Possible application of Extra-Polymeric Substances (EPS) for enhancement of water-solid separation in laboratory bench scale Dissolved Air Flotation system (DAF)

Additional Thesis Project

By

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Preface

This research project was carried forward in order to gain more experience in the laboratory and research practise. It was investigated the application of extra polymeric substances (EPS) in a lab-scale DAF column test to improve the separation performance of the total suspended solid. The experiments were performed in the Waterlab at the faculty of Civil Engineering in Delft.

I thankfully acknowledge Antonella Piaggio for the guidance and the patience in this research. Furthermore, I express my gratitude to Ralph, Merle, Matthijs and Bas without whom this project would not have been achieved.

Abstract

Dissolved air flotation (DAF) is a water treatment technology meant for the separation of suspended particles from the water. Since the fifties of the XIX century, it has gained an important role in many sectors of water treatment applications. In general, the flux variability, the small space requirement, and the limited energy consumption excel as some of the most relevant advantages of the DAF system. However, because of its not always excellent removal efficiency, DAF applications are usually considered as pre-treatment technologies to reduce the particles' load from more effective technologies as sand or membrane filtration technologies. Briefly, the amelioration of the suspended solids' separation is of particular interest because it decreases the maintenance cost of the next filtration units and, in some cases, it might substitute them. Coagulation and flocculation processes prove to be of extreme importance for the DAF performance as it is characterized by particles cut-off around 1-10 µm. The purpose of this research was the application of extra-polymeric substances (EPS) as a flocculant to enlarge the floc dimension of an anaerobic digested sludge and improve DAF efficiency. In the literature the flocculation ability of EPS is not completely acknowledged, but there are some succesfully results with microalgae and activated sludge. Specifically, the feasibility of producing EPS directly on-site, is interesting because it makes the treatment plant possibly independent from the flocculant purchase. Moreover, an extra amount of EPS might be sold (1$/kg) or used for the production of other valuable products (e.g. biodiesel production).

In collaboration with the Water Lab at the faculty of Civil Engineering in Delft and Royal Haskoning (DHV), it was possible to perform some experiments to understand the flocculation properties of EPS in the dissolved air flotation technologies. More specifically, the effects of the EPS were studied with two experiments: a jar test and a flotation column experiment. The sludge used for the experiment was collected from Harnashpolder facility after being digested for at least 25 days. With the jar test experiments, it was examined the effects of sludge settleability (5 gTSS/L): increasing EPS doses (200-1200 mgEPS/L), increment by 20% the original SVI value, on average. Furthermore, it was performed a small scale flotation experiment with two Alka seltzer pills. After a certain EPS dose (400 mgEPS/L), TSS in the formed foam resulted 1.78 times more concentrated. Finally, it was also analysed the particle size distribution (PSD) variation, but the measurements were characterized by a high standard deviation which reduced the reliability of the results. The scope of these first experiments was the individuation of a certain EPS dose to apply in the flotation column experiment simulating the DAF performance (800 mgEPS/L). The EPS addition did not improve the quality of the effluent (65%), and was slightly inferior to the blank series (69%). However, the obtained foam was almost 1.75 times more concentrated when compared to the blank solution. Towards the end of the experiment, a better removal efficiency was notated within the EPS series and it was correlated to the foam concentration (R^2= 0.989). Despite the errors, PSD of the EPS series were characterized by a higher frequency of small particles, between 1-10 µm. In the discussion chapter two explanations are proposed considering the effect of zeta potential variations after the EPS addition. In conclusion, the use of EPS to enhance the solid-liquid separation of the sludge was not successful. However, further research with different doses of EPS and different types of sludge should be studied to assess the potential use of EPS to improve the efficiency of a DAF system.

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1 Introduction

1.1 LOTHUS^{HR} project

Local Treatment of Urban Sewage stream for Health and reuse (LOTHUS^{HR}) is a research project started by the Indian Department of Biotechnology, in 2017. It proposes a new holistic approach in wastewater management aimed at the recovery of water, energy and nutrients from urban wastewaters produced by megalopolis all around the world. Since the beginning , this project has been run in close co-operation with many Dutch research institutes, among them TUDelft (LOTUSHR, 2018).

Nowadays, LOTHUS^{HR} is studying the feasibility of a Waste Water Treatment Plant (WWTP) for the Barapullah drain which collects wastewaters from many of New Delhi's canals conveying them into the Yamuna river, one of the most important drinking water resources for the municipality. The project is developing along three main research lines, related to the different steps of treatment of the drain's wastewater. The second line (Line 2) is focusing on the design of an anaerobic digestor and dissolved air flotation system (AD-DAF) to enhance organic removal and biogas digestion. Dissolved Air flotation (DAF) is a treatment technology for the removal of suspend solids by flotation which, even if not fully effective in the solids separation and removal, when compared with membrane system, it is widely recognized in coping with the flux variations. Due to monsoon climate, this last mentioned aspect is central for a correct design of the wastewater treatment plant (LOTUSHR, 2018). Therefore, DAF technology can be studied as a valid solids separation and recirculation system in the treatment line compared with more standard applications as gravity sedimentation tank or anaerobic membranes. Moreover, it can be also applied as a pre-treatment unit with the important objective of reducing the load of suspended solids which reach the anaerobic digestor (Crossley and Valade, 2006). In conclusion, with relatively low operational cost due to aeration and relatively little area requirement, the application of DAF technology could possibly remove a sufficiently large percentage of suspended solids out of the anaerobic digestor and efficiently increase the solids retention time in the reactor (Wang, Fahey and Wu, 2005).

Since the kick-off of the project, TUDelft university recreated a bench-scale DAF column system to investigate deeply the separation process and reach the optimum performance of the DAF. This technology works on the principle of solids' separation by flotation thanks to the interactions of particles and micro-bubbles, forming floating agglomerates. The removal efficiency is dependent on many parameters which have to be accurately defined. A recent research concluded that the critical operational parameters were the coagulation time, the retention time and the influent TSS concentration (Guleria, 2019). The addition of coagulant and flocculant (Ca(OH) and cellulose) did not result a crucial parameters for the suspended solids removal. However, it was recommended a more extensive study on the effects of different coagulants, focusing on their hydrophobicity and their density(Guleria, 2019).

For this research, it was decided to investigate the flocculation properties of extra-polymeric substances (EPS) as a flocculant to enlarge the floc dimension of an anaerobic digested sludge and suspended solids bench-scale DAF removal efficiency. EPS are defined as a large class of macromolecules bound to biological aggregates, with different functions for the microbial communities and many possible application for the industrial sector(Wingender et al, 1999). The flocculation ability of EPS is not completely understood nowadays, but some interesting applications are promising (Nielsen and Jahn ,1999). Because of the characteristic of the sludge, EPS was chosen to investigate the possibility of binding the suspend solids with what is called

entanglement, a bridging process between particles to increase their surface area. In general, wastewater treatment technologies are moving towards an increased utilization of natural and biodegradable compounds such as chitosan and tannin, because inorganic chemicals impact considerably the sludge discharge (Sia, Robinson and Chong, 2014). Furthermore, the possible extraction onsite of EPS out of the excess sludge or other sources would give an additional value to the LOTHUS^{HR} project as economical independency for the purchase of flocculants and sustainability.

1.2 Research question

The overarching objective of this research is the analysis of the flocculation performance of EPS and their effectiveness in enhancing the flotation of suspended solids of an anaerobic digested stream. The research questions that review this study are the following:

1. What are the effects of EPS addition in an anaerobic sludge solution during the process of coagulation and flocculation regarding the solids' flotation and separation?
2. What are the effects of EPS addition in the bench-scale DAF column system? Will it have an impact in the solid separation efficiency of the system?

To complete the research objectives and questions, this additional thesis was further divided into the following series of sections:

2 Literature Review

The objective of this chapter is a brief explanation and summary of the most relevant theoretical and experimental knowledge used to develop this study. Firstly, dissolved air flotation (DAF) theory and operation conditions are briefly discussed and summarized. Then, the EPS properties of biological sludge are investigated. Because of the broad and puzzled information of the subject, this section will focus exclusively on the flocculation properties concerning the EPS and biological sludge. Finally, it is discussed the relationship between flocculation and flotation of biological sludge to combine the two previous sections better clarify the reasons for these experiments.

2.1 Dissolved air flotation technology

Dissolved air flotation (DAF) is a water treatment technology developed in the second half of the XIX century to improve the separation of suspended particles both for drinking water and wastewater (Harnhoff, 2008). Compared with a standard sedimentation tank, a DAF system can tolerate a higher hydraulic rate ($\frac{m^3}{m^2 \times h}$) and face stronger hydraulic variations $\left(\frac{m^3}{h}\right)$ without an excessive increase of operational costs (Wang, Fahey and Wu, 2005). Other advantages of this technology are the smaller chemical requirements (coagulants, flocculants), a thicker sludge, the use of stainless steel instead of concrete(Wang, Fahey and Wu, 2005). Nonetheless, one particular aspect that slows down the application of this technology is the more complex and technical processes ruling the solid-liquid separation. The physics behind the flotation technology is more elaborated than a common settling tank because of the bubble-bubble and bubble-particles interactions forces. In general, the separation process is still not completely understood and it still under research (Edzwald, 2009). Overall, this technology is not so popular in the municipal wastewater sector and for instance, most of the literature reviews report cases of DAF application for the drinking and industrial sector (Crossley and Valade, 2006). As consequence, it was not found any specific review of flotation technology for municipal wastewater and this sector is commonly included as chapter in the drinking water part, though some relevant differences are present (Koivunen and Heinonen-Tanski, 2008).

2.2 Process description

A conventional air flotation system using DAF technology is schematized in Figure 2.1 below. Both for drinking and industrial processes DAF is typically applied as pre-treatment to reduce the load of suspended solid going into the mainline (membrane or sand filtration). Recently, more sophisticated systems were developed to enhance the removal efficiency and compact the design of the flotation vessel, usually incorporating different technologies in the same tank as CoCoDAFF, AquaDAF, DAFRapide (Crossley and Valade,2006). To give an example, DAFRapide combines in the same tank flotation and sand filtration: foam is collected on the top while the clean effluent is filtered by a sand layer, removing the settling particles. The main advantage of this set-up is the high loading rate, up to 40 m/h, reducing overall the tank volume requirement.

Two zones separate a standard DAF tank: the contact zone and the separation zone as indicated in Figure 2.2. In the contact zone, the influent is mixed with a pressurized flow (usually recycled to reduce cost and increase efficiency). The generation of microbubbles recreates turbulent conditions enhancing collision among particles and air bubbles with the objective to form floc-bubble-aggregates. Once the water flows in the separation zone, the laminar flow condition allows the low dense aggregates to float on the surface. It is usually formed a foam which can be hydraulically or mechanically collected by a scraper, discharging, and partially recirculating the water back into the system. A collection pipe pumps out the clarified water, from the bottom

of the tank, trying to minimize the up-taking of non-floated (sedimented) sludge as well as the disturbance of the laminar condition in the separated zone.

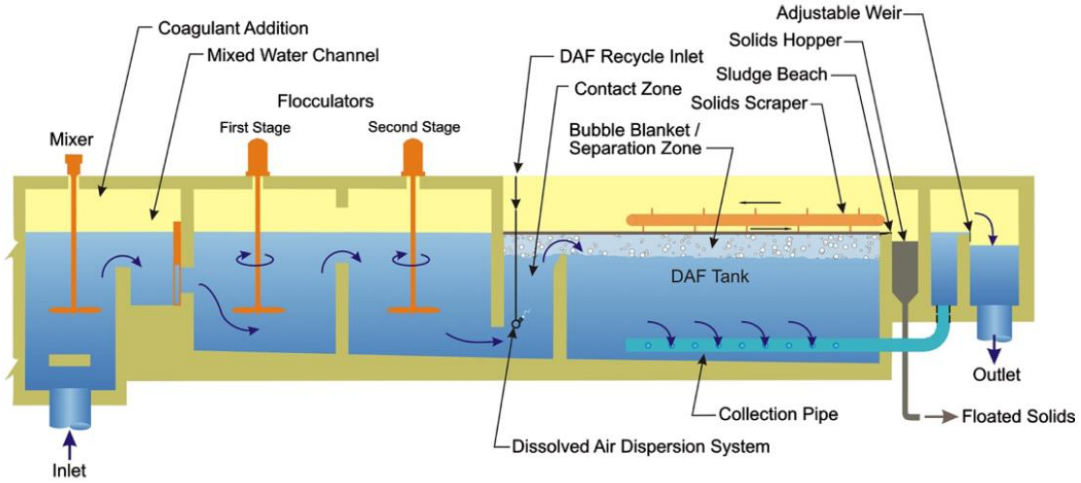


Figure 2.1 Schematic overview of a DAF line treatment plant (Crossley and Valade, 2006).

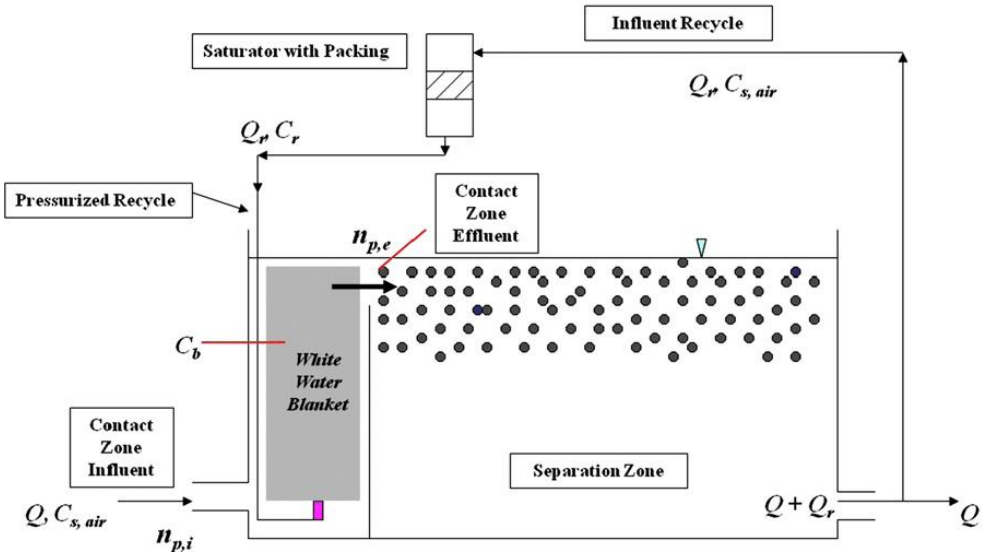


Figure 2.2 Representation of a standard DAF tank (Edzwald, 2009).

2.3 Theory

2.3.1 Bubbles formation and interactions forces

One aspect which characterises the DAF system is the application of pressurized gas, typically air for the separation of the particles. For that reason, one of the main parameter that rules the theory of the process is the air-solid ratio (A/S) expressed as the fraction between the volume of air and suspended solids in the tank (mLair/mgTSS). However this parameter can be defined in mgair/mgTSS and Shammas (Shammas, 2010) expresses it in a very compact and useful equation for the design of the DAF tank:

$$\frac{G}{S} = \frac{R \times C_s \times f \times \frac{p}{101.3}}{S_0 \times Q - S_e \times R}$$

Equation 1 air solid concentration expressed in mgair/mgTSS (Shammas, 2010).

On the left, G represents the gas concentration in mg/L, S gives the suspended solids concentration in the tank in mgTSS/L. On the right, R in L/d stands for the pressurized flow rate, C_s is the gas concentration at saturation in mg/L. The gas concentration at saturation is ruled by Henry's Law and constant (Henry,1803). At this regard, it is important to mention gas concentration is directly correlated with the air pressure and temperature (Appendix A). In the equation, p represents the saturation pressure gauge in kN/m^2. An important parameter is covered by *f*, defined as the "fractional system dissolving-efficiency factor (Bratby and Marais, 1975). This factor is fundamental to estimate the volume or mass of air released at a certain pressure and temperature (Appendix). In their research, Bratby and Marais concluded that among the main parameters influencing the release of air, the total pressure, the type of valve and the flow conditions were the most relevant to consider to estimate *f*.

In the contact zone, micro-bubbles starts to form due to the pressure difference. The dimensions and the rising velocity of those are particularly important. Bubbles dimension is mainly influenced by the pressure as it is shown from the paper of Han (Han, Park and Lee, 2002), even though also the nozzle and the valve at the outflow might have a considerable influence (Edzwald,2009). With deionized water Han found that with pressure varying between 2 and 6 atm the mean size of the bubble changed dropped from 71 to 28 µm, though, after 3.5 atm, it was not observed any change. In the DAF application, small bubble particles are usually preferred as they rise in a laminar flow according to the Stoke's Law and they have a more rigid and spherical shape than the bigger ones which tend to be more elliptic (Vigneswaran, 2009). Within 3 and 5 atmospheres, literature states most of the particles are in a range between 20-100 µm, but surface tension and temperature can decisively have an influence (Shammas, 2010; Han, Park and Lee, 2002; Vigneswaran, 2009). As said before also the rising velocity of the bubble has a significant influence in the process and dimension of the tank, both for the contact and separation zone. In the literature it is usually accepted that spherical micro-bubbles follow Stoke's Law in laminar condition, reported here below:

$$V_b = \frac{g(\rho_w - \rho_b)d^2}{18\mu}$$

Equation 2 Bubble rising velocity according to Stoke's Law

Where V_b is the velocity in m/s, g gravity in m/s^2, ρ_w and ρ_b stand for the density of water and bubbles respectively while µ figures the dynamic viscosity at a certain temperature in Ns/m.

2.3.2 Bubble-particles interactions and agglomerates formation

The theory behind the bubble formation and bubbles-bubbles interactions is overall well studied, though the bubbles-particles interactions turn to be the more realistic forces that determine the final separation in the DAF process. Unfortunately, defining these interactions is particularly complicated both from a theoretical and practical point of view. For that reason, the literature tends to divide the discussion into independent sub-topics, but then it struggles to recombine the acquired knowledge to some primary equations.

