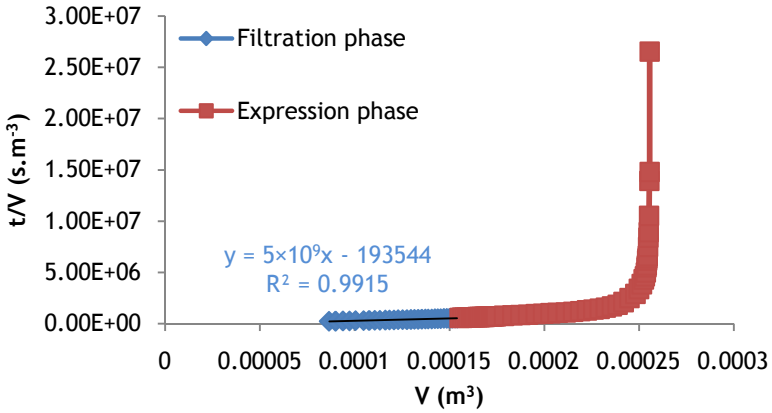

Figure 18 - Dewatering curve of a synthetic sludge with 0% of yeast.

This was the best adjustment that was possible to do. The first points just take a strange behavior, maybe because of the big quantity of water that leaves the sample in the beginning. The SFR and the volume of filtrate are, respectively, 1.24×10^{12} $s.m^{-3}$ and $1.54 \times 10^{-4} m^3$.

Other sample was tested, replacing fresh yeast by kaolin in the same proportions. The solution was even more difficult to filtrate than the other because in this case just a small quantity of water could pass though the filter.

After all these results, it was possible to construct the next table.

Table 4 - Review of the filtration results.

Component	%	Filtration	SRF ($s.m^{-3}$)	$V_{filtrate}$ (m^3)	$t_{filtrate}$ (s)
Reference	-	-	-	-	-
Calcium	0	+	6.53×10^{12}	1.23×10^{-4}	699
	0.5	-	-	-	-
	1	-	-	-	-
	3	+	5.34×10^{12}	2.16×10^{-4}	60
Alginate	0	+	1.22×10^{12}	2.26×10^{-4}	179
	2.5	-	-	-	-
	7.5	+	2.26×10^{13}	2.60×10^{-4}	107
MCC	0	+	-	-	-
	20	-	-	-	-
	40	-	-	-	-
Fresh yeast	0	+	1.24×10^{12}	1.54×10^{-4}	88

Analysing the results it is possible to verify that only 5 samples were filtrated (signal +), 3 of each in the absence of one component. In the absence of MCC there was no filtration (signal -) because all the solution passed through the filter.

The two curves from the concentration of calcium of 3% (10% of alginate and 7.5% of alginate) in the filtration phase, did not have a good adjustment to the linear curve, so the calculated values of SRF hardly to describe the permeability of the cake. So it is better not to compare these values of SRF to the same values of the other samples.

- 0 % of calcium: This concentration has the lower value correspondent to volume of filtrate, but has the bigger SRF and time of filtration. Analysing these values it is possible to say that the cake is more permeable but the water is more retained in the sample. With these values and with the knowledgement of the functionalities of each component it is possible to conclude that for the absence of calcium the water is well linked to other particles and calcium does not have a big impact in the attachment of the water in the solid (more than for the absence related to the other components.);
- 3% of calcium: Through this concentration, the lower time of filtration was found. With the increasing of the calcium ions the matrix becomes more attached and the quantity of water inside the matrix is inferior. Comparing this result to the one from 0% of calcium it can be said that the calcium only establishes connections between the components of the sludge. The increasing of calcium just makes the flocs more attached and into a closer matrix.
- 0% of alginate: Comparing the volume of filtrate of this sample to the other samples in the absence of one component it is possible to say that the water was not attached to the solid. This is related to the non existence matrix that can entrap the water.
- 7.5 % of alginate and 3 % of calcium: For these concentrations, and comparing with another one of 3 % of calcium it is verifiable that the increasing of alginate makes the volume of filtrate decrease. This happens because a bigger concentration of alginate means more material to be connected, so the matrix is more attached as well as the other material existent.
- 0 % of yeast: from this value the matrix was formed. Comparing the value of the volume of filtrate it can be state that the water was well attached in the matrix.

4.2. Isotherms

For thermodynamic assumption the water activity (a_w) is equal to the relative humidity in the equilibrium, as show the next equation:

$$a_w = \frac{P_v}{P_{sat}(T)} = RH_{eq} \quad (3)$$

Normally a sorption isotherm curve, in the case of the water vapour, has the following shape:

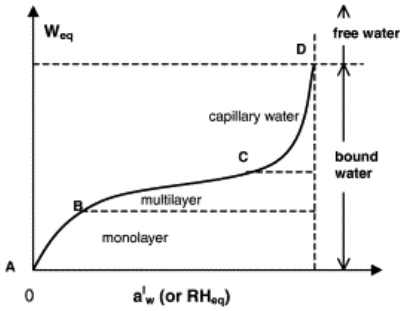

Figure 19- Classical isotherm of water.

It is possible to distinguish three different parts. In the first part, from A to B, the solid surface is covered with a monolayer of adsorbed water molecules. Here the interaction forces are short-range and very intense. In the second part, from B to C, there is a decreasing of the interaction forces and the solids are covered by multiple layers of water molecules. The last part, from C to D, layers of water molecules coalesce within the micro-pores of solid structure and the water is bound due to capillary forces. In a_w=1 this curve tends to an asymptote which corresponds to free water [(11)].

After several days of watching the evolution relatively to the weight of the samples, to observe the thermodynamically equilibrium, it was possible to trace the isotherms of each.

From next figure is possible to compare both gels and alginate.

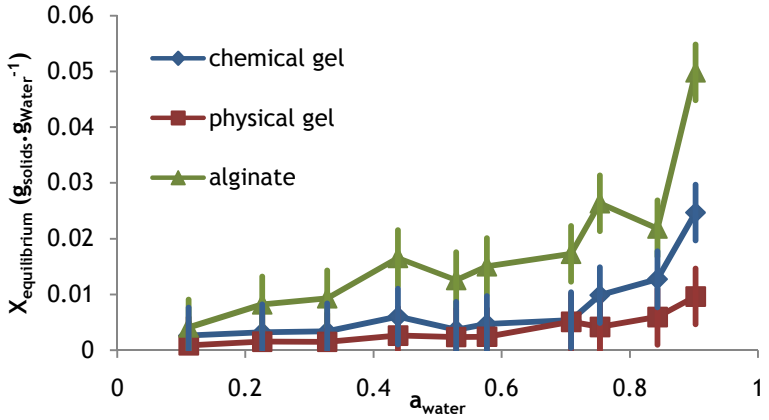

Figure 20 - Comparison of the isotherms of both gels and alginate.

The gels are polymers that have high ability to water absorption and a significant retention power. In other hand the alginate is a biopolymer that, in solution, behaves like flexible coils. But its behaviour changes when a divalent metal ion, such as calcium, is added, forming an ordered structure. In this experiment the alginate was just mixed with water [12].

The two gels have a similar behaviour and appear to have a small quantity of bound water. In the graph the little lines are the errors correspondent to each curve [13]. Having that in account it is also possible to say that alginate and the gel have a similar behaviour and the one that is closer to alginate is the chemical gel.

After a filtration step, the cake that is formed was put in the oven during several days to obtain the respectively isotherms of each sludge. In these three sludge the concentration of calcium was changed.

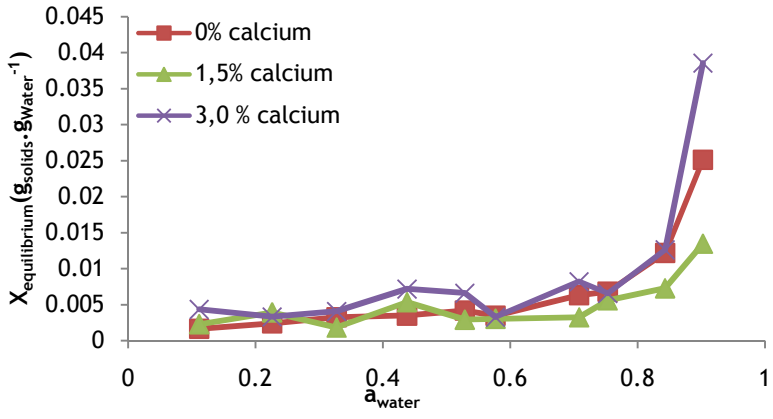

Figure 21 - Comparison of the sorption isotherms of synthetic sludge with three different concentration of calcium.

By this figure it can be observed that, the three different sludge have a similar behaviour. It was supposed that the quantity of free water would decrease with the increasing of calcium, because of the connection related to the gelatinous matrix to the others components. But by analyzing the curves it is possible to verify that calcium does not have a really influence in the attachment of water into the solids. Making a review of what has been studied; the calcium is the agent that has the function of bridging the matrix and does not really influences the bounding of the water in the solids.

4.3. Drying tests

With the experiment results, a drying curve can be drawn, and the evaporation flux can be calculated through the following equation:

$$F_m \cdot A(W) = m_s \cdot \frac{dX}{dt} \tag{4}$$

This curve can describes the evolution of the evaporation flux versus the mean moisture content. A normal drying curve is shown in the picture bellow.

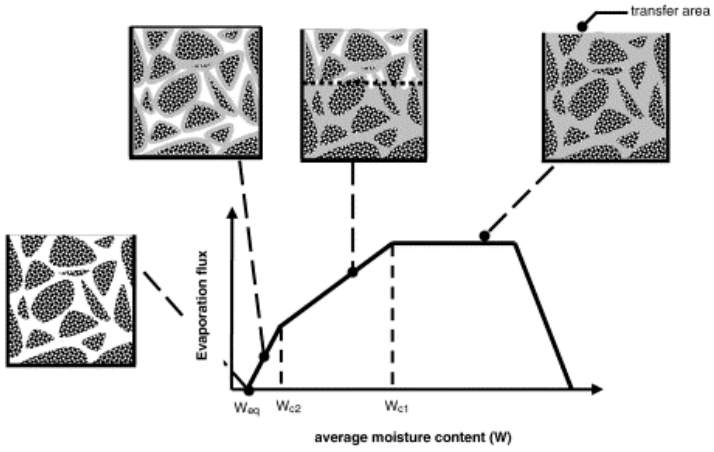

Figure 22 - Classical drying curve

By observing this curve it is possible to distinguish four different parts. Reading the graph from right to left, the first part corresponds to a period of increasing temperature. After that, a period of constant rate can be seen. This period correspond to the evaporation of free water at the surface of the material. Subsequently, a first period of falling rate which corresponds to the drying boundary progression into the material. In this point, the water starts to migrate into the solid (happens because activated sludge is a hygroscopic material). The second decrease just happens in hygroscopic materials [2]. Here the hardly bound water is slowly evaporated.

In the drying tests the experimental conditions were T=55° C, H=15% and v=1 m/s. Three samples were tested: Physical gel, Chemical gel and alginate slurry. On the beginning a support that had big walls was used but in this one a small part of the sample was touched by air current. To solve this problem another support was used. This one has smaller walls and the sample had bigger contact with the humid air.

However another problem appeared, the evolution of the diameter and thickness during the drying process. This evolution was not linear and so, using an approximation of the value of the area was not possible (see appendix J). To overcome this problem, the variation of moisture versus of the moisture content was plotted instead of plotting the evaporation flux.

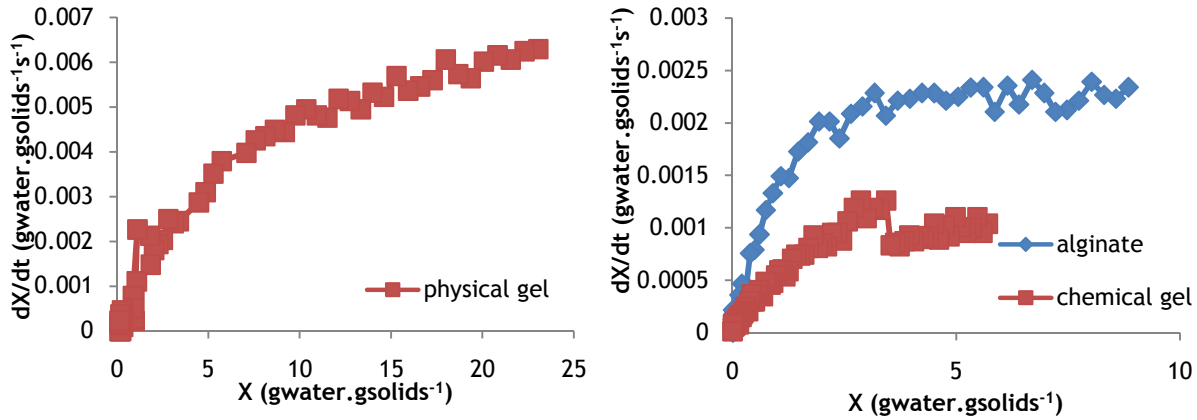

Figure 23 - Drying curve

Comparing the drying curves of the chemical gel and alginate it is possible to verify that the quantity of bound water is very close (the W_{c1} corresponding to the curve of the drying). Comparing this quantity to the one found by the isotherms, it is concludable that the bound water content is not as low as it appeared to be in the isotherms.

The level of the free water content was different in each gel. In order to understand this difference the next equation can give three parameters that can influence that level.

$$\frac{dX}{dt} = k \cdot S \cdot \big(C(sup) - C(exp)\big) \tag{5}$$

Reviewing the evolution of the volume and shape of the samples during the drying and comparing with the parameters of the equation it is possible to state that:

- In chemical gel the shape of the sample change progressively during the experiments. The *k* of the equation can change according to the passing air in the sample.
- It was observed a decreasing area in all the samples, this factor also influences the derivate.