For the purpose of this study, it was chosen to explain the DAF theory by showing one of the most used models simulating the solid-liquid separation, taking into account the fundamental concepts. Edzwald in one of his books, states that the models can be distinguished into two approach categories: heterogenous flocculation and white water blanket filtration models

(Edzwald, 2009). Both approaches start from assuming a second order rate to simulate the collision and attachment to the particles. As the aim of this research is not to discuss the accuracy and difference between the two approaches, but to give a general overview of the mechanism deterring the efficiency of the dissolved air flotation process, the white water bubble model will be only and briefly discussed, trying to explain the meaning of its variables. The white water bubble blanket model firstly proposed by Edzwald and then reviewed by Haarnoff proposed the following conclusive equation:

$$\frac{dn_p}{dt} = -\alpha_{pb}\eta_T v_b\left(\frac{\pi d_b^2}{4}\right)n_p n_b$$

Equation 3 White water bubble blanket model (Haarnoff and Edzwald, 2004).

Where, on the left, n_p , n_b are the number of particles and bubbles while α_{pb} stands for the attachment efficiency of the particles colliding with bubbles, η_T the single collector efficiency and $v_b\left(\frac{\pi d_b^2}{4}\right)$ the volume of suspension removed by a rising air bubble.

The variable α_{pb} is conceptually the number of successful collisions and it varies between 0 and 1. It considers many interactions forces between flocs and bubbles that are difficult to determine analytically as the van der Waals forces, the hydrophobic and the hydrodynamic effects and the electrostatic repulsion or attraction. The van der Waals forces were typically considered attractive but Lu found that in the interaction between particles and bubbles are effectively repulsive(Lu, 1991). The hydrodynamic interaction, also called hydrodynamic retardation, represents the removal of the water surrounding two particles to collide together. However, due to the state of agitation in the contact zone, this force is easily overcome and then is not particularly relevant in the equilibrium balance (Edzwald, 2009). The electrostatic forces take in consideration the surface charge of the particles. In the literature, they are evaluated through the DLVO theory (Verwey, and Overbeek, 1948). Gregory also found a useful direct correlation between ionic strength and the thickness of the double layer thickness, an relevant parameter in the DLVO theory theory (Gregory, 2005). At this point, it was not mentioned yet an attractive force to overcome the above mentioned forces which are in most conditions repulsive. Even though it mechanism in the dissolved air flotation process is not completely understood, the hydrophobic force is considered able to exceed repulsion between particles (Nguyen, 2007). Finally, the strength and the weakness of the variable α_{pb} is to gather all the above mentioned theory in one value. The coagulant addition reduces the double layer thickness, minimizing the range and power of the electrostatic repulsive force, as shown in Figure 2.3.

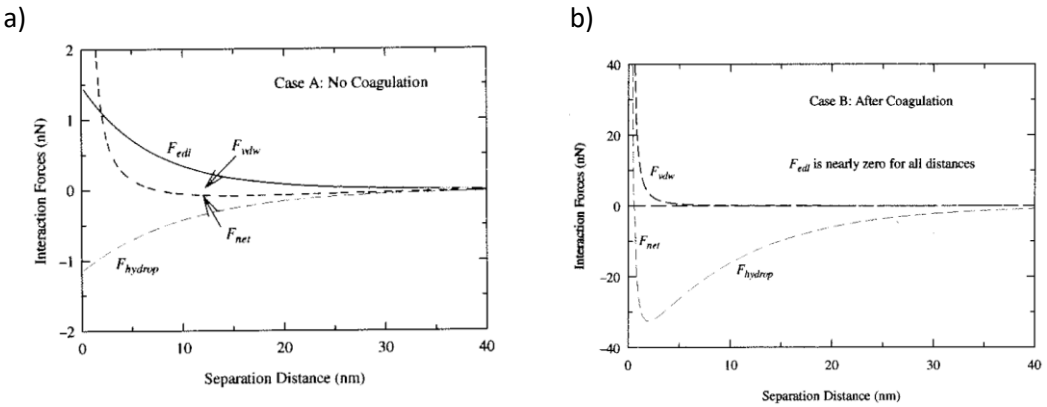


Figure 2.3 Representation of the particle-bubble interaction forces. Negative values are attractive ,positive repulsive. F_{hydrop} F_{edl} F_{vdw} are respectively hydrophobic, electrostatic and van deer Waals forces. Figure a is before coagulation, figure b is after coagulation and F_{edl} is nearly zero. (Edzwald and Haarnoff, 2012).

If the variable α_{pb} involves more aspects of the coagulation process as the surface charge, the single collector efficiency η_T covers as well considerable importance in the flocculation domain. Flocculation is defined as the process of collision and attachment of particles as to increase their size. As for coagulation, the theory behind the determination of this variable is complex and beyond the scope of this study. However, in the explanation of the model, Haarnoff arrived at the conclusion that η_T is both dependant on bubble and particle dimension (Haarnoff and Edzwald, 2004). In particular, particles above 1 µm positively influences flocculation; the size of ideal bubbles is around 10-20 µm, while temperature and density do not show any particular effect. To summarize, to optimize the flocculation, particles should have a mean dimension between 25-50µm and bubbles size below 100 µm (Haarhof and Edzwald, 2004).

While the number of suspended particles mainly depends on the concentration and the state of coagulation and flocculation, the number of bubbles can be acquired by the volume of air-bubbles. According to Vigneswaran, n_b can be expressed as :

$$n_b = \frac{\varphi_b}{\frac{\pi d_b^3}{6}}$$

Equation 4 number of bubbles estimation (Vigneswaran,2009).

Where φ_b is the bubble volume concentration expressed as the fraction between the concentration of the bubble in mL/mg_{air} and their relative saturation pressure (kPa).

The solution of the white water blanket bubble model can be expressed in the following formula, expressed by the removal efficiency of the flocs (E_{cz}) where t_{cz} is the detention time in the contact zone.

$$E_{cz} = 1 - \exp\left(\frac{\alpha_{pb}\eta_T \nu_b \varphi_b t_{cz}}{d_p}\right)$$

Equation 5. The conclusive solution of the white blanket bubble model

2.3.3 Design consideration

In the previous chapter, it was explained the white water model to explain the theoretical forces that determine the suspended solid removal efficiency. Nevertheless, the design and operation condition of DAF tank mainly relies on some other practical parameters that are used in the daily experience. The table below reports some of the most applied parameters usually found in the literature.

Table 2.1 most applied parameter found in the literature

	Parameter	Range	Unit	Literature
P	Air pressure	2.5-6	Bar	Shammas et al. , 2010
A_{eff}	Saturator efficiency	80-95	%	Gregory and Ezwald, 2010
A/S	Air to solids ratio	0.1-0.01	Kgair/KgTSS	Shammas et al., 2010
Q/A	Hydraulic load separation zone	5-15	$m^3/m^2/h$	Gregory and Ezwald, 2010

Θct	Retention time contact zone	1-2.5	min	Gregory and Ezwald, 2010
Θst	Retention time separation zone	20-60	min	Wang et al., 2005
R	Recycle ratio	5-50	%	Wang et al., 2005
F_c	Float solid concentration	2-10	%	Edzwald, 2009
Eff_{TSS}	TSS Removal efficiency	50-99	%	Edzwald, 2009

The first three parameters are related to the regulation of the white water flow. The air is usually filtered and then pressurized up to 600 kPa. The saturation concentration is a theoretical point not achievable in practice. In fact, the air transfer rate is first order kinetic reaction in function of pressure, surface area and many other parameters (Vigneswaran, 2009). For that reason, the saturator efficiency is an important factor to take into consideration for the design. As mention in Equation 1 the air solid ratio is a crucial parameter in the DAF process makes a balance between the air and the suspended solid load in the system.

In section 2.2, it was already showed the process description of the DAF system. From a design point of view, the tank is mainly defined by the hydraulic load and retention time of the separation zone. The contact zone is usually not significant in the dimension and design of the DAF tank. The standard depth varies between 2 and 3.5 m.

Finally, the recycle ratio is another important factor to take into consideration. It usually has the advantages to increment the removal efficiency, it saves some operational costs due to minor pressurization and the non-application of freshwater to produce the white water.

Then, with these few parameters, knowing the influent type of wastewater is possible to have a draft of the DAF layout.

2.4 Extracellular polymeric substances (EPS)

2.4.1 Definition

The definition of extracellular polymeric substances (EPS) has not still be clarified and in the literature authors identify them in different ways. Nielsen and Jahn (1999) applied a broad definition, because EPS represent all polymers outside the cell wall, not directly bounded to the outer protein layer that can be in both a soluble and dissolved form. Wingender, instead, prefers to identify EPS as different classes of macromolecules as polysaccharides, lipids, nucleic acids and lipids in the proximity of the biological aggregates (Wingender et al, 1999). Even though the scientific literature do not converge completely on the EPS definition, it agrees about the source of EPS which are mainly high-molecular-weight debris and fragment originated from the lysis and secretion of the microorganism.

Furthermore, at present, it is acknowledged the difference between bound and soluble form EPS due to the numerous extraction methods, whereas there are still some uncertainties about the differences between the tightly bound, TB-EPS, and loosely bound, LB-EPS (Sheng et al., 2006). Apart from the natural complexity and variety of microorganisms and communities of microorganisms, a possible reason might be that, at present day, it is not recognized a standard method to extract the EPS (Sheng et al., 2010). In the literature, the chemical composition of

EPS, intended as a fraction of polysaccharides, proteins, lipids and nucleic acids, has found particular interest because it is said to partly determine its characteristics, as biodegradability, adsorption, hydrophobicity, hydrophilicity, dewaterability and many other (Sheng et al., 2010). The following chapters will mainly focus on the influences of EPS in the flocculation process of the sludge.

2.4.2 Flocculation properties of EPS

In the scientific literature, the flocculation ability of EPS is mainly studied extracting these compounds and then analysing the effect on the flocculation of the sludge. This topic is commonly faced under two approaches. The first one directly studies the structural presence of EPS in the sludge, the second, once EPS was extracted and analysed, it is re-added to the sludge. Then, both approaches try to relate the effect of EPS presence or re-addition to some standard flocculation abilities of flocculants (e.g. SVI, particle diameter, hydrophobicity, etc.). Nowadays, little research has been carried studying the direct EPS effect on the flocculation of an external compound. Moreover, most of these publications used kaolin as standard compound to measure the flocculation ability of EPS (Sybramanian et al, 2010). However, before discussing the EPS influence is reasonable to define what is intended for the sludge flocculation ability. Bioflocculation is the capacity of forming stable, large and fast settling flocs in standard wastewater treatment processes (Suresh et al., 2018). An optimal bioflocculation would not require the addition of chemical coagulant or flocculants, because in a steady-state condition fast-settling flocs would prevail over the slow one. In practise, ideal conditions are difficult to maintain, and indeed inorganic coagulant and flocculants are typically dosed. For this reason, the necessity to comprehend which variables rule bioflocculation, more and more studies analysed the influence of EPS which seemed to have an important role. The next sub chapters will specifically explain the results of some relevant studied to asses afterwards a more general overview on the flocculation process due to the presence of EPS.

2.4.3 Surface charge and zeta potential

Liu and Fang examined more than 200 studies related to the influences of EPS in the flocculation ability in the activated sludge (Liu et Fang, 2003). Their researches showed that flocs and EPS were negatively charged (-0.2 to -0.6 meq/gVSS) and a zeta potential around -10 to -30 mV. Moreover, they suggested that those measurements are representative for the single cells and not the large flocs. In other studies, it was specified that, among the different macromolecules characterising EPS structure, proteins and humic substances were the most negatively charged (Wilen et al, 2003), while Liao found that carbohydrates components could have a positive charge (Liao et al, 2001). Liao et al. (2001) also supported the thesis by which the principal parameter influencing the surface charge is the ratio between proteins and carbohydrates instead of the total amount of EPS. The results from the paper of Li et al. (2015) might be another proof for the previous conclusion because it was not found a good correlation between the increase of the EPS content and a decrease measured a decrease of the absolute values in the zeta potential. Other researches focused on the difference between the LB-EPS and TB-EPS content to study the interaction energy (Liu et al., 2009). LB-EPS were discovered to be always negative, while TB-EPS were found to be negative for larger distances than 4 nm but positive for smaller distances. The pictures below reports some of the main findings regarding the zeta potential and the EPS content mentioned in the previous studies (Figure 2.4, Figure 2.5).

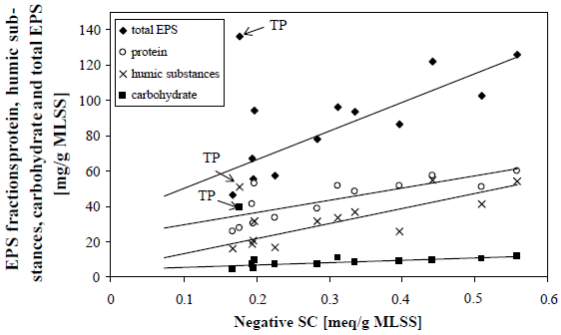


Figure 2.4 Correlation between surface charge and extracted EPS fractions (Liao et al, 2001).

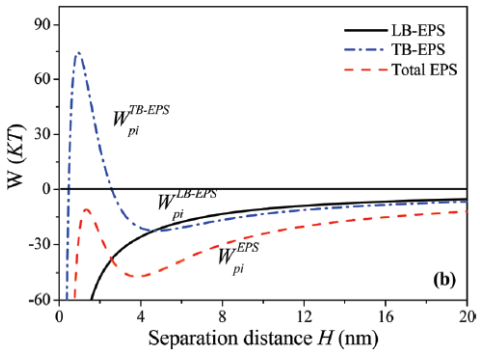


Figure 2.5 Interaction energy forces of EPS extracted from anaerobic granular sludge (Liu et al, 2010).

2.4.4 Hydrophobicity

Hydrophobic interaction is a crucial parameter for floc formation and flotation (Liu and Fang, 2003; Wang et al. 2006). The measure of hydrophobicity is standardly related to the surface contact angle and the adsorption on hydrocarbons, but it should be realized with homogenous suspensions. Floc morphology is characterized by heterogenous aggregates, so before measuring hydrophobicity, flocs have to be partially disrupted. Most recent studies usually agreed on the findings that proteins and humic compounds increment the hydrophobicity of the sludge, while carbohydrates keep hydrophilic nature (Wilen et al, 2003; Wang, Liu and Tay,2005). Nonetheless, when looking at most cited reviews, EPS hydrophobicity is regularly one of the most debated chapters (Liu and Fang, 2003). Liao et al (2001) arrived to the conclusion that hydrophobicity was more dependent on the type of EPS than from the load; moreover, hydrophobic interaction increased flocculation, but not settling (SVI). Other studies reported the negative effect on settling when carbohydrate EPS (EPS_c) are present(Liu and Fang, 2003). As for the previous chapter, many publications, instead of the distinction of EPS by its chemical composition, evaluated the influence of TB-EPS and LB-EPS. When LB-EPS are more concentrated, the settling capacity of the sludge is worsened (Li and Yang, 2006). Even though the hydrophobicity of EPS content in the sludge thoroughly discussed, the majority of scientific articles agree on the point that the load of EPS negatively influence the dewaterability and compressibility of the sludge, because of the retention water capacity of EPS. In the figures below are reported some of the most relevant findings related to the hydrophobicity of the flocs and the EPS content. The graphs below show some of the most important results obtained from different experiments and studies on hydrophobicity and sludge depending on the EPS content.

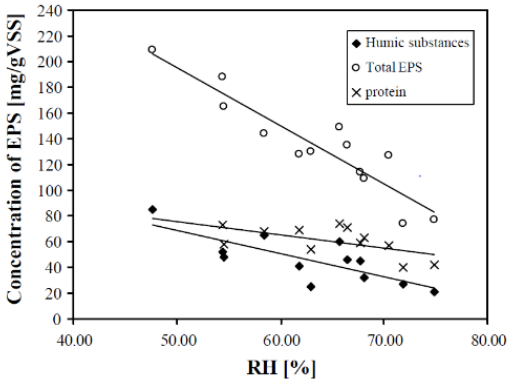


Figure 2.6 Correlation between EPS and hydrophobicity of the sludge (Wilen, Jin et al, 2003)

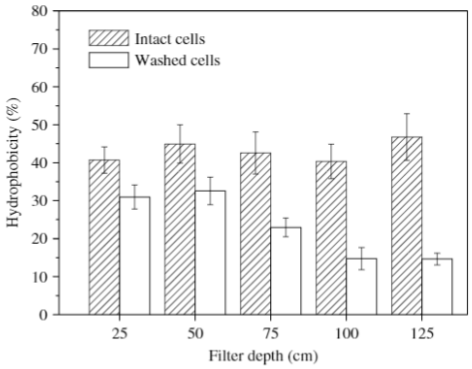


Figure 2.7 Impact on biofilm hydrophobicity when EPS is extracted (washed cells) (Bao et al. 2008).

2.4.5 Floc size

For the flocculation process, the particle diameter is a relevant parameter, especially when considering flocs larger than 1 µm (Smoluchowski, 1916). Most of the publications covering the influence of EPS in the sludge flocculation sludge do not mention their dimensions. The reason for this apparent paradox is justified by the fact that the dimension of the floc is mainly dependant on the feeding type and external conditions. Moreover, the type and the way bacteria access to substrate determines as well the type and load of EPS production. Thus, a standard way to investigate the EPS role in flocculation is to focus on the re-flocculation process after a certain shear rate or disturbance. The paper of Li et al. (2015) clearly shows the effect of EPS content for the dimension of re-flocculated flocs (Figure 2.8). Furthermore, another study assessed that EPS load and the VSS/TSS fraction were positively correlated with the floc size (Li et al, 2013). In general these researches proposed the thesis according to which EPS content enhances the floc strength and resistance to shear.