Taking in consideration that the value of the transfer area was not considerate in the drying curve and that the shape and the surface changed during the experiment, it can be concluded that there are too many values that are able to influence the results of the drying experiments [(4)].

Lots of assumptions were made so these values are not a good estimate regarding the water classification.

5. Conclusions

In this work it was possible to confirm the functionalities that each component have in the sludge.

The sludge described in the literature, used as a reference, did not filtrate. Further, many different changes in the proportion of the components were made. It was observed that in the absence of one component the solution was filtrated.

Changing the concentration of calcium and observing the changes that happen in the sludge, was possible to affirm that this contributes to the aggregation of the flocs. The increment on the calcium provokes a rise related to the agglomeration of the flocs.

At 2.5 % of alginate the flocs were not formed however, after filtration a small cake was created. Eventhough not all the solution was filtrated. Here, it is possible to conclude that a low quantity of alginate does not permit the formation of flocs but that the matrix exists inside the sludge and also the connection between this one and the others components of the sludge.

At 0% of MCC all the solution passes through the filter. This shows the weakness of the flocs and the formation of small aggregates of particles.

Without yeast, the formation of flocs was observed and the filtration was possible because of the non existence of fouling. It was possible to conclude that the presence of yeast did not influence the formation of flocs.

By observing all the results is not possible to verify of which one of the components have more influence in the dewatering because all of them have a particular influence in this process.

From the isotherms it was possible to conclude that the ion of calcium does not have an influence related to the attachment of the particle of water within the sludge. This can be explained by the fact that its functionality is the bridging

The experimental tests do not bring anything new, they only serve the purpose of confirming the functionalities of each component. With this study it was possible to assume that the fouling was forming because of the connection between the matrix and the yeast.

6. Assessment of the work

6.1 Aims achieved

In this work it was proposed to study the behaviour of each component of a synthetic sludge to see which one could influence more the dewatering process.

It was not possible to find the component that had more influence in dewatering process because some solutions did not filtrate. But the functionalities of each one of the components were observed.

6.2 Limitation and further work

Setbacks occurred all over this work. In the beginning, another method was proposed, the DSC test. But after a month it was altered to filtration because the DSC device was not working properly. Then, the filtration was just available in May, just two months before the delivery of the thesis. Even then the drying device was not available for some weeks. All this occurrences affected the quantity of the experiences that could be performed.

It would be interesting to do different solution but now with a reference solution of 3% of calcium because with this concentration the solution could be filtrated. Then this one should be dried just to observe how the water is attached to the particles.

It would also be interesting to, study in depth the process of fouling and try to overcome this problem by changing the substituent of bacteria.

6.3 Final Appreciation

In the beginning it was proposed to try and find the most influent component in a synthetic sludge doing mechanical and thermal tests. However one to the bad filtration it was not possible to verify how the water was attached to the solid by the thermal tests.

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Appendix A: Calculation of the SRF values

Adjusting the curve of the filtration phase to a linear equation it is possible to calculate the SFR through the next equation:

$$\frac{t}{V} = \frac{\mu \cdot SRF \cdot W}{2P_a \cdot \Omega^2} V + \frac{\mu \cdot R_{fm}}{P_a \cdot \Omega} \quad \text{(A1)}$$

With the slope of the curve, SRF can be calculated by:

$$\text{SRF} = \frac{a \cdot 2 \cdot P_a \cdot \Omega^2}{\mu \cdot W} \quad \text{(A2)}$$

a: Slope of the curve ($s.m^{-6}$)

P_a: Applied pressure (pa) = 4.0×10^5 pa

μ: Liquid viscosity (pa.s) = 1.0×10^{-3} pa.s

Ω: Cross-sectional area (m^2) = 3.9×10^{-3} m^2

W – Ratio of the mass of solid deposited by volume of collected filtrate ($kg.m^{-3}$)

In the next table is possible to see the values of SFR calculated for each sludge:

Table A1- Calculated values of a, W and SRF

	W ($kg.m^{-3}$)	a ($s.m^{-6}$)	SRF ($m.kg^{-1}$)
0% Calcium	72.58	4.0×10^{10}	6.53×10^{12}
3% Calcium	43.54	2.0×10^{10}	5.43×10^{12}
0% Alginate	63.05	3.0×10^{9}	1.22×10^{12}
7.5% Alginate	36.6	7.0×10^{10}	2.26×10^{13}
0% Yeast	47.73	5.0×10^{9}	1.24×10^{12}

Appendix B- Calculation of the mass necessary for the different quantities of each component

By the following system the mass necessary for each component in all the different percentages is calculated.

$$\begin{cases} m_{Alginate} + m_{MCC} + m_{YSC} + m_{calcium} = m_{total\ of\ solids} & (B2) \\ \frac{x}{m_{total\ of\ solids}} = \frac{new\ \%_{Component}}{100} & (B1) \end{cases}$$

The following table shows the different amounts of mass needed for each percentage.

Table B1 - Mass necessary for each different sludge

	%	m(g)
Calcium	0.5	0.18
	1	0.37
	3	1.13
Alginate	2.5	0.86
	7.5	2.7
MCC	20	3.56
	40	9.5

Appendix C – 0.5, 1 and 1.5 % of calcium curves.

For this concentration the filtration does not go as expected. After some hours, the solution, was not filtrated and remained inside the chamber. The next figures show the evolution of the volume of water all over the time.

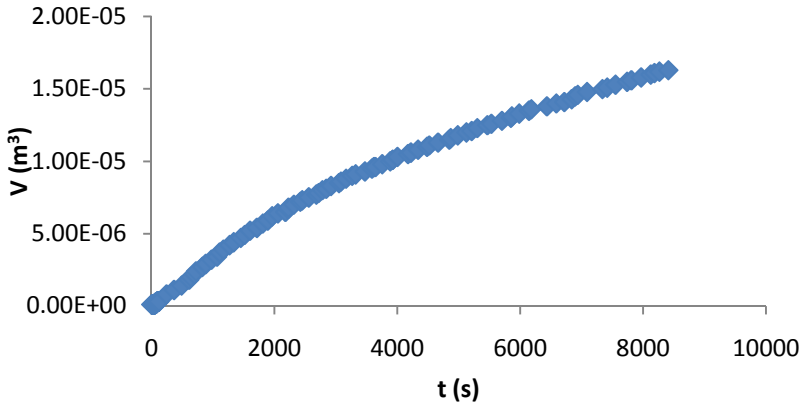

Figure C1 - V versus t of 0.5% of calcium

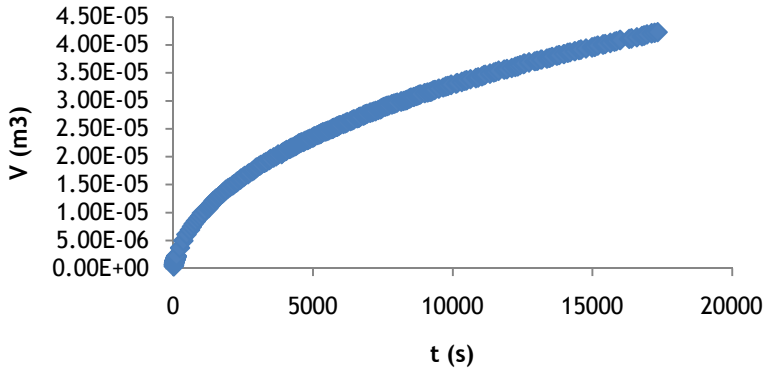

Figure C2 - V versus t for 1% of calcium

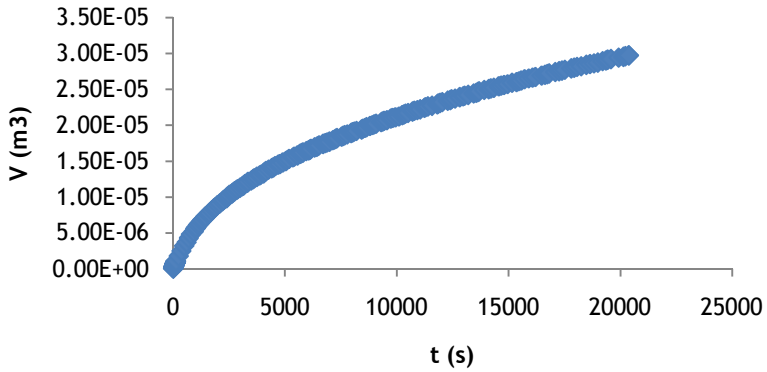

Figure C3 - V versus t for 1.5% of calcium

A filtration normally takes two hours (7200 seconds) but for these samples it took more time and it had to be stopped because there were always drops falling. When the chamber was open a big part of the solution remained inside. As it is possible to see, to the quantity of water that passed through the cake was very low considering that normally the volume of the solution is approximately 3.0×10^{-4} m^3.

Appendix D – 2.5% of alginate curves.

In this concentration a little cake was observed.

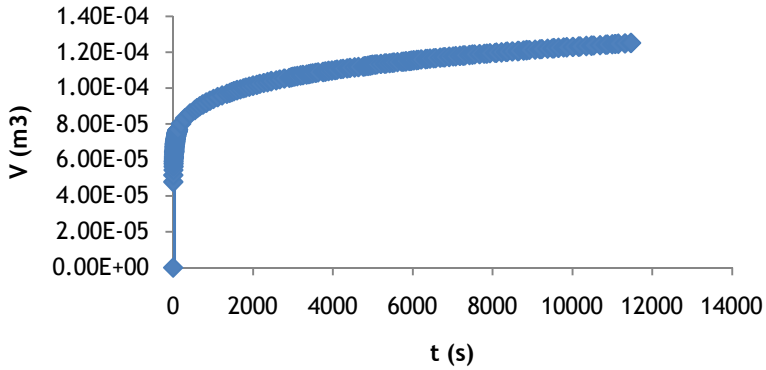

Figure D1 - V versus t for 2.5 % of alginate

Analyzing the graph, the quantity of water increases slowly over the time. But comparing with the graph in the previous appendix the quantity of water that passed through the cake was bigger. But, as it happened before, the experiment had to be stopped and the solution was not fully filtrated.

Appendix E – 0, 20 and 40% of MCC curves.

For this ranging of MCC content some strange graphs here observed.

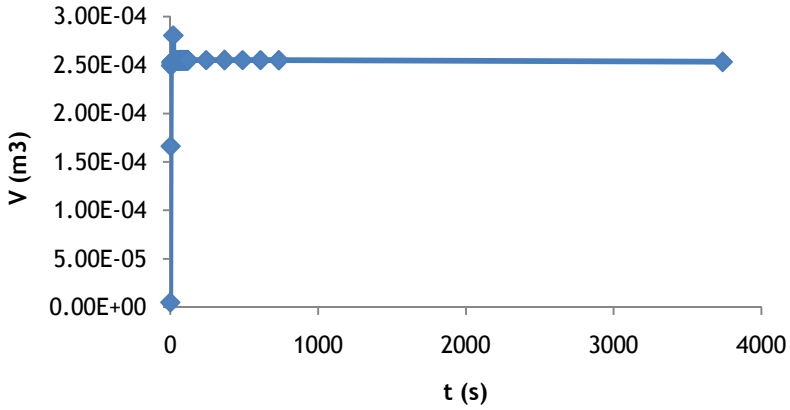

Figure E1 - V versus t for 0% of MCC

In 0% of MCC all the solution passed through the filter. As it is possible to observe in the picture, the stabilization of the curve happened very fast and the curve tended to the total volume of the solution since no cake was formed.

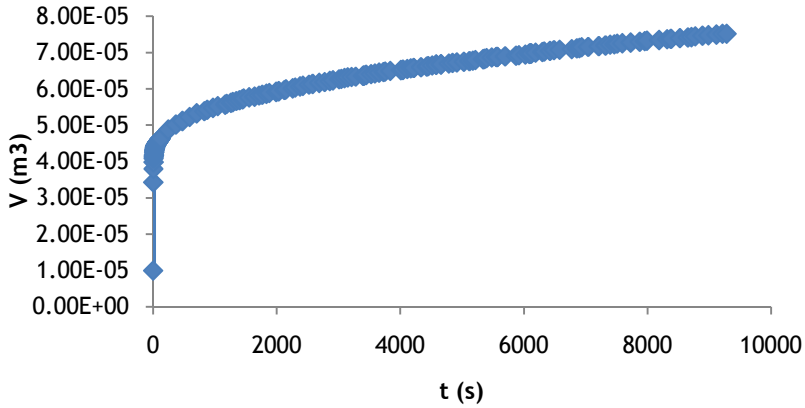

Figure E2 - V versus t for 20 % of MCC

By analyzing the figure above it is possible to affirm that on the beginning, the solution had a normal behavior but then the curve stabilized in a value very low compared to the value of volume.

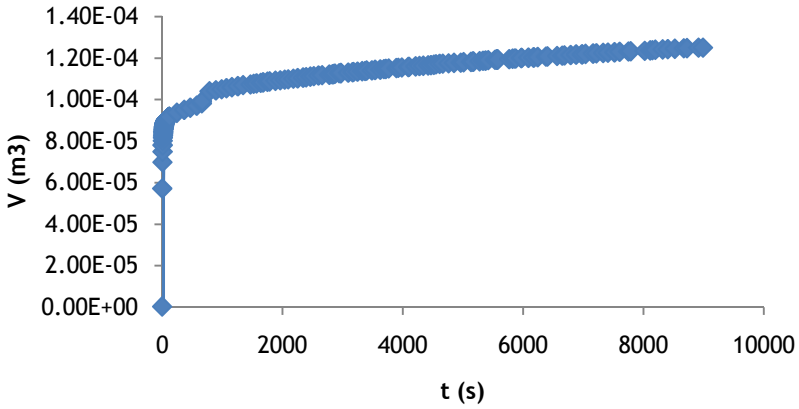

Figure E3 - V versus t for 20 % of MCC with 30 minutes of mixing

Comparing this figure to the previous it is possible to state that the mixing breaks some fibers and makes the solution more filterable. Here the volume of water that is not attached to the solids is bigger than for a solution without mixing.