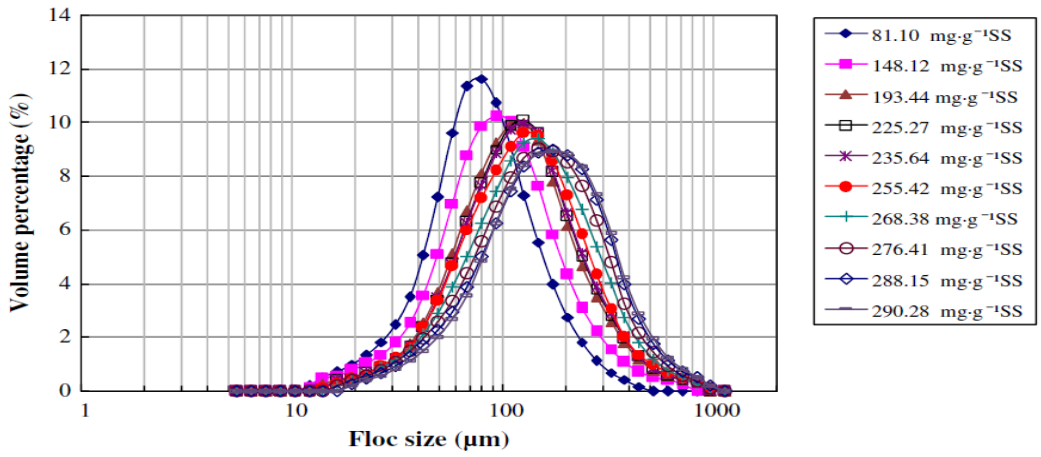


Figure 2.8 Floc size distribution of activated sludge with different EPS content at an average shear rate of 28.2 s^{-1} (Li et al, 2015)

2.4.6 Water ionic composition and metal bounding

EPS can be defined as a complex matrix of different and high weighted macromolecules composed by a considerable number of carboxyl and hydroxyl groups. For that reason, in the literature reviews, it is dedicated a chapter about their very high binding capacity with ions, heavy metals and also apolar compounds (Suresh et al., 2018; Sheng, Yu and Li, 2008). Due to the negative surface charge of EPS, multivalent cations as Ca^{2+}, Mg^{2+} and Fe^{2+} tent to bridge with those microbial structures and soluble EPS and LB-EPS more likely to re-flocculate in presence of Ca^{2+} (Higgins and Novak, 1997; Zita and Hermasson, 1994). In addition to these previous studies, in another research focusing on the comparison between bivalent, Ca^{2+}, and trivalent ions (Fe^{3+} and Al^{3+}), it also appeared the capacity of Ca^{2+} to merge to with LB-EPS (Li et al, 2012). On the contrary, trivalent anions directly interact with the TB-EPS and the pellet. In 2002, Sobeck and Higgins examined three processes for bioflocculation and finally, when treating wastewater, suggested the multivalent cation bridging theory. Thus, in the process of biological aggregation, the DLVO theory should be expostulated considering the cation polymer interaction and the polymer gelation (Nguyen et al, 2008).

2.5 EPS as external flocculant

Relatively few studies proposed the use of EPS as proper bio-flocculant. Among them, the majority used different clays and more specifically kaolin, a standard colloid `(Sun et al. ,2015). However, it is important to mention also the article of Sun et al. (2015) which proposed a series of experiments with *Microcysti Aeruginosas.* The maximum flocculation ability measured in these experiments was 80-90 % for clay and *Microcysti Aeruginosas* (Yu, He and Shao, 2009; Sun et al., 2015). In these studies, the results showed TB-EPS components as the best bio-flocculant while LB-EPS might have a negative effect on the settling of the suspension. The re-addition of previously extracted TB-EPS in a wastewater sludge repristinated the particles size distribution of the suspended solids almost to the original condition (Yu, He and Shao, 2009). Compared with other flocculants it was observed a decrease of the settling velocity, probably because of the low density of EPS and its capacity to retain water. Finally, Yu, He, and Shao (2009) proposed a thesis describing two different ways of EPS components binding the particles. TB-EPS is mainly responsible for the sweep flocculation and neutralization of the charge adsorbing trivalent ions as Al and Fe, while LB-EPS interacts more through the ion bridging and particles entanglement(Yu, He and Shao, 2009a). In their research Sun et al. (2015) proposed a slightly different conclusion. For kaolin suspension, Zeta potential analysis indicated that EPS contributed to the charge neutralization, enhancing kaolin flocculation. This process was not involved in the M. aeruginosa flocculation. Therefore, it was proposed the major role of metal ions, indicating a bridging mechanism during the flocculation process with EPS. In conclusion, cation interactions were found indispensable for a good flocculation, while zeta potential effects is still discussed.

2.6 Combination of EPS and flotation

In literature, no studies were found combining the application of extracted EPS as flocculant to increment the removal efficiency of the DAF system. Nonetheless, its application seems promising for several reasons that will be shortly intruded in this paragraph.

It was sufficiently explained that an increment of the particles size would increase the collision efficiency between aggregates which would lead to an improvement of the total separation efficiency of the DAF (section 2.3.2). With the correct addition of coagulant, the particles repulsion according to the DLVO theory is minimized and with the addition of a flocculant, aggregates can grow bigger and stronger. At present day, most of standard coagulants and

flocculants are inorganic, but for several reasons (biodegradability, ecological impact, on-site production, discharge) natural and organic polymers are preferable (Sia, Robinson and Chong, 2014).

In literature, there is a knowledge-gap on the interactions of flocculated EPS flocs with micro-bubbles, but some hypotheses and assumptions could be proposed. As already mentioned for other flocculants, the strength and the enlargement of the flocs, would increase the collision efficiency and reduce the breakage of agglomerates for certain shear stress. The negative variation of the zeta potential should be taken into consideration as the repulsive interactions of the particles might be partly repristinated. If so, this aspect could have also a negative effect on the electric equilibrium between agglomerates and bubbles. However, high ionic strength and bivalent ions concentrations should be able to overcome these repulsion force and enhance the bridging between particles. Another crucial parameter to research is the controversial hydrophobicity of the EPS. It was demonstrated that bubbles tend to better interact with hydrophobic substances, so the possible addition of hydrophilic EPS compounds like carbohydrates ought to be avoided. However, the number of the particles and the turbulence inside the contact zone should be sufficiently elevated to overcome these repulsive forces.

Apart from the floc strength and floc size enlargement in the contact zone, the separation zone in the DAF covers as well a central role in the separation efficiency of the system. When flocculation is researched, it is usually meant to form fast-settling flocs to decrease the area of the sedimentation tank. In the case of the DAF system, this aspect is not a priority and it could be even a drawback because they would be more likely uptake by the effluent pipeline on the bottom. Moreover, another parameter to consider in the separation zone design is the foam stability. Foam removal, both with a mechanical or hydraulic system, generates some turbulence and remix the separated solids into the water. Thus, the suspended solid concentration and the foam hydrophobicity are supposed to be crucial for the maintenance of this layer. The EPS content might improve the foam separation from the water. To support this hypothesis the experience with the membrane bio-reactor (MBR) reactor can be significant. Foam and scum created from the process of biofouling in the membranes are directly correlated with the EPS content (Alida et al., 2018). Another interesting example that might imply a correlation within EPS content and flotation, is the anaerobic self-flotation reactor (Zeng et al., 2015). In the latter article, the incoming suspended solids are firstly entrapped in the sludge bed by the EPS and then partly released forming a foam that has to be regularly removed.

Because of their interactions with the granules, proteins and humic substances are already been used in flotation and technology, as the experience with casein of Maruyama and Satoh proved in 2012. However, because the EPS are a matrix of different compounds, the flocculation and the foam stability enhancement are not for granted and should be verified.

3 Material and Methods

The experimental studies consisted of two steps: jar test experiments and the columns test experiments. The first stage was structured to assess the EPS influence on the flocculation properties of the sludge, with a series of jar test experiments, studying the sedimentation and flotation characteristics in various conditions. Thus, with this first experiment would it be possible the first research question. Then, the more promising EPS condition was used in a series of column test experiments to analyse it in a context more similar to the DAF system. These experiments focused on the solid removal efficiency, returning some possible solution for the second research question. In this chapter, the methodology, the measurement and the materials employed to study the effectiveness of the different experimental conditions are reported and explained.

3.1 Sludge characteristic

3.1.1 Harnashpolder sludge

The primary source of the sludge was collected from the anaerobic digestor of Harnaschpolder wastewater treatment plant, Den Hoorn, Zuid-Holland province. The sludge was firstly sieved with a 0.71 µm metallic sieve and then collected in a 10 L jerrycan. The sludge was kept in a fridge at the temperature of 4°C for less than two weeks. Among all parameters for the flocculation properties, some were fundamental for the flocculation properties studied and were specifically measured (Table 3.1).

Table 3.1 Measured digested sludge characteristic from Harnaschpolder

Parameters		Parameters	
TSS	30-34 g/L	**Fe^{2+}**	557 mg/L
VSS	20-23 g/L	**Ionic strength**	~0.3 M
Fe_{tot}	662 mg/L	**Particles size (volume distribution)**	~58 µm

a) The ionic strength was calculated based on inductively coupled plasma mass spectrometry (ICP-MS) of cationic atoms. Anions were estimated in the same equivalent concentration: 2/3 monovalent and 1/3 bivalent.

3.1.2 Influent sludge

For both the jar test and the column experiments, Harnashpolder sludge was diluted with tap water in order to have a sludge with a TSS concentration around 4.5 g/L (Appendix B). This step was necessary as to obtain in the column test experiment a concentration similar to the standard application of the DAF, around 300-700 mg TSS/L (Krofta and Wang, 1982). The table below reports some chemicals parameters measured in the influent sludge for all experiments.

Table 3.2 Influent sludge characteristic after tab water dilution

Parameters		Parameters	
TSS	4.3-4.8 gTSS/L	**pH**	7-8
VSS	3.0-3.3 gVSS/L	**Ionic strength[a]**	~0.17 M
COD	4000-6000 mg/L	**Particles size (volume distribution)**	~60 µm

b) The ionic strength was calculated based on inductively coupled plasma mass spectrometry (ICP-MS) of cationic atoms. Anions were estimated in the same equivalent concentration: 2/3 monovalent and 1/3 bivalent.

3.2 Flocculant characteristics

3.2.1 Cellulose

Chitosan, tannin and many other natural compounds among which cellulose are nowadays known to be the more promising bioflocculants substituting the chemical ones (Lee et al., 2014). Microcrystalline cellulose powder (Aldrich) was decided to be used as a comparative flocculant mainly because of its application in the previous studies with the same flotation column application (Guleria, 2019). In this research, the cellulose dose was established at 250 mg/L (5.5 mg/gTSS).

3.2.2 EPS

Structural EPS from aerobic granular sludge was extracted following the method of Felz (Felz et al, 2016) from the Kaumera wastewater treatment plant. The extraction was performed at the laboratory of Applied Sciences at TU Delft in November 2019. The solid concertation of the anionic EPS was measured around 7%. As for the cellulose, the dosage range was determined from the literature. In the article Yu (Yu et al., 2009), it was found that TB-EPS had a good flocculation ability with kaolin (0.4 g EPS/L for 5g/L). Because of the unknown concentration of TB-EPS in the EPS solution, the dose was set between 200 and 1200 mg EPS/L. This dose range was also in line with the re-flocculation ability on floc dimension studied by Li et al. (2015), once these values are converted in mg EPS/gVSS (50-300 mgEPS/gVSS)

3.3 Measurements

3.3.1 TSS and VSS measurements

Based on the APhA method (APhA, 1998), TSS was measured at the laboratory. Sampling volumes were chosen to minimize the standard deviation to a minimum of 10% and avoid clogging of the filter. For VSS analysis the ignition step of the glass filters was necessary. In the pictures below (Figure 3.1), it is shown some sample TSS and VSS sample ready for the measurements.

Figure 3.1 Foam TSS measurements before entering in the oven

3.3.2 Particles size distribution (PSD)

Floc properties were measured particle through light scattering technology(Blue wave, Microtac). This machine can measure particles in a range from 10.7 nm to 2000 µm using tri-laser beams differently scattered by size and collected by a Fouries lens. An Algorithm is used to calculate the volume percent as a function of particle size. The Bluewave is fitted with a sample circuit system (Sample Dispersion Controller The speed of the centrifugal pump can be adjusted according to the viscosity properties of the sample (sludge).An irregular and absorbing shape was chosen to estimate the flocs size distribution through the Fraunhofer or Mie calculation can be used depends on the irregular shape or of spherical particles.

The main outcomes form this measurement is particle size distribution (PSD). This is given as the cumulative curve and the frequency curve (channel distribution). As mentioned, these curves were measured based on the volume distribution, but other parameters can be found as the mean volume diameter, usually named D_{50}, but in this case will be called MV, the mean area diameter (MA) and mean number diameter (MN). MV represents the mean diameter of the volume distribution; MA and MN are estimated from the volume distribution where the coarse particles are minorly weighted showing a smaller particle size. For the purpose of this study, the attention was principally focused on the area distribution as the particles-bubble interactions happen on the surface of the particles. The standard deviation calculated by the Bluewave do not provide an indication of the statistical error, but it describes the width of the measured particles size distribution. All measurements were given in microns.

3.3.3 COD and NTU measurements

COD was measured following the HACH method (Lange, LCK014) diluting the samples, if necessary. Turbidity was evaluated with a turbidimeter (Hach, 2100N), measuring the nephelometric turbidity unit (NTU) even though values were over the detection limit for some samples (e.g. Harnashpolder sludge, diluted sludge, foam). These are relevant chemical parameters to assess the water quality, especially when examining TSS. While TSS and VSS analysis take around 32 hours to be evaluated, COD and NTU can be readily measured in few hours, so it is a common practice to correlate them, though case-specific, to have a first evaluation of the experiments.

3.4 Experiment 1: Jar test experiment

Jar test is a common laboratory experiment used for the simulation of coagulation and flocculation processes (Black et al., 1957; Clark and Stephenson, 1999). To evaluate the flocculation activity of EPS, cellulose and blank experiments were conducted in parallel as a comparison. One litre of sludge (5 g/L) was poured in a glass cylinder with a smooth corner to enhance hydraulic turbulence. Coagulation time was set at 1.5 minutes at 200 rpm whereas flocculation lasted for 15 minutes at 40 rpm. After 13 minutes 50 mL sample of the sludge was collected and used as reference (F_0). At the end of flocculation, the sludge was poured in a 1L graduated glass cylinder (VWR, ±5mL) for a 30 minutes sedimentation time. Every 5 minutes the volume of the sedimented sludge was measured. With this test, it was possible to calculate the sludge volume index (SVI) of the sludge over time as in the formula below where V (mL/L) is the volume of the settled sludge and TSS are the suspended solids (mg/L).

$$SVI = \frac{V\left(\frac{ml}{L}\right) \times 1000}{TSS\left(\frac{mg}{L}\right)}$$

Equation 6 SVI equation (Baird et al.,2012)

After sedimentation, the surfactant (S_f) was collected with a 50 mL glass pipette (±0.2mL) to measure the TSS, NTU, COD as well as the PSD curve after the sedimentation phase.

For the preparation of the flotation test, the sludge was slowly mixed again. From the graduate glass cylinder, 100 mL of sludge was collected and diluted with 900 mL of tap water. At this point, two solutions (S_1, S_2) of sludge were obtained: 800 mL of flocculated sludge and 1000 mL of diluted sludge, as to have S_2 in a range around 0.5-0.7 mgTSS./L. Concentrations of these solutions were calculated through a mass balance, based on the values of F_0 and S_f. Finally, two Alka seltzer tablets (325 mg acetylsalicylic acid, BAYER) were placed in a plastic net in the graduate glass cylinder with some weight to avoid flotation. Then S_1 and S_2 were poured. After gas formation stopped, the samples of foam (F_1, F_2) were collected with 50 mL glass pipette (±0.2mL). The dissolution of the Alka seltzer changed the pH of the original solution from 7.5 to 6. The pH is one of the main parameters influencing the flocculation (Ghanizadeh and Sarafpour, 2001), but in this research it was neglected. The dissolution of the acetylsalicylic acid boosted the COD concentration so the comparison with the other solutions were difficult to carry forward. The SVI, the TSS and the PSD curve of the different solutions were used to define the EPS concentration to apply in the column test experiments.

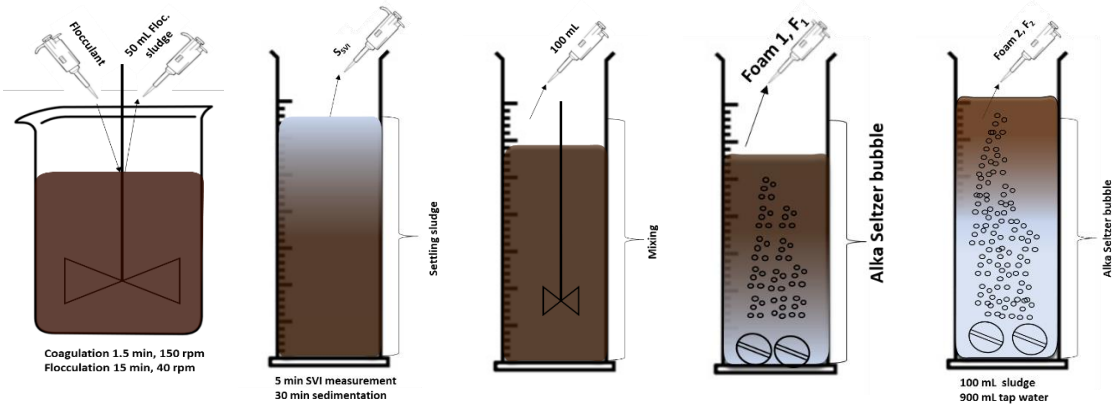


Figure 3.2 Visual representation of the Jar Test experiment: coagulation and flocculation with the mixer (a), sedimentation test in a graduated cylinder (b), preparation for the flotation test with Alka-Seltzer (c), flotation test with sludge S_1 (d), flotation test with sludge S_2 (e).