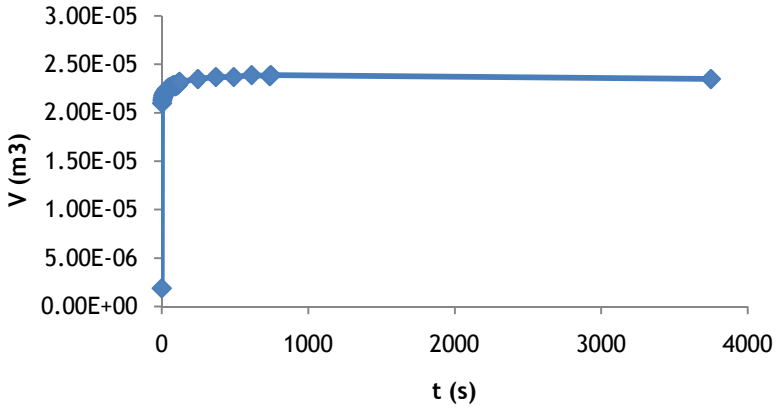

Figure E4 - V versus t for 40 % of MCC

This curve seems a normal curve of filtration but with a better analyzes one can verify that it tends to a very low volume. With this range of concentrations, eventually after a while the fouling will not let the water pass.

Appendix F – Kaolin curve.

This curve shows a really strange behavior that is impossible to explain with increase or decrease volume. The results maybe inaccurate due to device malfunctions.

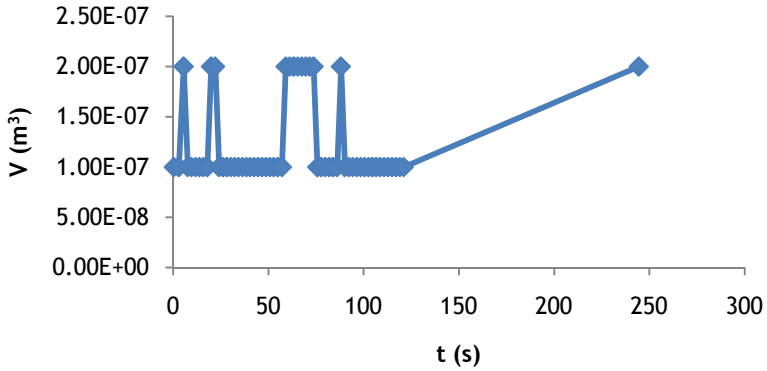

Figure F1 - V versus t replacing yeast by kaolin

Appendix G: Deduction of the activity equation for isotherms.

The liquid vapour equilibrium of pure water can be described by the equality of the fugacities:

$$f_l(T,P,x) = f_v(T,P,x) \quad \text{(F1)}$$

The fugacity of the liquid is defined as:

$$f_l = \gamma(T,P,x) \cdot x \cdot f_l^0(T,P) \quad \text{(F2)}$$

Where the f_l^0 and γ are the respectively the fugacity of the pure substance and the activity coefficient.

If the pressure influence is neglected (below 10 bar) the fugacity of the liquid water (pure substance as reference stage) at fixed T and P is:

$$f_l^0 = P_{sat}(T) \quad \text{(F3)}$$

Otherwise the fugacity of the vapour is defined as:

$$f_v = \phi_v(T,P,y) \cdot y \cdot P \quad \text{(F4)}$$

If the vapour is considered as an ideal gas the coefficient of fugacity is: $\phi_v = 1$ Then the equation (a1) becomes:

$$y \cdot x = y \frac{P}{P_{sat}(T)} \quad \text{(F5)}$$

The introduction of the activity ($a = \gamma \cdot x$) and the partial pressure ($P_w = y \cdot P$) of the water leads to:

$$a_w = \frac{P_v}{P_{sat}(T)} = RH_{eq} \quad \text{(F6)}$$

Appendix H: Values of isotherms.

After several days of measurements weight of sample the equilibrium was reached. The next two tables show the salts that were used as well as the constitution of the samples.

1	**Lithium chloride**	**1**	**Alginate**
2	**Potassium acetate**	**2**	**0 % Calcium**
3	**Magnessium chloride**	**3**	**1.5 % Calcium**
4	**Potassium chloride**	**4**	**3% Calcium**
5	**Magnessium nitrate**		
6	**Sodium bromide**		
7	**Strontium chloride**		
8	**Sodium chloride**		
9	**Potassium chloride**		
10	**Barium chloride**		

1	**Lithium chloride**	**1**	**Chemical gel**
2	**Potassium acetate**	**2**	**Physical gel**
3	**Magnessium chloride**	**3**	**MCC**
4	**Potassium chloride**		
5	**Magnessium nitrate**		
6	**Sodium bromide**		
7	**Strontium chloride**		
8	**Sodium chloride**		
9	**Potassium chloride**		
10	**Barium chloride**		

Table H1 - Values of the weight of the samples of chemical and physical gel and MCC.