3.5 Experiment 2: Flotation Column

The aim of these experiments was the simulation of a DAF system on a laboratory scale DAF column. Previous studies were done at Delft University (Guleria, 2019) and they were used as the starting point for this research. The setup of the experiment is shown here below (Figure 3.3), representing all tools and instruments necessary for the its realization.

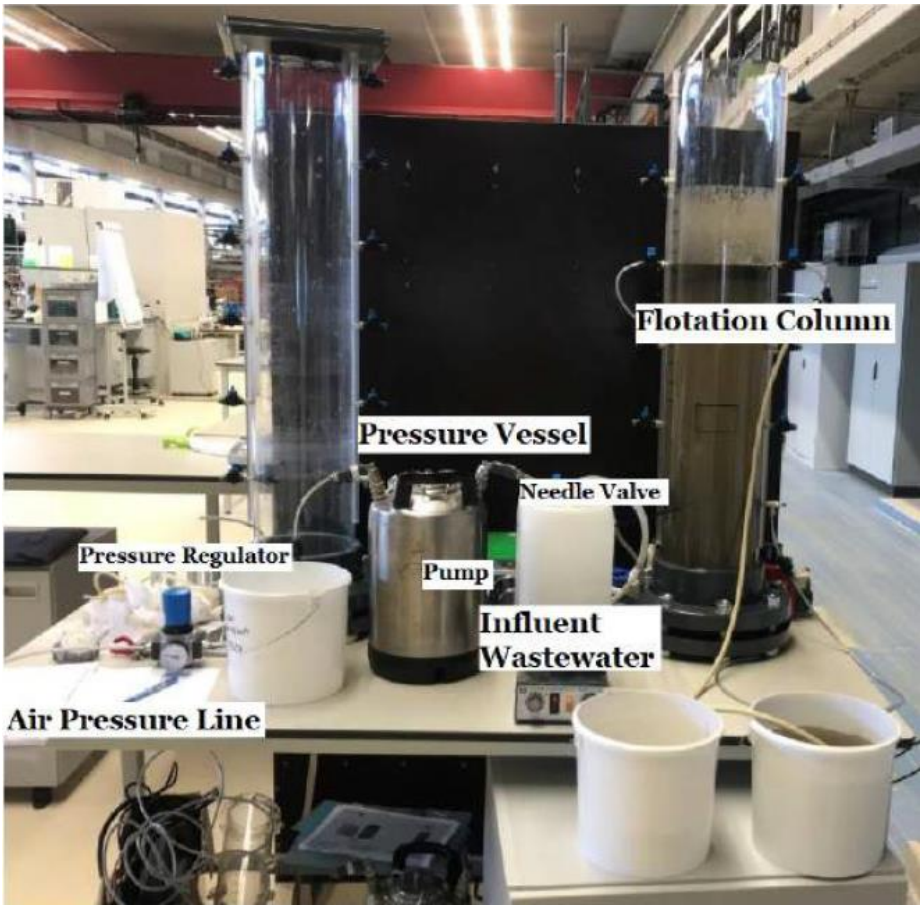


Figure 3.3 Laboratory DAFset up (Guleria, 2019)

The pressurized vessel (Thielmann stainless steel pressure containers) was filled with 5 L of tap water, then closed and pressurized with air at 5 bar. The inlet pressurized air was regulated with a Festo HE Series Pneumatic Manual Control Valve. For the correct realization of the experiment, the water has to reach the saturation state with the air. So, the pressure vessel was manually shaken for 10 minutes each time previous experiment or let it stay for at least 12 hours, as demand the oxygen transfer rate. At the outline was located a manual ball valve (Festo, G1/4") to open and close the line and a needle valve (Festo, G1/4") to manually regulate the flow. The flow regulation was defined with the help of a scale (Kern, 0.1 g SD), a chronometer (Hanhart) measuring the weight over time and assuming a water density of 1g/mL . From now on, the pressurised outflow will be called white water, a term usually applied in the DAF process (Rodrigues and Rubio, 2007).

The influent sludge (5L, 4.5 gTSS/L) was prepared as mentioned in the previous section (3.1.2), poured in a plastic bucket of 5.5 L and located on a magnetic mixer (Heidolph). Samples of sludge were collected every time before the experiment. The sludge was continuously mixed with a magnetic stirrer at 40 rpm to avoid the settling of the sludge. When flocculants were added, the same coagulation and flocculation mixing parameters were recreated. The container was connected to a peristaltic pump (Watson Marlow 520s) which allowed the regulation of the flow. Because of the influent sludge viscosity, higher than water, the flow was checked in the same way of the white water, still assuming a density of 1g/mL. The white water and the influent sludge were connected through a T-valve (Festo, G1/4") and directly connected to the flotation column.

The flotation column was a plexiglass cylinder (20 cm diameter, 1.2 m height), which was previously graduated with different ball valves (Festo, G1/4") at different height to regulate the

influent and effluent time. For each experiment, 20L of tap water was poured in the flotation column (64 cm). The influent line was located to spray the flow at the centre of the column at 25 cm height. From some previous studies (Guleria, 2019) it was assed flow and operational the table below (Table 3.3).

Table 3.3 Chemical and operational parameters of the flotation column experiment.

Chemical Parameters		**Time Parameters**	
White water	4.5 mL/s	Influent sludge in	0 min
Diluted sludge	5.0 mL/s	Open Clean eff.	5 min
Air pressure	5 bar	Stop Clean eff.	10 min
TSS concentration	4.5 gTSS/L	Stop Influent sludge	13.5 min
A/S ratio	0.005 -0.015 gAir/gTSS	Open concentrate	15 min
Temperature	15-25 °C	Sample clean eff. 17 min	17 min
pH column	7-8	Sample concentrate 17 min	17 min
Influent sludge	9.5 mL/s	Close concentrate (expected)	20 min
TSS column	200-800 mgTSS/L	Final volume	20 L

The figure below (Figure 3.4) represents the flotation column experiment and shows the names used to identify the different flows. The influent sludge was composed by the white water and the diluted sludge solutions. Theoretically, 18.2 g of TSS were added in the column in 13.5 minutes. At the end of the experiment, whether the column was considered as a CSTR reactor, the suspended solid concentration in the reactor would be around 657 mg TSS/L. This latter value was specifically calculated for each experiment and used as a mean of comparison to calculate the efficiency of removal of the other samples. The clean effluent was collected for 5 minutes from the bottom manual valve (16 cm). In the standard DAF application, the effluent pipe is located at a relative low height to avoid the intake of floating and heavy sedimented flocs. The clean effluent flowed into a jerry can and it was weighted, mixed and then samples were taken. The same procedure was used for the concentrate from the 15-20 minutes of the experiment, but from a different height (64 cm). Moreover, 180 mL samples were taken after 17 minutes at the same height of the previous two measurements. In this way, it was possible to verify the effectiveness of the plug flow behaviour of the flotation column and compare the bottom and upper part solution at the same time. Seventeen minutes were defined because of the raising velocity of the bubbles, around 25-55 cm/s at a pressure of 5 bar (Vigneswaran, 2009). Thus, even though Vigneswaran studied bubbles and not agglomerates, which have a different density, it was assumed that after 3.5 minutes the closure of the influent sludge all agglomerate should have reached the surface. Foam thickness was also measured after 17 minutes with a ruler.

C_0 = initial concentration diluted sludge (gTSS/L);

M_n = Suspended solids added (gTSS/L);

C_{rs} = Concentration residual sludge (gTSS/L);

$C_{cl,eff}$= Concentration clean effluent (gTSS/L)

C_{conc}= Concentration concentrate (gTSS/L) ;

$t_{0\text{-}13}$ = eperiment time 0-13 (min);

$t_{5\text{-}10}$ = eperiment time 5-10 (min) ;

$t_{15\text{-}20}$ = eperiment time 15-20 (min) ;

S_{ct17} = sample concentrate 17

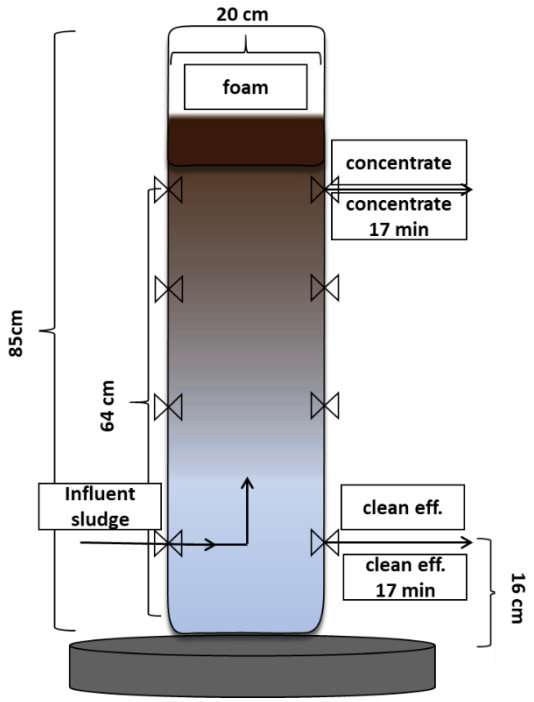


Figure 3.4 Representation of the column test experiment

V_0 = initial volume diluted sludge (L);

S_s = sample diluted sludge (mL);

V_{rs} = residual dilutaed sludge (L);

V_{ds}= volume diluted sludge (L);

V_{ww} = volume white water (L);

V_{ce} = vole clean eff. (L);

S_{ce17} = sample clean eff. 17 min (mL);

V_{ct} = volume concentate (L);

S_{ct17} = sample concentrate 17 min (mL).

At the end of the experiment, foam samples were taken with a spoon. The effluents and the samples were weighted also to estimate the balance, defining the volumes of diluted sludge and white water truly added in the experiment. The system (Equation 7) below assesses the equations (Figure 3.4):

$$\begin{cases} V_{ds} = V_0 - V_{rs} - S_s & (1) \\ V_{ww} = (V_{ce} + V_{ct}) + (S_{ce17} + S_{ct17}) - V_{ds} & (2) \end{cases}$$

Equation 7 Mass balance calculation of the experiment

Once these volumes were measured, in combination with the TSS results, it was possible to assess a mass balance. The total load of suspended solids introduced into the column was equal to:

$$M_{in} = V_0 \times C_0 - V_{rs} \times C_{rs}$$

Equation 8 Total influent sludge during the experiment

As said, in order to compare the particle separation efficiency between the experiments, it was estimated a concentration as a CSTR behaviour. That results equal to M_{in} divided by the column volume at the end of the experiment, 20 L ($C_{cstr,0\text{-}20\ min}$). Furthermore, to evaluate the hydrodynamic behaviour of the column and better asses the removal efficiency of the clean effluent, a dynamic mass balance was simulated. The main reason for this calculation lies in the fact that the clean effluent is extracted between 5-10 minutes, when not the suspended solids

load was added into the column. Similarly to the final concentration, this mass balance was estimated as the column was a CSTR reactor. To structure this calculation, several assumptions were taken. All flow rates were estimated constant during the experiment and a 0.5 minute time step was used for the calculation. In the first equation, it is showed the theoretical mass balance with a variable volume over time, while in the following one is showed how it was discretized (Equation 9, Equation 10).

$$\frac{\partial C_{cstr} \times \partial V}{\partial t} = QC_{in} - QC_{out}$$

Equation 9 Theoretical mass balance for the CSTR reactor with variable volume

$$\Delta C_{cstr,t} = \frac{\left(\frac{M_{in}}{t_{0-13}} - \frac{V_{ce} \times C_{cl.eff}}{t_{5-10}} - \frac{V_{ct} \times C_{conc}}{t_{15-20}}\right)}{\left(\frac{V_{ds} + V_{ww}}{t_{0-13}} - \frac{V_{ce}}{t_{5-10}} - \frac{V_{ct}}{t_{15-20}}\right)} \times \Delta t$$

Equation 10 Discretization of the mass balance to calculate the $C_{cstr,t}$

Lastly, $C_{cstr,5\text{-}10\ min}$ and $C_{cstr,15\text{-}20\ min}$ were estimated as the mean of the simulated concentration over time and they were used to assess the removal efficiency for the clean effluent and the concentrate respectively.

4 Results

In this chapter, the most relevant results obtained in one month of experiments are reported. Two subchapters were chosen, separating between the jar and flotation column test experiments. After the jar test, it would be shortly motivated the reason why a certain dose of EPS (800 mg/L) was chosen to perform the column test experiment.

4.1 Results: experiment 1

4.1.1 SVI

Table 4.1 reports the values obtained during the SVI test, mentioning as well TSS, VSS and EPS. In order to dose the correct EPS amount in mgEPS/gVSS, firstly it was estimated a certain VSS concentration (67% of TSS) of the sludge. Four different dosages of EPS were tested: 200, 400, 800 and 1200 mgEPS/L which almost correspond to a range between 50 and 300 mgEPS/gVSS. However, from the experiment, the VSS/TSS fraction resulted around 75%, so the dosage need to be slightly adjusted.

Table 4.1 Jar test experiment results: TSS, VSS, $SVI_{5,10,30\ min}$

Test	Flocculant [mg/L]	TSS [g/L]	VSS [g/L]	$\frac{mgEPS}{gVSS}$	$SVI_{5\ min}$	$SVI_{10\ min}$	$SVI_{30\ min}$
Blank	-	4.45±0.7%	3.51±4.6%	-	179	121.	88
Cellulose	200 mg/L	4.74±1.7%		-	154	106	77
EPS_1	200 mg/L	4.57±13.0%	3.41±6.6%	58.7	197	140	101
EPS_2	400 mg/L	4.60±1.4%	3.47±3.6%	115.3	202	154	102
EPS_3	800 mg/L	4.84±1.5%	3.69±3.3%	216.8	208	172	108
EPS_4	1200 mg/L	4.79±0.6%	3.71 ±2.3%	323.0	200	185	111

With the addition of EPS and cellulose, SVI values changed over time. As ascertained some previous researches (Wilen et al, 2003; Liu and Tan, 2005) the addition of EPS increased the SVI of the sludge. On the other hand, the addition of cellulose decreased its value. More in detail, the final values varied from 77 mL/mgTSS (cellulose) to 111 mL/mgTSS (1200mgEPS/L). However, SVI values were significantly different for the first 5-10 minutes, resulting 10-50% higher than the blank solution as shown in Figure 4.1 and Figure 4.2. After ten minutes, the difference between EPS_3/EPS_4 and the blank counted 51 and 64 mL/mgTSS. In the graduated cylinder, these values represent around 15 cm height variation. On the contrary, with cellulose addition, at 5 minutes it was measured 5 mL/mgTSS difference which represents around 6 cm sedimentation difference compared with the blank solution. The sedimentation process for the EPS series seemed to start with some delay. Only after 15-20 minutes the difference with the blank was considerably reduced (Figure 4.1).

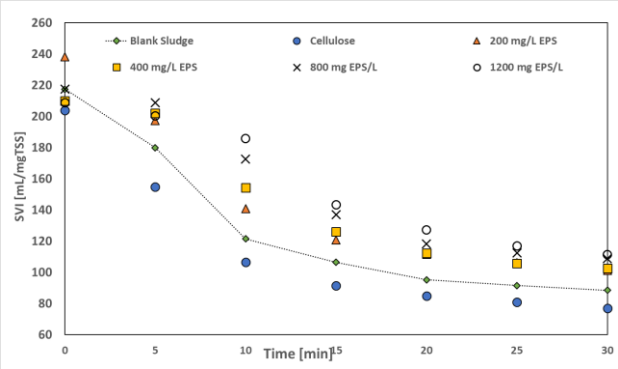


Figure 4.1 SVI results plotted over time. The dotted line represents the blank experiment. Higher values imply a slowest sedimentation (EPS) and viceversa (cellulose).

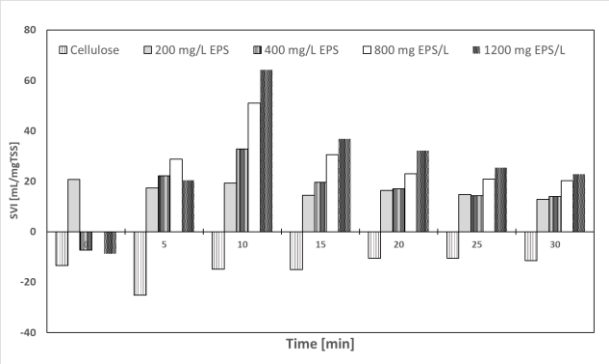


Figure 4.2 Difference between SVI using the blank as reference.

4.1.2 TSS measurements

During the jar test experiment, TSS samples were collected at three different moments: S_f, F_1 and F_2 as mentioned in chapter 3.4.

The highest concentrations in the supernatant were measured with the highest EPS doses (800, 1200mgEPS/L), whereas the lowest was with 400 mgEPS/L. For the blank, cellulose solutions EPS_1 and EPS_2 doses, the S_f values were relatively close to 0.50 g/L, while for the last two, EPS_3 and EPS_4, slightly higher, respectively 0.64 and 0.78 g/L. For F_1, from the blank solution it was collected the greatest value (7.09 gTSS/L); the lowest was measured in the experiment with 200 mgEPS/L (5.25 gTSS/L). In this case, EPS_3 series created a foam that was the most concentrated (6.62 gTSS/L) among the experiments with the flocculants. Similarly, for the diluted sludge (F_2), with the addition of 800 mgEPS/L the collected foam was the highest among the EPS doses, and, in this case, among all solutions (1.53 gTSS/L). In this experiment, the addition of a considerable amount of EPS (>200 mgEPS/L), the formed foam was about two times more concentrated than the one from the blank solution. In general, it is interesting to notice how the addition of cellulose did not enhance either the reduction of TSS in the surfactant (0.51 gTSS/L) or increased the foam concentrations.