	Weight (g)							
Sample	**cuvete**	**0 hours**	**1 day**	**2 days**	**3 days**	**4 days**	**5 days**	**6 days**
11	4.5331	6.9344	4.9172	4.8779	4.8739	4.8715	-	-
12	4.2656	6.9532	4.4487	4.4697	4.4038	4.4043	-	-
13	4.2123	7.8591	5.4621	5.4767	6.3088	-	-	6.1666
21	3.8402	5.6573	4.1229	4.1084	4.0955	4.1038	-	-
22	3.884	6.4878	4.022	4.0189	4.0178	4.0184	-	-
23	3.4641	7.3897	4.8092	4.8063	4.8082	-	-	4.8046
31	4.3806	6.0926	4.6502	4.632	4.6305	4.6285	-	-
32	4.286	6.4471	4.4144	4.4141	4.4129	4.4121	-	-
33	4.5171	8.164	5.8022	5.8001	5.7971	-	-	5.7968
41	3.6914	5.9054	4.069	4.0289	4.0218	4.0195	-	-
42	3.9354	6.4248	4.1078	4.0676	4.0666	4.0663	-	-
43	3.8567	7.4496	5.1542	5.1504	5.1502	-	-	5.151
51	4.5184	6.4192	5.0367	4.8209	4.8113	4.8039	-	-
52	3.7882	5.9603	4.2547	3.9101	3.9096	3.9042	-	-
53	4.6244	8.849	6.2359	6.054	-	-	6.0507	6.0485
61	4.0066	5.5378	4.2841	4.2486	4.2436	4.2403	-	-
62	3.8204	5.8193	3.9307	3.9292	3.928	3.9268	-	-
63	4.4453	8.5698	5.9332	5.9209	5.9116	-	-	5.9052
71	4.456	6.1269	5.032	4.7335	4.7195	4.7125	-	-
72	3.8969	7.1142	4.908	4.0811	4.0752	4.0739	-	-
73	4.4592	8.5567	6.3515	5.9696	5.9622	-	-	5.9541
81	4.3119	5.8096	4.8148	4.5676	4.5594	4.5581	-	-
82	4.295	6.3423	4.71	4.4203	4.4146	4.4144	-	-
83	4.4563	8.612	6.7003	5.9962	5.9911	-	-	5.9775
91	4.6029	6.1889	5.5564	4.9945	4.887	4.8812	-	-
92	4.5439	7.0079	5.92	4.8896	4.7051	4.6986	-	-
93	4.5583	8.4159	7.225	6.1279	6.0314	-	-	6.0168
101	4.0107	5.7158	5.1925	4.804	4.5072	4.4158	-	-
102	3.6867	6.1348	5.4725	4.9477	4.3392	3.9043	-	-
103	3.9914	7.7368	7.197	6.566	5.826	-	-	5.467

Table H1 - Values of the weight of the samples of chemical and physical gel and MCC.

	Weight (g)							
Sample	**7 days**	**8 days**	**9 days**	**10 days**	**11 days**	**12 days**	**13 days**	**14 days**
11	4.8677	4.8667	4.8663	4.8651	4.8648	-	-	5.8636
12	4.4036	4.4024	4.4022	4.401	4.4012	-	-	4.4011
13	6.1464	6.1416	6.1106	6.1106	-	-	6.1004	6.102
21	4.0993	4.0985	4.099	4.0978	4.075	-	-	4.0969
22	4.0172	4.0167	4.0164	4.0162	4.0164	-	-	4.0161
23	4.8026	4.8015	4.802	4.8027		-	4.802	4.8018
31	4.6263	4.6259	4.6261	4.6258	4.6255	-	-	4.6252
32	4.4111	4.411	4.4112	4.4111	4.4109	-		4.4108
33	5.7942	5.7944	5.7965	5.7963		-	5.7949	5.7965
41	4.0158	4.0154	4.0162	4.0154	4.0152	-	-	4.0145
42	4.0659	4.0665	4.0662	4.0661	4.0658	-	-	4.0655
43	5.147	5.1471	5.1444	5.1435		-	5.1441	5.1446
51	4.7993	4.7985	4.7975	4.7976	4.775	-	-	4.7967
52	3.904	3.9041	3.9041	3.9038	3.9036	-	-	3.9034
53	6.0493	6.0493	5.7962		-	6.047	6.0463	6.044
61	4.2367	4.2368	4.2358	4.2354	4.2364	-	-	4.2343
62	3.9257	3.9259	3.9258	3.9256	3.9253	-	-	3.9254
63	5.9058	5.906	5.9044	5.9052		-	5.904	5.9054
71	4.7102	4.7085	4.7082	4.7081	4.708	-	-	4.7085
72	4.0718	4.0703	4.0707	4.071	4.0698	-	-	4.0704
73	5.9534	5.9537	5.9556	5.953		-	5.9485	5.9462
81	4.5584	4.5558	4.5556	4.557	4.5549	-	-	4.5581
82	4.4125	4.4115	4.4122	4.412	4.4118	-	-	4.4106
83	5.9758	5.9537	5.979	5.9754		-	5.9762	5.9714
91	4.8747	4.8748	4.8753	4.8782	4.8728	-	-	4.872
92	4.6943	4.693	4.6929	4.6934	4.6933	-	-	4.6937
93	6.0125	6.0108	6.008	6.0094		-	6.007	6.0091
101	4.3601	4.3387	4.342	4.342	4.3377	-	-	4.3389
102	3.8523	3.8476	3.8535	3.8466	3.8481	-	-	3.8407
103	5.4653	5.469	5.4626	5.4578		-	5.452	5.559

Table H1 - Values of the weight of the samples of chemical and physical gel and MCC.

	Weight (g)							
Sample	**15 days**	**16 days**	**17 days**	**18 days**	**19 days**	**20 days**	**21 days**	**22 days**
11	4.8636	4.863	4.8629	4.8627	-	-	-	4.8625
12	4.4011	4.4009	4.4011	4.005	-	-	-	4.4006
13	6.0993	6.1009	6.0969	-	-	-	6.093	6.0956
21	4.0967	4.0964	4.0965	4.0963	-	-	-	4.0961
22	4.0159	4.0156	4.0157	4.0157	-	-	-	4.0156
23	4.801	4.8021	4.8016	-	-	-	4.8024	4.8008
31	4.6252	4.625	4.6252	4.625	-	-	-	4.6251
32	4.4107	4.4105	4.4107	4.4105	-	-	-	4.4106
33	5.7951	5.7962	5.7955	-	-	-	5.7957	5.7945
41	4.014	4.014	4.0136	4.0136	-	-	-	4.0133
42	4.0651	4.0649	4.0653	4.065	-	-	-	4.0647
43	5.1444	5.1414	5.1415	-	-	-	5.1706	5.1631
51	4.7969	4.7959	4.7958	4.7953	-	-	-	4.7962
52	5.9036	3.9038	3.904	3.9039	-	-	-	3.9038
53	6.0447	6.0468	-	-		6.0453	6.0467	6.0481
61	4.2344	4.2341	4.2342	4.2339	-	-	-	4.2334
62	3.9254	3.9252	3.925	3.9253	-	-	-	3.9253
63	5.9054	5.9026	5.904	-	-	-	5.9041	5.904
71	4.7066	4.7065	4.706	4.7067	-	-	-	4.7065
72	4.0704	4.0705	4.0704	4.0696	-	-	-	4.0697
73	5.9472	5.9462	5.9482	-	-	-	5.9495	5.95
81	4.5588	4.557	4.5559	4.5532	-	-	-	4.554
82	4.4113	4.4112	4.4108	4.4105	-	-	-	4.4101
83	5.974	5.9706	5.9715	-	-	-	5.9772	5.9726
91	4.8783	4.8755	4.8756	4.8779	-	-	-	4.8784
92	4.6935	4.6944	4.6903	4.693	-	-	-	4.693
93	6.0085	6.003	6.0032	-	-	-	6.0063	6.0054
101	4.3458	4.3415	4.3442	4.3479	-	-	-	4.3461
102	3.8429	3.8389	4.8387	3.8414	-	-	-	3.841
103	5.446	5.4435	5.4447	-	-	-	5.4461	5.4359

Table H1 - Values of the weight of the samples of chemical and physical gel and MCC.