Table 4.2 and reports the values of the above mention experiments, while Figure 4.3 illustrated the TSS concentration for S_f, F_1 and F_2 over the EPS doses.

Table 4.2 Supernatant and foam concentration form the sedimentation and flotation test

Test	Flocculant [mg/L]	S_f [gTSS/L]	F_1[gTSS/L]	F_2 [gTSS/L]
Blank	-	0.548±4.3%	7.09±5.5%	0.63±3.93%
Cellulose	200 mg/L	0.509±8.7 %	6.04±3.3%	0.54±1.6%
EPS_1	200 mg/L	0.509±5.8%	5.25±3.6%	0.64±1.0%
EPS_2	400 mg/L	0.537±3.6%	5.84±4.1%	1.21±2.2%
EPS_3	800 mg/L	0.637±2.9%	6.62±4.3%	1.53±4.0%
EPS_4	1200 mg/L	0.779±6.2%	5.88±6.0%	1.18±3.2%

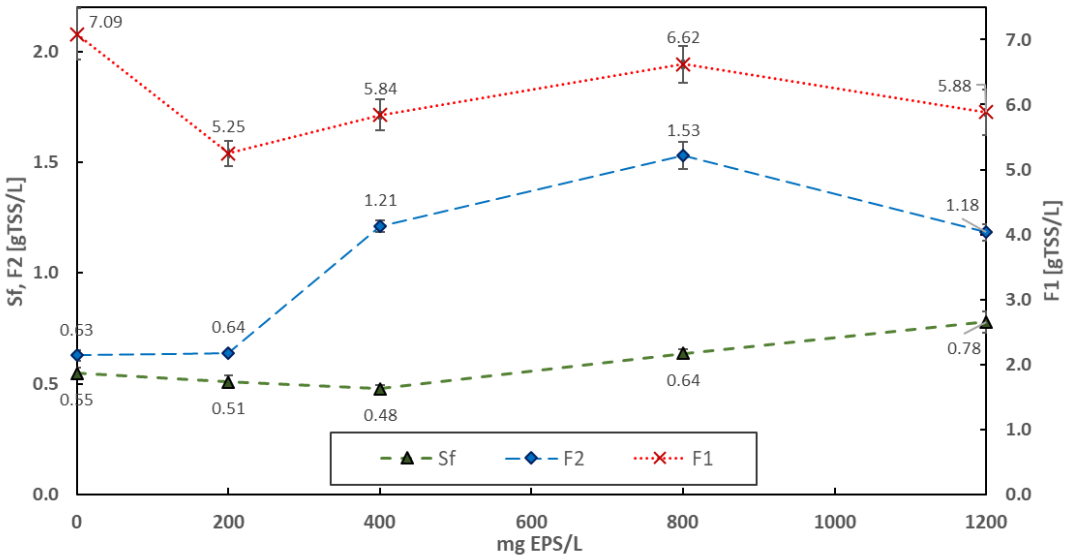


Figure 4.3 TSS concentration over EPS doses in mg/L. On the left vertical axes S_f and F_2 concentration are reported, on the right F_1 concentration in gTSS/L.

4.1.3 PSD analysis

In the Jar test experiments, the particle size distribution of sludge extracted after 15 minutes of flocculation was compared among all the solutions. An example of the measured data is reported as from the Microtac software(Appendix D). The mean volume diameter (MV), the mean area diameter (MA), and of the mean number diameter (MN) are reported in Table 4.3. The present standard deviation refers to the MV calculation, and, in general, it is noticeably high. The range of particles size is around 60-70 µm for MV, 33-37 µm for MA and 11-19 µm for MN. The highest value for the MV was found in the cellulose series (70.03 µm) and the lowest in the blank solution (58.90 µm). The largest diameter for the MA distribution was obtained with 800 mgEPS/L, 36.62 µm. Lastly, for the MN measurement, EPS_4 series measured the largest number, 19,08 µm. With the addition of EPS, MV and MA values seemed to gradually increase, but this behaviour was not noticeable for MN. However, MN results for EPS_3 and EPS_4 was considerably higher than other values.

Table 4.3 mean volume and area diameter obtained from the PSD analysis

Solution	MV [µm]	MA [µm]	MN [µm]	SD [µm]
Blank	58.9	33.04	11.56	20.5
cellulose	70.03	34.19	11.42	41.5
EPS_1	63.95	34.03	11.66	20.9
EPS_2	64.49	34.12	11.39	37.7
EPS_3	67.9	36.62	13.37	21.95
EPS_4	69.3	37.03	19.08	22.99

The graph below represents the channel distribution, or frequency, of the different samples over the diameter on a logarithmic scale (Figure 4.4). The distribution was calculated between 0.001-2000 µm, but the graph reports only those between 5-500 µm as the majority of particles was

in that range. Even though in a qualitatively way, from this type of chart it is possible to appreciate the variations in the particles distributions. In general, a right-shift of the curve implies bigger particles, while a higher peak signifies a greater frequency on a certain particular range, as also indicated in Figure 4.4. For cellulose, it is not visible any particular change in the chosen range when compared with the blank solution. This is not the case for the EPS solution: EPS_1 and EPS_3 curves show a significant shift on the right (floc enlargement) in a range between 30 and 50 µm. For EPS_3 and EPS_4, it also appreciable the reduction of small particles in the range between 5 and 10 µm. To have a more quantitively overview of the different PSD curves, the frequency difference compared with a standard channel distribution gives the percentual variations within a certain gap (Figure 4.5). Results were compared with the blank solution: negative values imply a decrease of the floc frequency in that range, and viceversa. EPS_1 flocs were around 5% bigger in a range between 30 and 100 µm; for EPS_3 an 10-20% flocs augmentation between 36-176 µm was measured; for EPS_4, around 20 and 80 µm.

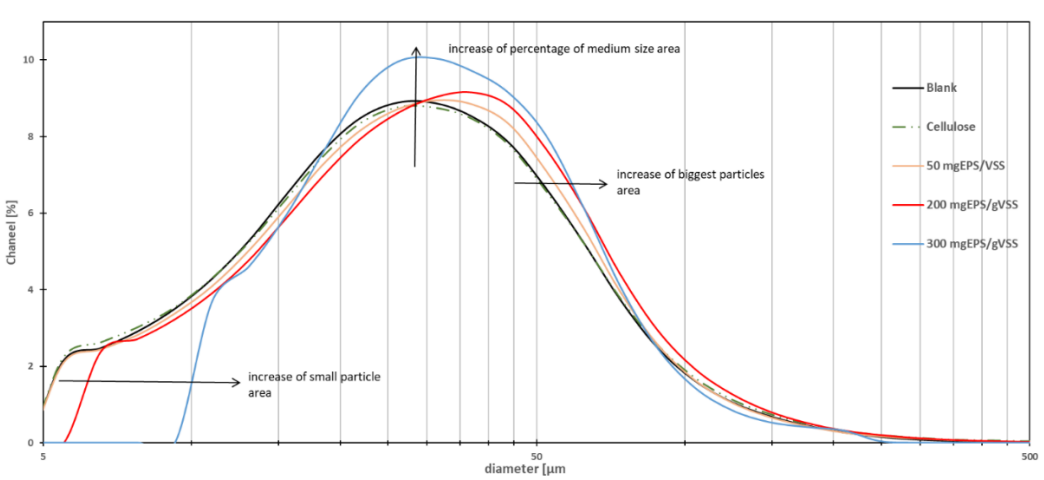


Figure 4.4 Channel distribution of the mean area size (µm)

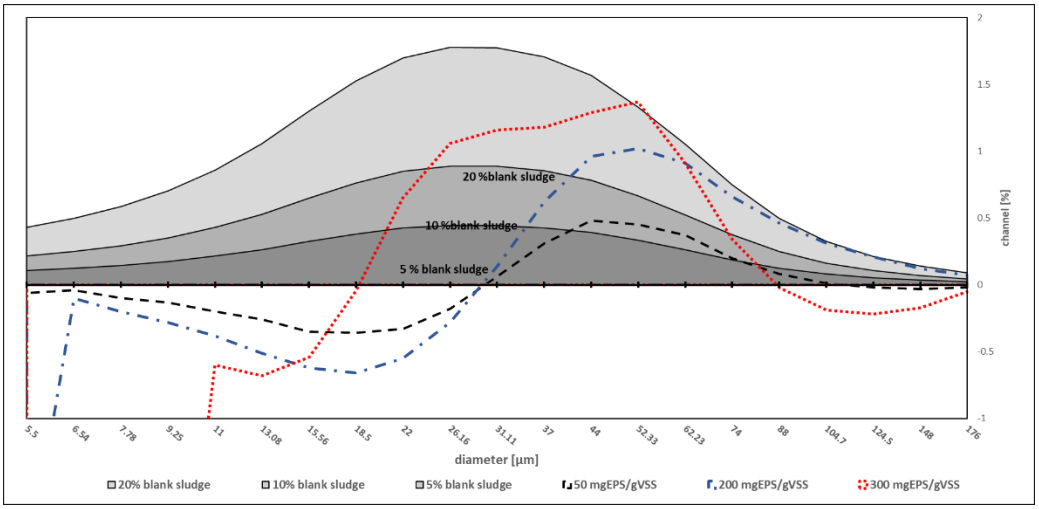


Figure 4.5 Channel difference between flocculant and blank solutions. Positive values state an increases of particle size in specific interval, negative values a decrease.

4.1.4 EPS dose for experiment 2

To progress to experiment 2 an EPS dose had to be chosen. From this first set of experiments it can be concluded that EPS_3 and EPS_4 doses showed the best flocculation performance in order to achieve a better solid separation efficiency in the flotation column test. For both trials, it was measured the greatest SVI and PSD value. For PSD results, EPS_4 would have been the best candidate, but these measurements were characterised by a considerable uncertainty. Meanwhile, the difference between the two SVI values were not considered such significant. On the other hand, F_1 and F_2 samples indicated EPS_3 as preferable dose as it was possible to collect the most concentrated foam. These last results were considered the most relevant and close to achieve a better flotation performance. In conclusion, experiment 2 was performed with the EPS_3 dosage, 800 mgEPS/L.

4.2 Results: experiment 2

4.2.1 Mass balance calculation and C_{cstr} estimation

The flotation column experiments were dependant on the total load of suspended solid introduced into the reactor as well as from the amount of white water used for the generation of the microbubble. Thus, Table 4.4 summarizes the mass balance calculations and the results of the dynamic mass balance over time for the experiments, explained in chapter 3.5. The load of suspended solid varied between 17.3-19.8 of gTSS introduced and the A/S ratio between 0.8-0.93 gair/gTSS. Overall, the mean concentration of the in the reactor varied 0.42-0.48 gTSS/L after 10 minutes ($C_{cstr\ 5\text{-}10min}$), while 0.71-0.819 gTSS/L, after 20 minutes ($C_{cstr\ 15\text{-}20min}$). $C_{cstr,0\text{-}20min}$ estimated with the static mass balance differ within 0.637-0.710 gTSS/L. At the end of the experiment, it was measured the thickness of the foam which resulted 1.8, 2.4 and 2.2 cm respectively for the blank, cellulose and EPS experiments. This layer was assumed homogeneous and, measuring its concentration (Table 4.5), it was calculated the suspended solid mass ended in the foam.

Table 4.4 Relevant parameter calculated from the mass balance obtained during the experiment

Solution	Introduced mass [gTSS]	A/S ratio [gair/gTSS]	$C_{cstr\ 0\text{-}20\ min}$ [gTSS/L]	$C_{cstr\ 5\text{-}10\ min}$ [gTSS/L]	$C_{cstr\ 15\text{-}20min}$ [gTSS/L]	Foam Mass [gTSS]
Blank	17.4	0.00926	0.637	0.425	0.714	6.9
Cellulose	19.7	0.00871	0.710	0.479	0.819	12.9
EPS_3 (800 mgEPS/L)	19.3	0.00802	0.708	0.457	0.813	15.8

4.2.2 Chemical results: TSS,VSS, COD,NTU

TSS, VSS,COD and NTU from the more relevant samples measured during the experiments are reported in Table 4.5.

As expected, the clean effluent showed the lowest concentration. In the blank experiments, it was measured the lowest TSS concentration, 0.137 g/L, while with the addition of flocculants these values were higher, 0.156 gTSS/L for EPS_3 and 173 gTSS/L for cellulose. As well, the same pattern was obtained for concentrate and the $C_{cl.eff,\ 17min}$: the lowest TSS values were measured in the blank experiments, 0.257 gTSS/L and 0.258 gTSS/L respectively. On the contrary, the minimum value of $C_{conc,17\ min}$ was measured in the EPS series, 0.259 gTSS/L. Meanwhile, foam samples were much denser: 13.8, 19.5 and 24.0 gTSS/L respectively for the blank, cellulose and EPS solutions. Comparing the values of the clean effluent and the concentrate at 17 minutes, it is noticeable how these values do not differ considerably, but blank and EPS series measured around 0.05 gTSS/L difference.

The addition of EPS influenced the concentration of COD and in as in all samples, it is found the greatest values. As consequence, it was not possible to correlate TSS and COD (R^2 = 0.249) as appears in Figure E.1, Appendix . Finally, turbidity varied between 68 to 172 NTU. In this case, in EPS it was always measured the lowest turbidity, especially for the samples measured after 17 minutes. Furthermore, it revealed a good correlation (R^2 = 0.927) with the TSS values (Figure E.2,Appendix EAppendix).

Table 4.5 Chemical results from the flotation column experiment. The values are reported as mean of the experiments.

	Solution		TSS [g/L]	VSS [g/L]	COD [mgO_2/L]	Turbidimetry [NTU]
1	Blank	$C_{cl.eff}$	0.137±0.011	0.126±0.007	199±23	70±10
2	Cellulose	$C_{cl.eff}$	0.173±0.005	0.134±0.006	162±6	92±4
3	EPS `	$C_{cl.eff}$	0.156±0.017	0.142±0019	213±17	68±5
1	Blank	$C_{conc.}$	0.257±0.011	0.225±0.032	359±49	152±1
2	Cellulose	$C_{conc.}$	0.316±0.005	0.233±0.008	255±1.7	167±2
3	EPS `	$C_{conc.}$	0.292±0.027	0.239±0.029	462±31	146±10
1	Blank	$C_{cl.eff,\ 17min}$	0.258±0.013	0.187±0.028	375±4	141±1
2	Cellulose	$C_{cl.eff,\ 17min}$	0.324±0.007	0.234±0.014	226±2	165±4
3	EPS `	$C_{cl.eff,\ 17min}$	0.259±0.018	0.203±0.005	399±21	126±3
1	Blank	$C_{conc,17\ min.}$	0.307±0.012	-	407±7	152±3
2	Cellulose	$C_{conc,17\ min.}$	0.316±0.029	0.236±0.019	250±5	172±4
3	EPS `	$C_{conc,17\ min.}$	0.291±0.033	0.228±0.008	445±10	134±3

1	Blank	Foam	13.798±0.676	10.088±0.623	18196±867	-
2	Cellulose	Foam	19.543±2.069	14.637±1.407	19886±1510	-
3	EPS `	Foam	24.052±1.412	17.545±1.062	25923±2387	-

When comparing these results, it should always consider that the incoming suspended solid load slightly diverged (Table 4.4). As consequence, the possibility to compare the measurements with their relative efficiency can give other interesting outcomes. Figure 4.6 reports TSS removal efficiencies compared with the different C_{cstr} at the respective time or interval. Then, for the clean effluent, it was considered $C_{cstr\ 5\text{-}10\ min}$, whereas for the concentrate the $C_{cstr\ 15\text{-}20\ min}$. Besides, the latter estimation was used to compare the separation efficiency for the samples measured at 17 minutes($C_{cl.eff,\ 17min}$, $C_{conc,17\ min}$). In general, the efficiency did not change significantly in the different experiments, varying from 57-69%. From the cellulose series, it was obtained the lowest efficiency for most of the samples ($C_{cl.eff}$, C_{conc} and $C_{cl.eff,\ 17min}$). The concentrated showed very similar results among the three series (63.9%, 61.4%, 64%) while the highest separation was found in clean effluent samples from the blank series, 69%. However, the EPS series performed the best particles' separation for the samples collected at 17 minutes: 68.1% for the clean effluent and 64.2% for the concentrate. Though it is not reported in the graph, it is possible to calculate the efficiency with $C_{cstr\ 0\text{-}20\ min}$, giving an indicative estimation of the overall experiment. For the clean effluent, in the cellulose series was obtained the least removal efficiency, 75,6%, whereas for the blank and EPS solution results were 78,5% and 78,0% respectively.