	Weight (g)							
Sample	**23 days**	**24 days**	**25 days**	**33 days**	**34 days**	**35 days**	m_{dry}	X_{eq}
11	4.8522	4.8624	4.8619	-	-	4.8614	4.8506	0.00268
12	4.4002	4.4005	4.4007	-	-	4.4006	4.3972	0.000887
13	6.0934	6.0945	-	-	6.0871	5.8471	0.051188	
21	4.096	4.0934	4.0959	-	-	4.096	4.0835	0.003233
22	4.0154	4.0156	4.0157	-	-	4.0155	4.0097	0.001546
23	4.8021	4.8014	-	-	4.8013	4.7832	0.004056	
31	4.625	4.6252	4.625	-	-	4.6251	4.6095	0.003406
32	4.4105	4.4106	4.4106	-	-	4.4103	4.4039	0.001544
33	5.7951	5.7946	-	-	5.7954	5.7556	0.006707	
41	4.0131	4.0133	4.0137	-	-	4.0128	3.9899	0.00604
42	4.0645	4.0647	4.0644	-	-	4.0645	4.0542	0.002639
43	5.1611	5.1609	-	-	5.1574	5.0992	0.009374	
51	4.7966	4.7975	4.7971	-	-	4.7959	4.7781	0.003704
52	3.9037	3.9039	3.9044	-	-	3.9034	3.8947	0.002388
53	6.0493	-	-	6.0462	5.9962	0.008339		
61	4.2335	4.2334	4.2335	-	-	4.2332	4.2141	0.004746
62	3.925	3.9252	3.9253	-	-	3.925	3.9158	0.002452
63	5.9033	5.9028	-	-	5.9023	5.8371	0.011701	
71	4.7074	4.7067	4.7062	-	-	4.7082	4.6812	0.005405
72	4.0695	4.0695	4.0693	-	-	4.0699	4.0497	0.005111
73	5.9491	5.9487	-	-	5.9487	5.8726	0.01381	
81	4.5568	4.5583	4.5565	-	-	4.5563	4.5117	0.009885
82	4.4114	4.4108	4.11	-	-	4.4115	4.3928	0.004189
83	5.9743	5.9729	-	-	5.9747	5.8604	0.019504	
91	4.8747	4.8714	4.8716	-	-	4.872	4.8135	0.012735
92	4.692	4.6928	4.6918	-	-	4.6911	4.665	0.005981
93	6.0059	6.007	-	-	6.006	5.8803	0.0209	
101	4.3476	4.3451	4.3492	-	-	4.3461	4.2374	0.024685
102	3.8385	3.84	3.8392	-	-	3.8362	3.8043	0.009647
103	5.4457	5.4393	-	-	5.4424	5.2777	0.031207	

Table H2 - Values of the weight of the samples of different % of calcium an alginate.

	Weight (g)							
Sample	**cuvete**	**0 hours**	**6 days**	**7 days**	**9 days**	**10 days**	**15 days**	**16 days**
11	4.5328	7.3235	4.883	4.8827	4.8823	4.8822	4.882	4.8817
12	4.2656	5.2474	4.666	4.66	4.6659	4.6664	4.6662	4.6661
13	4.2124	7.4921	4.5524	4.5523	4.5522	4.5613	4.5586	4.5585
14	3.6935	5.056	4.2968	4.2967	4.2967	4.2966	4.2962	4.296
21	4.84	6.983	4.2637	4.2637	4.262	4.2619	4.2614	4.2612
22	3.8843	4.8939	4.3011	4.3009	4.3001	4.3005	4.3002	4.3003
23	3.4635	7.2236	3.8257	3.8259	3.8256	3.826	3.8252	3.8381
24	3.7488	4.4966	4.09	4.09	4.0908	4.0901	4.09	4.1001
31	4.3803	7.273	4.8363	4.8357	4.8344	4.8346	4.8341	4.8336
32	4.2975	5.552	4.8171	4.8169	4.816	4.8163	4.8159	4.8159
33	4.5164	7.1391	4.7582	4.7582	4.7577	4.7584	4.7581	4.7583
34	3.7823	4.6678	3.172	3.1719	4.1716	4.1713	4.1709	4.1711
41	3.6902	6.9536	4.2361	4.2356	4.2341	4.2344	4.2345	4.2331
42	3.9346	4.8352	4.3085	4.3096	4.3087	4.3086	4.3088	4.3089
43	3.8563	7.14	4.2349	4.2303	4.2284	4.2277	4.2242	4.2246
44	3.9712	4.8614	4.3695	4.3694	4.3856	4.3821	4.4159	4.4045
51	4.5187	7.6649	4.9991	4.9977	4.9992	4.9976	4.9971	4.9975
52	3.7881	4.836	4.2203	4.2209	4.2227	4.2231	4.221	4.2218
53	4.6219	7.4115	4.9063	4.908	4.9078	4.9094	4.9095	4.909
54	4.4838	5.766	5.0722	5.075	5.0748	5.0738	5.075	5.0752
61	4.0066	7.047	4.4799	4.4789	4.4779	4.4785	4.4776	4.4772
62	3.8204	4.6682	4.1798	4.1795	4.1797	4.1798	4.1788	4.1788
63	4.4457	4.6961	4.7331	4.7331	4.7331	4.733	4.7326	4.7326
64	4.4226	5.367	4.892	4.8615	4.8608	4.8608	4.8604	4.8602
71	4.4557	7.4828	4.9741	4.9752	4.9709	4.972	4.971	4.9714
72	3.8967	5.0389	4.3884	4.3885	4.388	4.388	4.3863	4.388
73	4.4593	7.0576	4.6964	4.6957	4.6947	4.6955	4.6951	4.6953
74	3.866	5.0087	4.3843	4.3844	4.3817	4.3821	4.3819	4.3817
81	4.4311	7.899	4.9727	4.9719	4.9679	4.9809	4.9754	4.9618
82	4.2947	5.228	4.7021	4.7021	4.7024	4.7036	4.6978	4.6975
83	4.4556	6.7353	4.5972	4.5979	4.5951	4.5959	4.5946	4.5946
84	4.3068	5.2379	4.8172	4.8162	4.8136	4.8124	4.8141	4.8136
91	4.6022	7.5286	5.0634	5.0624	5.0497	5.0619	5.0629	5.0556
92	4.5436	6.0222	5.187	5.1841	5.1815	5.1853	5.1791	5.1807
93	4.5578	7.5602	4.8631	4.8634	4.8615	4.8631	4.8597	4.8603
94	3.8401	4.8983	4.3516	4.3528	4.3482	4.3502	4.349	4.3477
101	4.011	7.1944	4.9653	4.7034	4.6222	4.6396	4.6192	4.5905
102	3.6864	5.0305	4.418	4.3964	4.3325	4.3452	4.3408	4.332
103	3.9912	7.5818	4.647	4.4098	4.3739	4.3765	4.3739	4.3718
104	4.306	5.7676	5.0922	5.0686	5.0537	5.0503	5.5197	5.1484

Table H2 - Values of the weight of the samples of different % of calcium an alginate.