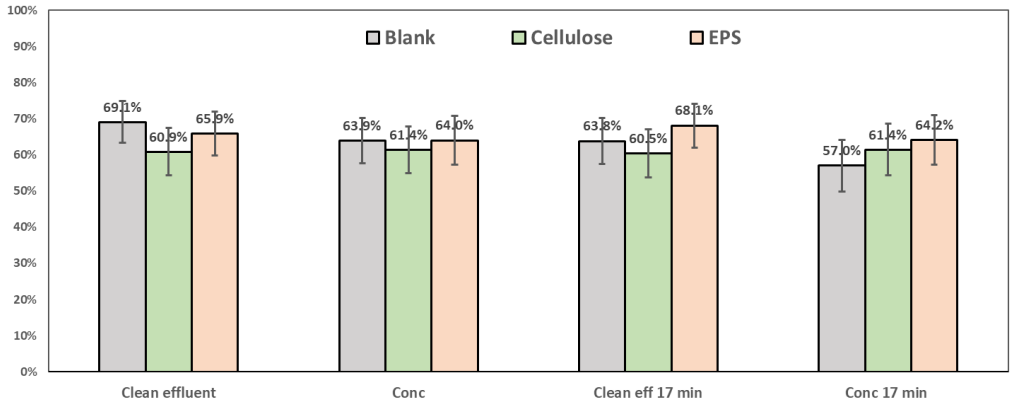


Figure 4.6 Removal efficiency compared with the different C_{cstr}

4.2.3 PSD measurements

The influent sludge characteristics had on average a normal PSD distribution with the mean volume and area particle size MV and MA around 59 µm and 32.5 µm. An example of the standard results obtained from the PSD curve is shown in Figure 4.7 (EPS_3 distribution) . In this case, it is not appreciable a particular difference between sludge and the flocculated sludge, but the same considerations mentioned in Figure 4.4 are valid. The foam is typically characterised by a higher frequency between 20 and 50 µm, a lower concentration of small particles for diameter minor than 10 µm. The clean effluent and the concentrate had a smaller mean diameter than the flocculated sludge. They are characterized by a more pronounced peak around their mean (~20 µm) and inferior fraction of particles larger than 30 µm. Also, especially for the concentrate its distribution was marked by a peak in the small particle range (< 5µm).

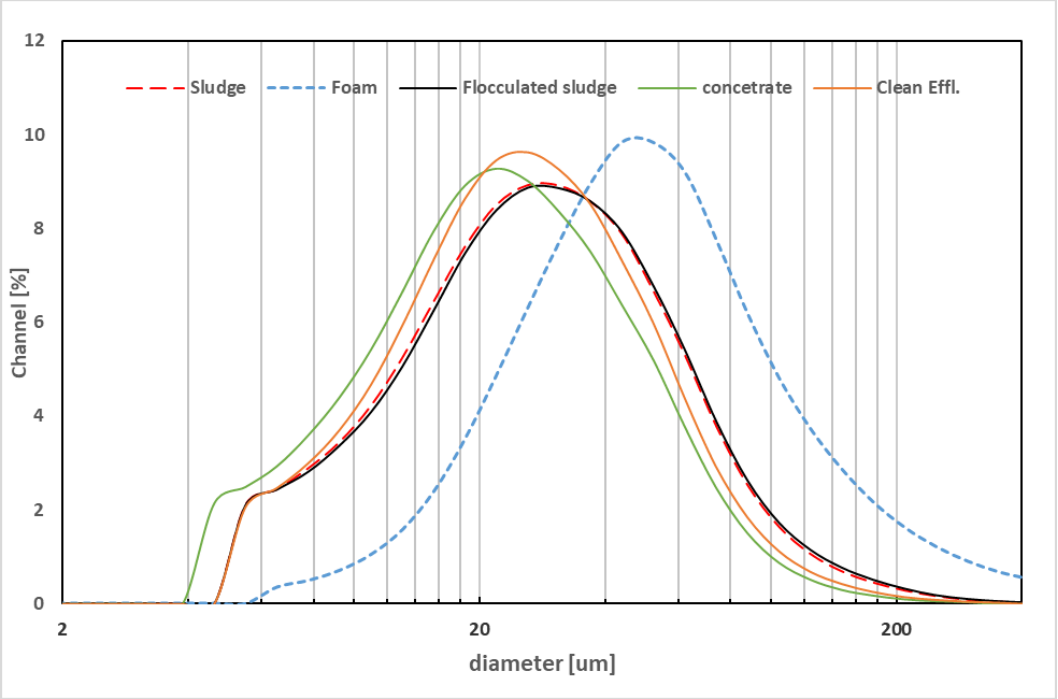
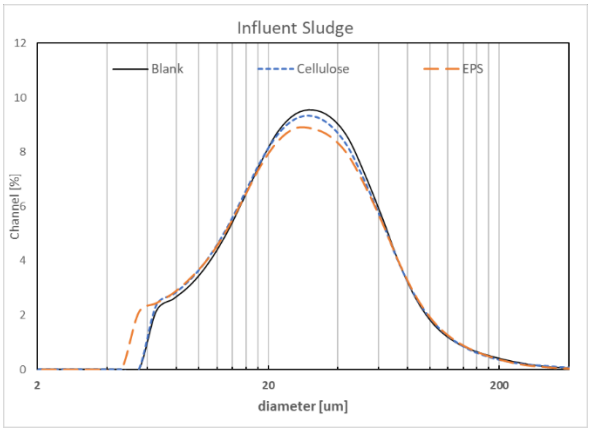
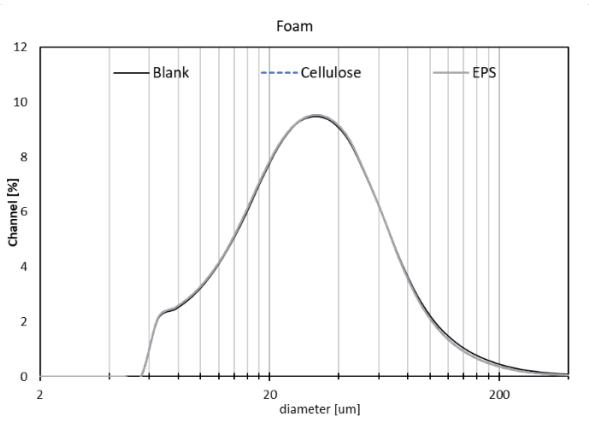


Figure 4.7 Standard channel distribution for MA from EPS series of column test flotation.

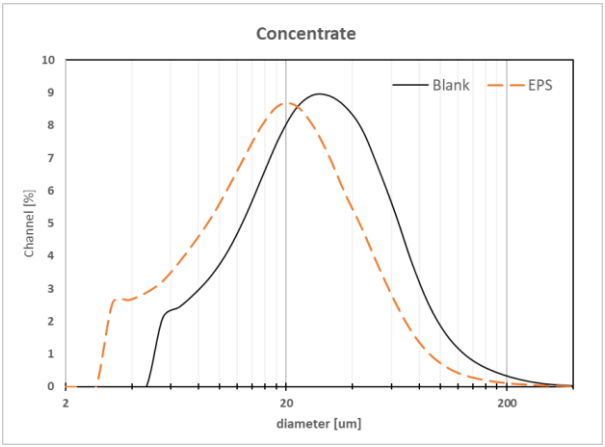
Figure 4.8 reports the average channel distribution for MA results of the collected samples during all column experiments. The flocculated sludge for the different solutions varied between 60-71 µm, 34-37 µm for MA and 11-13 for MN. The EPS series were marked by a peak in the small particles' size range and also by the smallest MA, 34.12 µm (Figure 4.8.a). In all series, PSD of the foam presented very similar pattern, with a MA which varied between 35-37µm (Figure 4.8.b). Both for the concentrate and for the clean effluent, the blank and EPS solutions presented a different significant patterns, with EPS distribution marked by smaller particles. For these samples, MA distributions were 22 and 26 µm for the blank solution, at 25 and 27 µm for the EPS solutions. (Figure 4.8.c,d). The comparison between the influent sludge and foam distribution evidences the different frequency of the particle size in the samples. For the EPS experiments, the channel distribution of the foam was on average 10% more concentrated in the range between 20-50 µm (Figure 4.8.e). In addition, specifically in the EPS series, the concentrate distribution was characterized by a frequency of very small particles (2-4 µm) which they were not present in the flocculated sludge. As it appears in Figure 4.8.f, between 4 and 12 µm, the concentrate is around 30-50% more frequent than the influent sludge.

a) *b)*

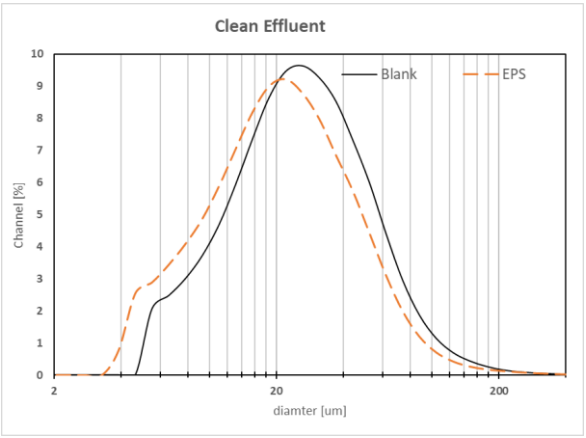




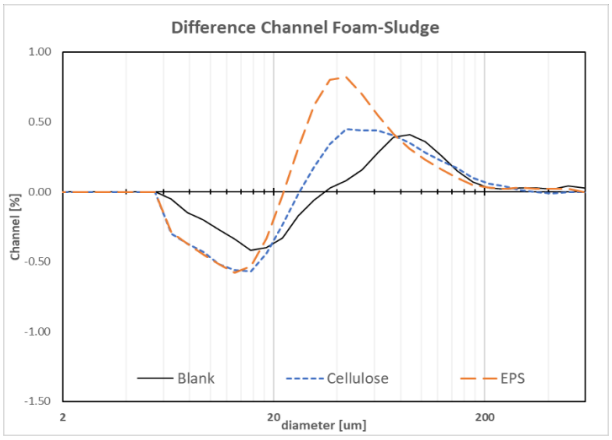
c)



d)



e)



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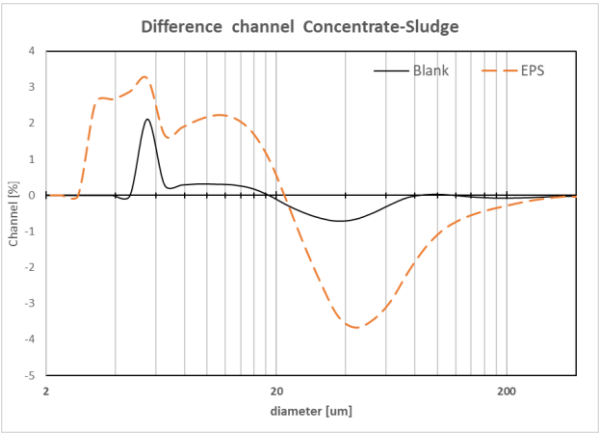

Figure 4.8 Mean area size PSD results from the flotation column experiments: a) flocculated influent sludge; b) PSD of the foam; c) PSD of the concentrate; d) PSD clean effluent; e) channel difference between foam and sludge f) Channel difference between concentrate and sludge.

5 Discussion

5.1 Sludge solution

At Harnashpolder's wastewater treatment facility, a considerable quantity of iron, calcium and magnesium are dosed to enhance coagulation and flocculation. As consequence the particle size distribution of the sludge measured MV of 60 µm on average, so it can be stated that the sludge is already flocculated, as shown in Appendix C (Houghton, Burgess and Stephenson, 2002). Moreover, because of the digestion process which takes at least 25 days, flocs can be assumed in stable conditions. As result, the little difference between the blank and flocculant solutions (Figure 4.4, Figure 4.8) was a possible outcome.

Another important consideration of the Harnashpolder's sludge is the elevated ionic strength, estimated around 0.30 M. In the laboratory, it was not possible to measure zeta potential, but, because of the considerable presence of divalent cations and floc size, it might be considered close to zero. The dilution process of with tap water to obtain the influent sludge with 4.5 gTSS/L reduced the ionic strength to an estimated value of 0.17 M. As well, in the flotation experiment, the ionic strength was estimated to decrease down to 0.0132 M, very close to the tap water value. The drop of the ionic strength is responsible for an increase of the repulsive force in the DLVO forces and an extension of the double layer (Verwey, and Overbeek, 1948). Furthermore, in section 2.4.3, it was mentioned that EPS are negatively charged, so their dosage would have intensified even more zeta potential of the particles. In conclusion, the assumed negative trends of the zeta potential and the extension of the double layer could have decisively affected the flocculation performance of the EPS. Additionally, the increase of zeta potential might have also negatively influenced the bubbles particles electric forces, as bubbles are negatively charged (Kwak and Mi-Sug, 2013). For future analysis, the evaluation of the zeta potential would be of great help to determine dosage and the flocculation potential of EPS, as it would give an estimation of the electrical interaction between particles.

5.2 Jar test discussion

The jar test experiments did not simulate the same physical conditions of the flotation column experiment. However, it was helpful to determine some characteristics of the sludge in response to flocculation, sedimentation and flotation.

PSD results were marked by a high standard deviation, so their results were difficult to take into consideration. In the Microtac manual, the standard deviation is stated to be the width of the measured particle size distribution and not the common-used statistical error. With this interpretation, on average, due to the little difference between two PSD measurements, any conclusion from becomes unreliable. As consequence, it is not possible to draw the relationship between the flocs' dimension and EPS dosages present in Table 4.3 mean volume and area diameter obtained from the PSD analysis. The SVI clearly showed how an increasing EPS dosage decreased the sludge settleability, especially in the first 5-10 minutes. As mentioned in the study of Wilen et al. (2013), this is a possible sludge behaviour, particularly with a considerable LB-EPS and carbohydrates fraction. The supernatant concentration slightly increased with a dosage higher than 400 mgEPS/L. The combination of these results might suggest that particles are more disposed to flotation. Lastly, Alka seltzer dissolution simulated the foam formation ability of the sludge. This test was not meant to simulate the performance in the flotation column experiment. The addition of Alka seltzer generated microbubbles of CO_2 with different diameters, between 100-300 µm (Chui, Fan and Park, 2004), while in the flotation column it was used pressurized air which generated particle between 20-70 µm (Han, Park and Lee, 2002). Moreover, the A/S ratio as the contact time in the reactor was not comparable between the experiments. However,

because CO_2 bubbles are negative charged, though at a lower extent than air, the agglomerates-bubble interaction was not affected by and agglomerates-bubble interaction (Kwak and Mi-Sug, 2013). From the collection of the foam (F_2), three out of four EPS dosage fostered foam formation. At this regard, it is important to mention that the collection of the foam might have been inaccurate. In these experiments, the formed foam created a thin layer of solid which was hard to collect uniformly with a glass pipette.

Thus, as already mentioned at the beginning of chapter 4, EPS_3 was chosen as the most favourable dose. More attempts and a broader range of EPS dose would have clarified the effects of EPS on the flocculation, and especially for the F_2 results. In this respect, it should be studied the accuracy of the foam collection with a glass pipette or it should be devised a new system for the scope.

5.3 The difficult interpretation of the flotation column tests.

The flotation column tests were more sophisticated experiments than the jar test and they included more variables and uncertainties. The total amount of TSS added into the column was on average in line what expected, around 5% (5.8% STD). Likewise, on the same magnitude, the volume of influent sludge varied between 3.8-4.2 L (5.8% STD) and the one of white water between 3.3-3.8 L (6.7% STD). Another important factor that might have affected the results is the volumes of the clean effluent and concentrate were extracted during the trials. They fluctuated between 2.7 and 3.1 L (6.3% STD) and 4.3 and 5.0 L (5.8% STD). In the chemical measurement as well, error measurements were always lower than 10% (Table 4.4). The experiment errors were on the same magnitude with the separation efficiency among series. Consequently, it is possible to say that neither cellulose or EPS addition improved the separation efficiency of the flotation column test and it was not observed any significant size enlargement in the flocculation process.

Nevertheless, some more reflections can be discussed. In the blank experiment, most of TSS values were lower than the cellulose and EPS runs, apart for the $C_{conc,17\ min}$, but the removal efficiency results showed a slightly different behaviour (Figure 4.6). Moreover, it is interesting to notice how the foam thickness and concentrations increased when flocculants were dosed blank (Table 4.4). To explain the different behaviour of these results, the following explanation can be considered. The higher efficiency in $C_{cl.eff,17\ min}$ and $C_{conc,17\ min}$ and in the EPS series might imply a better flotation ability of the agglomerates as well as a better foam formation. After the closure of the inlet valve, the turbulence in the column decreased, allowing the floating aggregates to rise to the surface and forming the foam whereas denser agglomerates to settle down, both according to Stoke's Law (Equation 2). Then, for the EPS series the minor presence of suspended particles in $C_{cl.eff,17\ min}$ can be interpreted as the restrain to settleability. Aligned with the SVI results, this result was expected (Table 4.1).

The higher removal efficiency in the $C_{conc,17\ min}$ both for the EPS and cellulose samples can be explained by the denser foam concentration (Table 4.4, Table 4.5). Foam formation in the column was not measured over time, but some theory can help to understand this phenomenon. When the influent valve is closed, laminar conditions are recreated and floating aggregates can travel to the surface forming the foam layer. However, in the experiments, foam formation was observed during the injection of the influent, implying that foam can develop also in contact zone simulation. In conclusion, the EPS addition seemed to hinder the settling velocity of the aggregates and promote the foam formation. It is not possible to asses if EPS increased the foam formation during the turbulent or laminar condition increasing the up-rising velocities of the aggregates or enhancing the foam formation during influent injection, but it is possible to say that $C_{conc,17\ min}$ and the foam concentration are inversely correlated. The graphs below try to asses a correlation with the above mentioned explanations. Although the number of data are not

statistically sufficient, the measured R-squared values were significantly high (Figure 5.1,Figure 5.2).

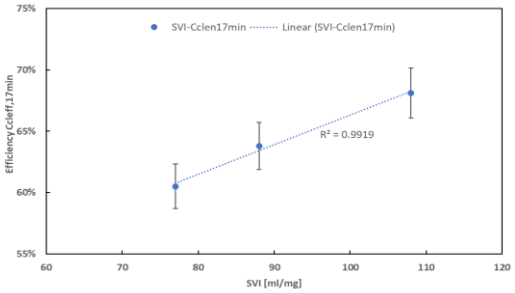

Figure 5.1 Correlation between removal efficiency of $C_{cl.eff,17\,min}$ and SVI test

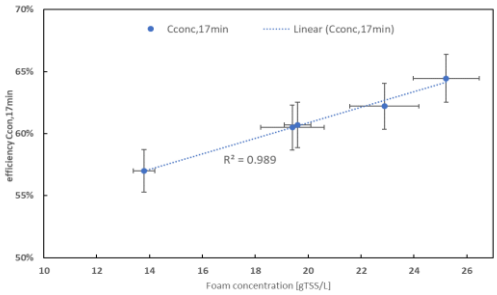

Figure 5.2 Correlation between removal efficiency of $C_{conc,17\,min}$ and foam concentration

Another important consideration that should be discussed is related to the collection and composition of the foam. During the experiment, it was measured the foam layer thickness and then it was extracted some sample. Then, assuming the layer homogeneous and uniformly distributed over height and area, it was estimated the TSS load in the foam layer (Table 4.4). When compared with the total incoming sludge, these values can give also an idea of the particles' separation efficiency in the experiments (40%, 65%, 82% respectively for blank, cellulose and EPS series). These percentages were expected to be to the removal efficiency obtained in Figure 4.6, whereas they decidedly diverged. As a matter of fact, previous assumptions can not be confirmed. Furthermore, this result raises some issues, as for the jar test experiment, about the collection of the foam, this time performed with a spoon. Moreover, it might be a possibility that the increase of the foam was provoked by the flotation of EPS and cellulose itself and not increase of the anaerobic sludge. Thus, for future research, this aspect should be better analysed. A more accurate collection of the foam might help to determine as well as verify the removal efficiency of the flotation column test.

Also for these experiments, the PSD analysis gave results with a high standard deviation, so any clear comparison is unreliable. Nonetheless, EPS series were characterized by a particular frequency of small particles that they were not noticed in the other solutions and in the jar test measurements (Figure 4.4, Figure 4.8). This result can be attributed to an error measurement, as, especially small particles of a PSD distribution measurement are less accurate. However, concentrate samples were characterized by a more pronounced distribution difference (Figure 4.8.c,f). Mainly two possible explanations were proposed. In the EPS series, concentrate samples were influenced by EPS particles size distribution (Appendix). Thus, EPS did not efficiently bound to the flocs and remained in the upper zone of the column, without forming a foam. Secondly, the EPS addition, due to the change of zeta potential and the extension of the diffuse layer, provoked a floc breakage mechanism which induced to a reduction of the particle size distribution (section 5.1). It was not possible to prove these phenomena but, in the end, this phenomena did not affect the removal efficiency of the two series (Figure 4.6).

In conclusion, the analysis of the particle distribution with the Microtac instrument was not sufficient to add any relevant result on the flocculation process because of the high standard deviation. For the future researches, when using coagulated digested sludge Microtac could be used to assess only qualitatively the particle size distribution. Therefore, it is suggested to apply a more accurate Fiji analysis, even though they are more time demanding

5.4 Comparison with previous studies

For anaerobic digested sludge, pressure was found the only DAF critical parameter with a statistical significance (Guleria, 2019). Temperature and TSS load were other relevant parameters, though it was not found a strong statistical evidence. These three parameters influence the air-solid ratio which is the main parameter controlling the DAF removal (Chapter 2.3.1). A direct measure of the A/S ratio is difficult to assess and control, but it can be calculated successively to validate the consistency of experiments.

Guleria obtained a solid removal efficiency around 85-90% with a standard deviation of 6%. In this report, solid removal was measured differently, based on the final mass balance; not as mentioned in chapter 3.5. Based on Guleria's method, the calculated removal efficiency becomes 78%, 78% and 75% respectively for the blank, EPS and cellulose solutions. The outcome of this method does not change the global conclusion of these experiments, in fact any variance between the runs is appreciable. However, it emerges a 5-10% difference with Guleria's experiment. In this report, temperature was not precisely monitored, but it is reasonable to assume it around 20°C. Guleria worked in a different range of temperature, between 25 and 35 °C. Temperature has a negative effect on the A/S ratio as it reduces the air solubility (Appendix A). Thus, the lower temperature should have even improved the solid separation. Within the two studies, the average TSS load was similar, around 18 gTSS per experiment, with a standard deviation below 5%(Table 4.4; Guleria, 2019). In conclusion, it results difficult to motivate valid reasons for the difference in the removal efficiency. At this regard, it is important to highlight an aspect of the experiment set-up. Pressure, temperature and TSS load are previously measured and controlled parameters determining the A/S ratio. Nonetheless, white water flow is measured backwards, based on the effluents of the and the added volume in the column (Appendix D). A direct measure of the added white water volume would improve the accuracy of the calculated A/S ratio. Meanwhile, the addition of a control flow valve in the pressurized water line would improve the regularity of the white water flow and estimate a reasonable pressure drop. In the actual condition, it is difficult to regulate the white water line with the needle valve.

Finally, it can be stated that, for Harnashpolder's sludge, DAF efficiency is mainly influenced by physical parameters. Thus, a sensitivity analysis of the influencing parameter of the A/S ratio should be assessed in order to optimize the removal efficiency of the DAF.

6 Conclusion

This study investigated the effects of EPS addition in a solution prepared with digested sludge and tap water in order to enhance the separation efficiency in a DAF system. The digested sludge was collected and sieved from the Harnashpolder's wastewater facility and sieved. Total suspended solids and other relevant chemical parameters as VSS, NTU, COD were measured to analyse the separation performance. Furthermore, the morphology of the sludge was studied through a particle size distribution analysis (Microtac, Bluewave). Two types of experiments were proposed to verify whether the EPS addition enhanced flocculation and flotation of suspended particles.

The jar test experiment showed that the EPS addition affected the settleability of the sludge and the foam formation after the dissolution of Alka seltzer. SVI_{10min} and SVI_{30min} of EPS series were 34,5% and 20,0% higher than the blank solution and 62,8% and 36% higher than the cellulose runs. With the EPS addition, it was collected a foam 1.78 times more concentrated than the blank solution. Although the high standard deviation, a gradual increase in the volume particle size distribution is appreciable after the dosage of EPS and cellulose, varying from 60 to 70 µm. In the end, from the jar test experiment the chosen EPS dose to use in the flotation column experiment corresponded to 800 mgEPS/L.

With the EPS addition the solid-liquid separation remained around 65%. Thus the effluent quality in the flotation experiment did not improve compared to the blank condition. Apart from the foam, for all other extracted samples, the separation efficiency varied between 57-69% samples. From the EPS and cellulose series, foam samples were 1.75 and 1.41 times more concentrated than the blank solution, even though some constraints emerged because of the collection method with a spoon. Towards the end of the experiment, in the extracted samples $C_{conc,17}$ and $C_{cl.eff,17}$, a better removal efficiency was obtained within the EPS series. Moreover, a good correlation is present between these concentrations and the foam concentration (R^2=0.989). Despite the error of the Microtac instrument (30%), the particle size distribution were characterized by a frequency of smaller particles, not present in the other solutions. Two possible reasons were proposed to explain this behaviour. For the flotation column test the EPS dose might have enhanced the breakage of the flocs, or the EPS did not sufficiently bind with the sludge.

In conclusion, the use of cellulose or EPS to enhance the solid-liquid separation of the sludge did not turn successful. The application of Harnashpolder's sludge negatively affected the flocculation process with EPS because it was already coagulated during the digestion process. At the same time, the EPS composition was not assessed and might have strongly influenced the final outcome of the experiment. A comparison with a previous study evidenced a little difference in the removal efficiency. This aspect suggested that, for digested anaerobic sludge, physical parameters are the most relevant in the DAF removal. For further researches, different types of sludge and a broader range of EPS doses should be analysed to assess the potential improvement of a DAF system. In particular, enlargement of smallest particles should be studied more rigorously with microscopical and zeta potential analysis. Furthermore, a more precise measurement of the white water flow and foam collection would improve the result accuracy.

7 Recommendations

These results demonstrated that the application of cellulose or EPS did not improve the solid-liquid separation of a down-scale DAF system when anaerobic sludge was used. Further researches are recommended to better understand the possible application of EPS as flocculant as well as to increase the separation efficiency when anaerobic sludge is treated in the DAF system.

More detailed analysis on the type of EPS should be achieved to understand its chemical composition (proteins, carbohydrates and humic substances) and the fraction of TB-EPS, LB-EPS and SL-EPS.

Different types of sludge or solutions with high suspended solids concentrations should be studied as the anaerobic sludge seemed disinclined to flocculation.

A series of experimental adjustments should be forward to increase the accuracy of the jar and flotation column test. It should be studied a more accurate foam collection method, as foam results very distant from homogeneity. For the jar test, the use air microbubbles instead of CO_2 would get the two experiments more comparable. For the flotation column test, a better flow regulation in the influent or in one of the effluents will reduce the error and the difficulties of trials.

Finally, the zeta potential measurements, both for the influent and EPS solutions would help the definition of the optimal flocculant dose. Additionally, it should be found another way of analysis of the particle size distribution, especially when using already flocculated sludge as Bluewave software did not give sufficiently accurate results.

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A. Appendix A

In this appendix the main phenomena related to the air pressurisation in the DAF process are shortly summarized.

Gas solubility is governed by Henry's Law (). The concentration in the water of a gas is directly proportionated to the Henry's constant and the partial pressure of the compound in the gaseous solution.

$$C_g = HX_gP$$

Equation 11 Henry's Law (1803)

In the equation, C_g is the gas concentration in the water (kg/mol), H is the Henry's constant (kg/mol/kPa), X_gP is the partial pressure of the gas in the air.

Temperature and salinity of the water solution are important factor that influence the values of the Henry constant. In the table below, oxygen saturation concentrations are reported in mg/L with different temperature and salinity and 1 atm. Table A.1 is to give as an demonstrative example of the variability of the Herny's Law. In practise, the efficiency factor *f* (section 2.3) has to be take into consideration. Different type of saturator and retention time in the saturator vessel determine the its value and , standardly, it fluctuates between 60-90%.

Table A.1 Oxygen saturation concentration in mg/L

Temp	**Solubility [ppt]**				
[°C]	**10**	**20**	**30**	**40**	**50**
0.0	14.6	13.6	12.7	11.9	11.1
20.0	9.1	8.6	8.1	7.6	7.2
25.0	8.2	7.8	7.4	7.4	6.6

B. Appendix B

In the table below the mean values the tap water from the Water lab at TUDelft.

Table B.1 Water matrix of the Water Lab tap water

Productielocatie Kralingen - Gemiddelde drinkwaterkwaliteit per maand en voortschrijdend jaar

Parameter	Eenheid	Wettelijke norm minimum	Wettelijke norm maximum	SEP 2018	OKT 2018	NOV 2018	DEC 2018	JAN 2019	FEB 2019	MRT 2019	APR 2019	MEI 2019	JUN 2019	JUL 2019	AUG 2019	Gemiddeld
Temperatuur	°C	-	25	19,9	17,1	11,9	8	6,1	6,2	7,6	10,4	13,5	17,2	20,8	21,4	13,5
Zuurstof	mg/l O2	2	-	7,2	7,9	9,1	10,5	-	11,4	10,8	10,2	8,7	7,7	6,4	5,6	8,8
Troebeling	FTE	-	1	0,03	0,03	0,03	0,01	0,02	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03
Geur	-	-	geen afw*	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	-
Smaak	-	-	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	geen afw.	-
Zuurgraad	pH	7	9,5	8,1	8,02	7,96	7,9	7,94	7,9	7,9	8,0	8,02	8,1	8,11	8,1	8
Verzadigingsindex	SI	-0,2	-	0,32	0,26	0,23	0,12	0,17	0,09	0,05	0,09	0,25	0,29	0,31	0,33	0,2
Geleidingsvermogen 20°C	mS/m	-	125	46	47	49	50	50	49	48	46	46	45	45	46	47
Waterstofcarbonaat	mg/l HCO3	60	-	140	140	140	130	130	120	110	110	130	120	120	130	130
Chloride	mg/l Cl	-	150	61,7	63,5	67,4	72	70,3	72,7	70,8	66,3	58,8	57,2	56,6	57,1	64,6
Sulfaat	mg/l SO4	-	150	49	49	49	52	54	57	57	52	47	48	46	48	51
Natrium	mg/l Na	-	150	40	41	46	47	45	48	46	40	42	40	41	40	43
Calcium	mg/l Ca	-	-	44	46	50	47	46	47	43	44	48	45	46	46	46
Magnesium	mg/l Mg	-	-	6,9	7,3	7	7,9	7,8	8	7,5	6,7	6,6	6,4	6,7	6,7	7,1
Totale hardheid	mmol/l	1	-	1,39	1,45	1,53	1,5	1,48	1,51	1,38	1,37	1,46	1,38	1,42	1,41	1,43
Ammonium	mg/l NH4	-	0,2	<0,03	<0,03	<0,03	<0,03	<0,03	<0,03	<0,03	<0,03	<0,06	<0,05	<0,05	<0,05	<0,05
Nitraat	mg/l NO3	-	50	7,2	5,7	5,7	4,7	5,7	6,8	9	11	13	12	12	9,7	8,6
IJzer	µg/l Fe	-	200	<5	<5	9,8	<5	2,4	3,6	2,4	3,4	2,1	1,9	1,3	1,6	<5
Aluminium	µg/l Al	-	200	1,7	1,9	3,9	<1,2	2,5	<1,2	2	1,2	1,4	2,7	2	3,3	2
Fluoride	mg/l F	-	1	0,15	0,18	0,2	0,2	0,2	0,2	0,17	0,19	0,15	0,17	0,16	0,19	0,18
Kleurintensiteit (Pt/Co-schaal)	mg/l Pt	-	20	<2	<2	2	<2	<2	2	2	2	3	<2	<2	<2	<2
Trihalomethanen (som)	µg/l	-	25	2,2	2,9	1,5	0,96	0,76	0,73	1,3	2,4	2,2	2	1,8	1,9	1,8
Bacteriën van de coligroep	KVE/100 ml	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Escherichia coli	KVE/100 ml	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Enterococcen	KVE/100 ml	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clostridium perf. (incl sporen)	KVE/100 ml	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

*geen afw. = geen afwijking

NB. In verband met de doorloop- en analysetijden in ons laboratorium lopen de gegevens doorgaans 1 tot 2 maanden achter.

C. Appendix C

The tables below gather all the results from the Bluewave Microtac software. In this case, the measurements reports the values of the trial with the digested sludge (34 gTSS/L).

Table C.1 Summary of data, percentile and peaks of the volume distribution

Summary data		Percentile		Peaks	
		%Tile	Size(um)		
MV(um):	60.17	95	157.8	Dia(um)	46.02
MN(um):	18.84	90	117.8	Volume %	100
MA(um):	38.04	80	82.77	Width (um)	69.17
CS:	0.158	70	65.55		
SD:	34.59	60	54.46		
		50	46.02		
Mz:	54.46	40	38.97		
si:	38.76	30	32.63		
Ski:	0.472	20	26.56		
Kg:	1.337	10	20.15		

Table C.2 Volume PSD distribution

Volume PSD distribution					
Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass
2000	0	100	5.5	0	0
1674	0	100	4.63	0	0
1408	0	100	3.89	0	0
1184	0	100	3.27	0	0
995.6	0	100	2.75	0	0
837.2	0	100	2.313	0	0
704	0	100	1.945	0	0
592	0	100	1.635	0	0
497.8	0	100	1.375	0	0
418.6	0	100	1.156	0	0
352	0.41	100	0.972	0	0
296	0.66	99.59	0.818	0	0
248.9	1.04	98.93	0.688	0	0
209.3	1.57	97.89	0.578	0	0
176	2.21	96.32	0.486	0	0
148	2.97	94.11	0.409	0	0
124.5	3.9	91.14	0.344	0	0
104.7	5.08	87.24	0.289	0	0
88	6.56	82.16	0.243	0	0
74	8.23	75.6	0.204	0	0
62.23	9.7	67.37	0.172	0	0
52.33	10.37	57.67	0.145	0	0
44	10.32	47.3	0.122	0	0
37	9.46	36.98	0.102	0	0
31.11	8.18	27.52	0.086	0	0
26.16	6.63	19.34	0.072	0	0
22	4.96	12.71	0.061	0	0
18.5	3.37	7.75	0.051	0	0
15.56	2.09	4.38	0.043	0	0
13.08	1.21	2.29	0.036	0	0
11	0.69	1.08	0.03	0	0
9.25	0.39	0.39	0.0255	0	0
7.78	0	0	0.0215	0	0
6.54	0	0	0.0181	0	0

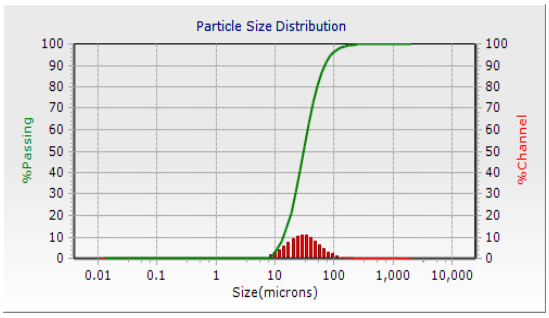

Figure C.1 Volume particule size distribution example

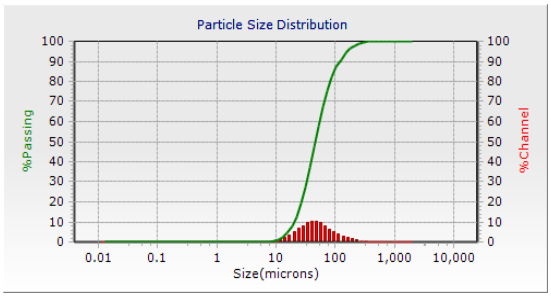

Figure C.2 Area particle size distribution example

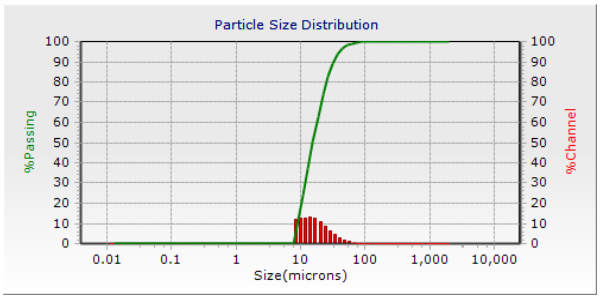

Figure C.3 Number particle size distribution example

D. Appendix D

In this appendix, it is reported a complete example of a flotation column test. This experiment was performed with EPS_3 dose (800 mgEPS/L).