	Weight (g)				
Sample	**17 days**	**20 days**	**23 days**	**mseco**	**X**
11	4.9258	4.9133	4.9094	4.8894	0.00409
12	4.6659	4.6659	4.6659	4.6582	0.001653
13	4.5583	4.5585	4.5581	4.5477	0.002287
14	4.296	4.296	4.2966	4.2779	0.004371
21	4.2612	4.2607	4.2606	4.2258	0.008235
22	4.3003	4.3002	4.3001	4.2898	0.002401
23	3.8365	4.8359	4.8547	4.8357	0.003929
24	4.098	4.0976	4.098	4.0844	0.00333
31	4.8336	4.8336	4.8333	4.7888	0.009293
32	4.8159	4.8162	4.8156	4.8	0.00325
33	4.7582	4.7581	4.758	4.7493	0.001832
34	4.171	4.1711	4.1711	4.1542	0.004068
41	4.2333	4.2332	4.2331	4.1643	0.016521
42	4.3119	4.3078	4.3022	4.2872	0.003499
43	4.2236	4.2218	4.2213	4.1988	0.005359
44	4.4078	4.4048	4.4026	4.3712	0.007183
51	4.9978	4.9989	4.9989	4.9368	0.012579
52	4.2222	4.2218	4.2221	4.2045	0.004186
53	4.9086	4.9088	4.9097	4.8954	0.002921
54	5.076	5.0761	5.0757	5.0424	0.006604
61	4.4776	4.4771	4.4774	4.4109	0.015076
62	4.1791	4.1789	4.1789	4.1644	0.003482
63	4.7328	4.7323	4.7324	4.718	0.003052
64	4.8604	4.8602	4.8501	4.8342	0.003289
71	4.9722	4.9726	4.9723	4.8877	0.017309
72	4.3874	4.388	4.3879	4.3603	0.00633
73	4.6952	4.6954	4.6953	4.6801	0.003248
74	4.3829	4.3822	4.3824	4.3467	0.008213
81	4.962	4.9611	4.9607	4.8334	0.026338
82	4.6976	4.698	4.6957	4.6639	0.006818
83	4.5954	4.5947	4.593	4.5674	0.005605
84	4.8154	4.8148	4.8138	4.7824	0.006566
91	5.0521	5.0541	5.05	4.942	0.021854
92	5.1801	5.1785	5.1778	5.1155	0.012179
93	4.8614	4.8586	4.8595	4.8244	0.007276
94	4.3482	4.3473	4.348	4.2938	0.012623
101	4.5962	4.5816	4.6021	4.3837	0.049821
102	4.3261	4.3225	4.3242	4.2182	0.025129
103	4.3719	4.3724	4.3704	4.3123	0.013473
104	5.1623	5.1693	5.1667	4.975	0.038533

Appendix I – Sorption isotherm of MCC

This result was not presented in the results since there was nothing to compare. But, as the other isotherms, the water content of bound water is low.

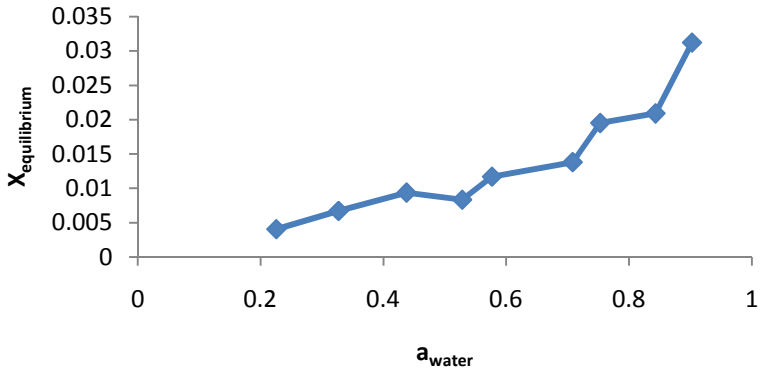

Figure I1 - Sorption isotherm of MCC

By comparing this curve to the isotherms of the gels it is possible to conclude that the water content in this component is bigger.

Appendix J – Drying test (evolution of the diameter all over the experiment)

In the beginning the evolution of the diameter and the thickness was followed. But a non linear behavior was found.

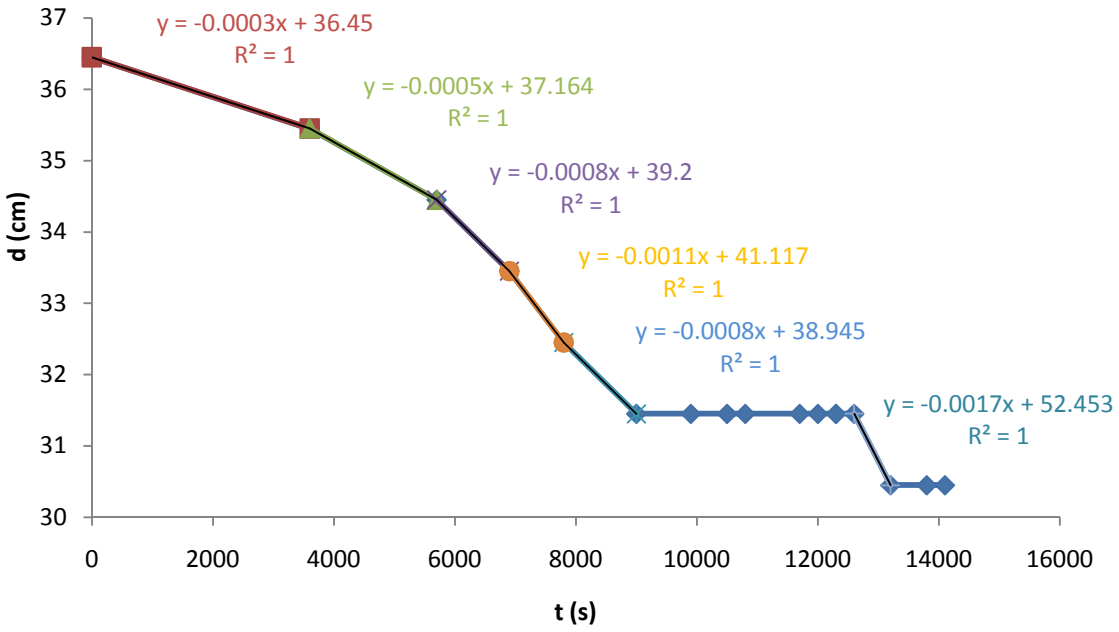

Figure J1 - Evolution of the diameter over the time of the chemical gel

As is possible to observe the evolution was very irregular and is was difficult to have a real equation that gives a good adjustment.

In the physical gel and alginate the diameter just remained the same but the thickness decreased over the experiment. This increase was impossible to measure, though.