Table D.1 Sample collection and weight.

Name	Weight	Tara	Sample [mL]	Volume [g]
Total sludge	5007	-	342.63	**4664.37**
Total clean effluent	2852	185.6	-	**2666.4**
Residual sludge	833.6	182.4		**651.2**
Total concentrate	3894.7	189.3		**3705.4**
Total supernatant (foam)			211.49	211.49
17 min clean effluent			337.25	337.25
17 min dirty effluent			341	341
Total white water introduced				**3248.37**

Table D.2 Mass balance and efficiency

	TSS g/L	STD g/L	STD %		T=20 min	T=0-10 min	T=15-20 min
Clean Effluent	0.15	0.00	1.1%	**Total TSS inlet (g)**	17.39	13.37	17.4
Concentrate	0.28	0.00	0.0%	**Total TSS diluted (g/L)**	0.63	0.41	0.73
Sludge	4.47	0.04	1.0%	**Efficiency**	77.2%	65.3%	60.9%
Foam	13.22	0.32	2.4%				

Table D.3 Chemical measurement results (TSS,VSS,COD,NTU)

		filter+metal g	Vol mL	After incub. g	TSS g/L	COD mgO2/L	NTU	OVEN 500 C	VSS g/l
clean Effluent	1	2.5367	60	2.5471	0.173	226	72.3	2.5388	0.138
	2	2.5504	60	2.561	0.177	229	75.7	2.551	0.16
	3	2.6122	60	2.622	0.163	226	70.6	2.6128	0.153
	Average	2.5664	60	2.5767	**0.17**	**227**	**72.8667**	**2.5675**	**0.1528**
	STD	0.0402	1.6%	0.0398	**0.01**	**0.76%**	**3.56%**	**1.55%**	**9.28%**
Concentrate	1	2.5297	50	2.5431	0.268	432	135	2.5301	0.262
	2	2.5734	50	2.5866	0.264	431	139	2.5738	0.256
	3	2.5247	50	2.5384	0.274	442	139	2.5258	0.252
	Average	2.5426	50	2.5560	0.27	435	137.6667	2.5432	0.2560
	STD	0.0076	0.3%	0.0266	0.01	1.40%	1.68%	1.04%	1.56%
Sludge	1	2.5411	10	2.5868	4.700	5469	-	2.5518	3.532
	2	2.5346	10	2.5802	4.720	5239	-	2.5455	3.472
	3	2.5259	10	2.5711	4.730	5309	-	2.5362	3.493
	Average	2.5339	10	2.5794	4.72	5339	-	2.5445	3.486
	STD	0.0076	0.3%	0.0079	0.02	2.21%	-	0.31%	0.44%
Foam	1	2.5587	10	2.7853	22.660	24020	-	2.6184	16.691
	2	2.5394	10	2.7684	22.900	24140	-	2.5996	16.882
	3	2.5614	10	2.7923	23.090	23510	-	2.6227	16.966
	Average	2.5532	10	2.7820	22.88	23890	-	2.6136	16.8433
	STD	0.0120	0.5%	0.0123	0.22	1.40%		0.47%	0.82%
remaining sludge	1	2.5634	10	2.6162	5.280	6153	-	2.5788	3.74
	2	2.5366	10	2.5933	5.670	5963	-	2.5551	3.82
	3	2.5479	10	2.6037	5.580	6070	-	2.566	3.77
	Average	2.5493	10	2.6044	5.51	6062	-	2.5666	3.7767
	STD	0.0135	0.5%	0.0115	0.20	1.57%	-	0.46%	1.07%
Clean effluent 17	1	2.5448	60	2.56	0.253	414	130	2.5456	0.24
	2	2.6034	60	2.619	0.260	415	129	2.6052	0.23
	3	2.5406	60	2.5567	0.268	426	127	2.5523	0.073
	Average	2.5629	60	2.5786	0.26	418	128	2.5677	0.181
	STD	0.0351	1.4%	0.0351	0.01	1.59%	1.19%	1.27%	51.61%
Concentrate 17	1	2.5655	50	2.5799	0.288	456	138	2.5661	0.276
	2	2.5607	50	2.5781	0.348	441	131	2.5646	0.274
	3	2.5877	50	2.6015	0.276	459	131	2.5885	0.268
	Average	2.5713	50	2.5865	0.30	452	133.	2.5731	0.2687
	STD	0.0144	0.6%	0.0130	0.04	2.13%	3.03%	0.52%	3.01%

Table D.4 CSTR data summary

Check of the CSTR		
Volume added	7.26	L
Concentration of TSS added	2.67	g/l
Q inflow rate	0.54	L/min
Cin	2.67	g/l
Q flow out (clean effluent	0.53	L/min
Cout	0.17	g/l
Q flow out 2 (conc)	0.88	L/min
Cout	0.27	g/L

Table D.5 Dynamic CSTR simulation of the experiment

T (min)	Concentration (gTSS/L)	Inflow (mL/min)	Outflow (mL/min)	Volume (L)	T (min)	Concentration (gTSS/L)	Inflow (mL/min)	Outflow (mL/min)	Volume (L)
0.0	0.000	0.269	0.000	20.00	**10.0**	0.632	0.269	0.267	22.45
0.5	0.035	0.269	0.000	20.27	**10.5**	0.664	0.269	0.000	22.71
1.0	0.070	0.269	0.000	20.54	**11.0**	0.695	0.269	0.000	22.98
1.5	0.105	0.269	0.000	20.81	**11.5**	0.726	0.269	0.000	23.25
2.0	0.139	0.269	0.000	21.08	**12.0**	0.756	0.269	0.000	23.52
2.5	0.172	0.269	0.000	21.34	**12.5**	0.787	0.269	0.000	23.79
3.0	0.206	0.269	0.000	21.61	**13.0**	0.816	0.269	0.000	24.06
3.5	0.238	0.269	0.000	21.88	**13.5**	0.846	0.269	0.000	24.33
4.0	0.271	0.269	0.000	22.15	**14.0**	0.846	0.000	0.000	24.33
4.5	0.303	0.269	0.000	22.42	**14.5**	0.846	0.000	0.000	24.33
5.0	0.333	0.269	0.267	22.42	**15.0**	0.841	0.000	0.438	23.89
5.5	0.363	0.269	0.267	22.43	**15.5**	0.836	0.000	0.438	23.45
6.0	0.393	0.269	0.267	22.43	**16.0**	0.831	0.000	0.438	23.01
6.5	0.423	0.269	0.267	22.43	**16.5**	0.826	0.000	0.438	22.58
7.0	0.453	0.269	0.267	22.43	**17.0**	0.820	0.000	0.438	22.14
7.5	0.483	0.269	0.267	22.43	**17.5**	0.815	0.000	0.438	21.70
8.0	0.513	0.269	0.267	22.44	**18.0**	0.809	0.000	0.438	21.26
8.5	0.543	0.269	0.267	22.44	**18.5**	0.804	0.000	0.438	20.82
9.0	0.572	0.269	0.267	22.44	**19.0**	0.798	0.000	0.438	20.38
9.5	0.602	0.269	0.267	22.44	**19.5**	0.792	0.000	0.438	19.94

E. Appendix E

In the flotation column test results, measurements of NTU and COD were performed to analyse whether it was possible to find any correlation with these two units that are faster to complete.

Firstly is important to mention that the COD of the diluted sludge changed over the time and it was not constant between the trials, varying between 4000-7000 mgO_2/L (Table 4.4). Moreover, Moreover the addition of EPS influenced the COD of the solution. In conclusion it was not found any correlation between COD and TSS as shown in the picture below (R^2 = 0.248). To create this graph, the average data of the samples were applied ($C_{cl,eff}$, $C_{conc.}$, $C_{cl,eff,17}$, $C_{conc.17}$).

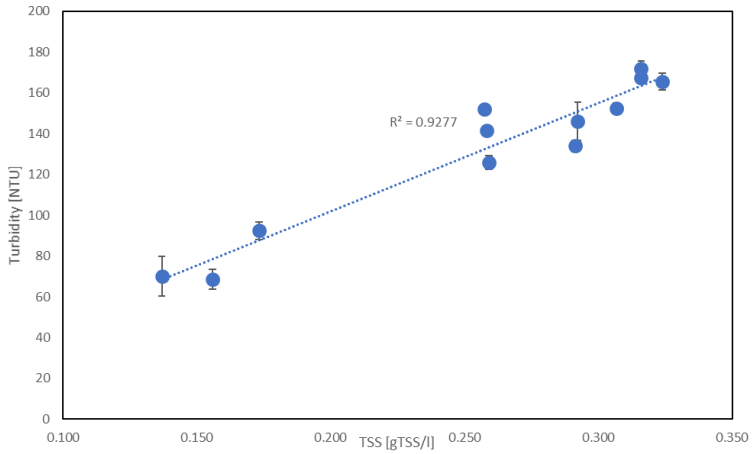

Figure E.1 Correlation between COD and TSS

On the opposite, in the flotation column experiment it was found good correlation (R^2= 0.928) between the turbidity and the suspend solids as depicted in the figure below. A for the previous graph, the average data of the samples were applied ($C_{cl,eff}$, $C_{conc.}$, $C_{cl,eff,17}$, $C_{conc.17}$). Even though it was calculated a good correlation between the two parameters, it seemed not sufficiently accurate its application for the assessment of the separation efficiency of the particles.

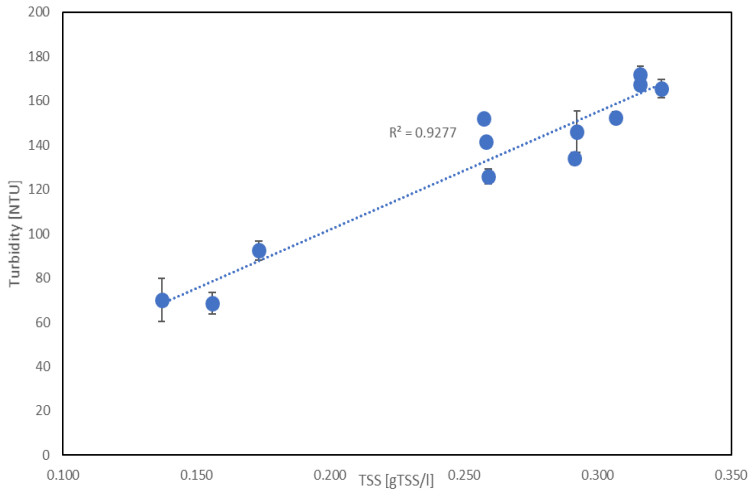

Figure E.2 Correlation between NTU and TSS

F. Appendix F

The tables below gathers all the results from the Bluewave Microtac software. In this case, the measurements report the values of the trial for the solution of EPS with tap water (800 mgEPS/L).

Table F.1Summary data of PSD distribution from water+EPS distribution

Summary data		Percentile		Peaks	
		%Tile	Size(um)		
MV(um):	22.98	95	35.05	Dia(um)	16.3
MN(um):	10.5	90	29.52	Volume %	100
MA(um):	17.97	80	24.15	Width (um)	16.55
CS:	0.334	70	20.9		
SD:	8.27	60	18.41		
		50	16.30		
Mz:	21.94	40	14.33		
si:	10.49	30	12.36		
Ski:	0.2758	20	10.25		
Kg:	1.159	10	7.82		

Table F.2 Area PSD distribution

Area PSD distribution					
Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass
2000	0	100	5.5	1.92	2.89
1674	0	100	4.63	0.97	0.97
1408	0	100	3.89	0	0
1184	0	100	3.27	0	0
995.6	0	100	2.75	0	0
837.2	0	100	2.313	0	0
704	0	100	1.945	0	0
592	0	100	1.635	0	0
497.8	0	100	1.375	0	0
418.6	0	100	1.156	0	0
352	0	100	0.972	0	0
296	0	100	0.818	0	0
248.9	0	100	0.688	0	0
209.3	0	100	0.578	0	0
176	0	100	0.486	0	0
148	0	100	0.409	0	0
124.5	0	100	0.344	0	0
104.7	0.02	100	0.289	0	0
88	0.11	99.98	0.243	0	0
74	0.22	99.87	0.204	0	0
62.23	0.46	99.65	0.172	0	0
52.33	1	99.19	0.145	0	0
44	2.13	98.19	0.122	0	0
37	4.18	96.06	0.102	0	0
31.11	7.27	91.88	0.086	0	0
26.16	10.8	84.61	0.072	0	0
22	13.41	73.81	0.061	0	0
18.5	14.13	60.4	0.051	0	0
15.56	12.64	46.27	0.043	0	0
13.08	10.2	33.63	0.036	0	0
11	7.79	23.43	0.03	0	0
9.25	5.78	15.64	0.0255	0	0
7.78	4.13	9.86	0.0215	0	0
6.54	2.84	5.73	0.0181	0	0

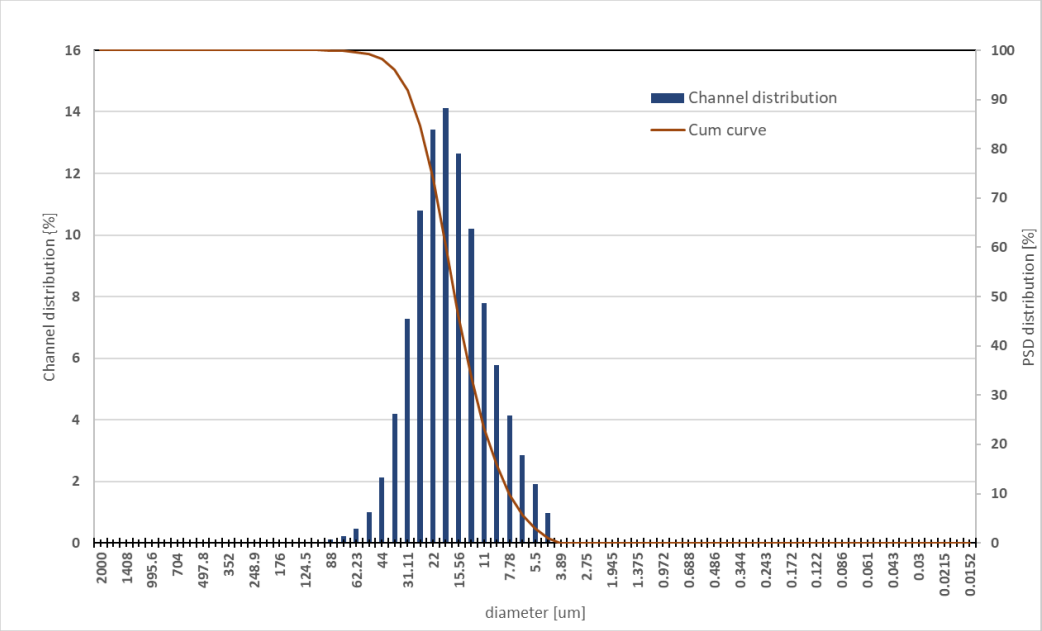

Figure F.1 PSD results for EPS in water (800 mgEPS/L)

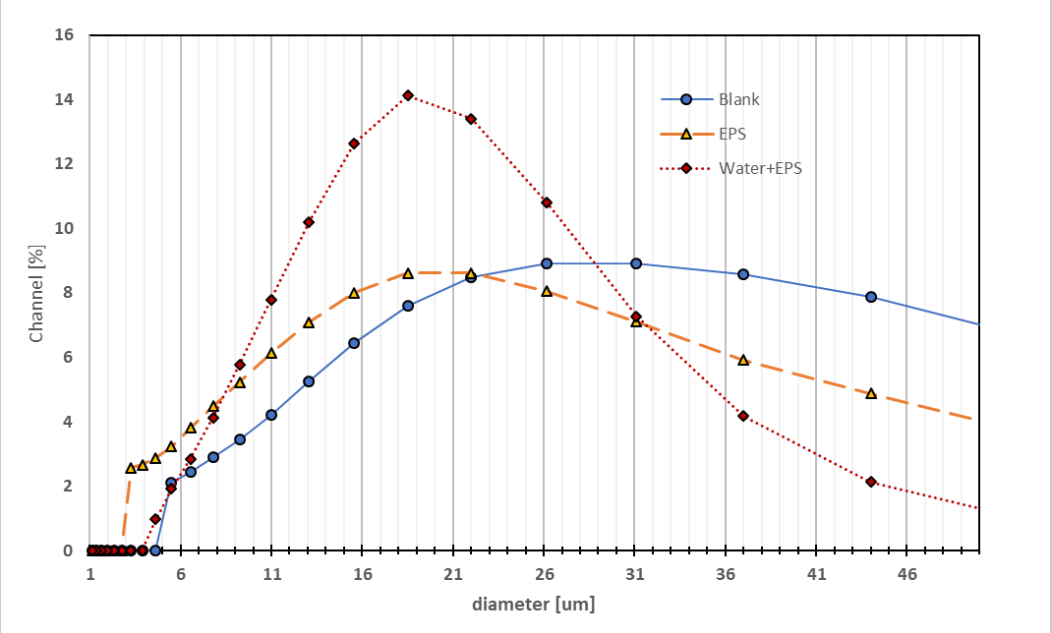

Figure F.2 Concentrate sample PSD channel distribution for blank, EPS and Water+EPS solution.