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Electro-dewatering of wastewater sludge: influence of water distribution in sewage sludge

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Abstract

This work the influence of conditioning, mechanical dewatering and electro-dewatering (EDW) on the types of water in sludge samples from five different wastewater treatment plants (WWTPs) was evaluated. The sludge samples have been taken after different stabilisation methods and mechanical dewatering techniques. First, thickened sludge samples have been characterized in the lab, in terms of dry solid and volatile solid content, pH, conductivity, CST, zeta potential and polyelectrolyte dosage. Then, the influence of potential values, cake thickness and duration of the tests on EDW of two anaerobically and aerobically stabilised sludge samples was studied. For the EDW tests two types of samples have been used: (i) thickened conditioned sludge (TC), conditioned in the lab with the selected polyelectrolyte dosage, and (ii) mechanically dewatered sludge (MD). The EDW tests allowed the dewatering of the MD samples from 16-18% dry solid (DS) content up to 47%. It has been shown that the operating conditions have considerable influence on the efficiency of the EDW process, both on TC and MD sludge. Moreover, different mechanical dewatering techniques, including centrifugation, vacuum filtration and compression in the lab-scale device have been studied.

Finally, by means of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), the influence of conditioning, mechanical dewatering and EDW on water content, its distribution among free and bound water and on the bond strength between water and particles has been studied. The effect of polyelectrolyte on free and bound water content depends on types of polymer and its dosage. Application of pressure driven electro-dewatering to 15-mm thick sludge samples under 25 V electric potential for 35 min duration showed the best compromise between high final DS content and specific energy consumption in both TC and MD sludge samples (from 100 to 220 Wh/kg of water removed). In general, aerobically stabilized sludge allows more efficient removal of water content than anaerobically digested sludge.

Sommario

Questo lavoro ha valutato l'influenza del condizionamento, della disidratazione meccanica e della elettro-disidratazione (EDW) sui tipi di acqua in campioni di fanghi provenienti da cinque diversi impianti di trattamento delle acque reflue (WWTP). I campioni di fanghi sono stati prelevati dopo aver subito diversi processi di stabilizzazione e diverse tecniche di disidratazione meccanica. Innanzitutto, i campioni di fango ispessito sono stati caratterizzati in laboratorio, in termini di contenuto di solidi totali e contenuto di solidi volatili, pH, conducibilità, CST, potenziale zeta e dosaggio di polielettrolita. Successivamente, è stata studiata l'influenza dei valori di potenziale elettrico, dello spessore della torta di fango e della durata dei test sul processo EDW di due campioni di fango stabilizzati anaerobicamente e aerobicamente. Per i test EDW sono stati utilizzati due tipi di campioni: (i) fango ispessito condizionato (TC), condizionato in laboratorio con il dosaggio di polielettrolita selezionato e (ii) fango disidratato meccanicamente (MD). I test EDW, partendo da un contenuto di solido secco (DS) iniziale del 16-18%, hanno consentito la disidratazione dei campioni MD fino al 47%. È stato dimostrato che le condizioni operative hanno una notevole influenza sull'efficienza del processo EDW, sia su fanghi TC che MD. Inoltre, sono state studiate diverse tecniche di disidratazione meccanica, tra cui la centrifugazione, la filtrazione sottovuoto e la compressione nel dispositivo su scala di laboratorio.

Infine, mediante la calorimetria differenziale a scansione (DSC) e l'analisi termogravimetrica (TGA), è stata studiata l'influenza del condizionamento, della disidratazione meccanica e del processo EDW sul contenuto d'acqua, la sua distribuzione tra acqua libera e legata e la forza di legame tra acqua e particelle.

L'effetto del polielettrolita sul contenuto d'acqua libera e legata dipende dal tipo di polimero e dal suo dosaggio. L'applicazione del processo di disidratazione elettro-assistita su campioni di fango TC e MD di 15 mm di spessore con potenziale elettrico di 25 V per una durata di 35 minuti ha mostrato il miglior *compromesso tra elevato contenuto finale di DS e consumo specifico di energia (da 100 a 220 Wh/kg di acqua rimossa). In generale, il fango stabilizzato aerobicamente consente una più efficiente rimozione del contenuto d'acqua rispetto al fango digerito anaerobicamente.*

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List of Abbreviations

BW	Bound water
C.C.	Constant current
CFG	Centrifugation
CST	Capillary suction time
C.V.	Constant voltage
DC	Direct current
DS	Dry solid
DSC	Differential scanning calorimetry
DSp	Dry solid of pressure-driven phase
DTA	Differential thermal analysis
DTG	Differential thermogravimetry
EDW	Electro-dewatering
EPS	Extracellular polymeric substances
FIL	Filtration
FW	Free water
LB-EPS	Loosely bound EPS
MCFG	Multiple centrifugation
MD	Mechanical dewatering
PRS	Pressure
PTFE	Polytetrafluoroethylene
PTT	Poly-trimethylene terephthalate
SEC	Specific energy consumption
SRT	Solid retention time
TC	Thickened conditioned sludge
TGA	Thermogravimetric analysis
MMO	Mixed Metal Oxide
TU	Thickened unconditioned sludge
VS	Volatile solid
W	Water content
WWTP	Wastewater treatment plant

1. Introduction

1.1 Background

Treatment and disposal of sewage sludge are complex procedures for municipalities and industries since it contains a large amount of water which is difficult to remove by using only mechanical dewatering (MD) techniques. Indeed, the presence of large amount of water in sludge leads to an increase in the cost of transport and disposal. The selection of an efficient sludge dewatering technique is a crucial part to get a cost-effectiveness process. Among the conventional dewatering processes (e.g. gravitational settling, mechanical dewatering and thermal drying), mechanical dewatering is widely used due to the lower consumption of electric energy and/or the higher dry solid (DS) content in sludge. Compared to mechanical dewatering processes, electro-dewatering (EDW), which combines conventional dewatering technique with electro-kinetic phenomena, is considered an efficient process to improve separation of liquid-solid phases in order to increase the final dry solid content of sludge, by using a significantly lower energy consumption than thermal drying (Mahmoud et al., 2010). The cake thickness, the duration of the EDW test, the initial DS content of sludge and the developed electric current are considered important operating factors that can affect the efficiency of the EDW process.

Different factors such as extracellular polymeric substances (EPS), organic matter, metal ions, microbial population, cake porosity, particle size and water distribution in sludge affect the dewaterability of sludge. According to Zhang and Sun (2012), moisture distribution in sludge is considered a main factor. The different types of water distributed in sludge can be classified depending on the type and intensity of their physical bonding to the solid particles, while, a continuous classification can provide a global information about the moisture distribution in sludge, improving the efficiency evaluation of different dewatering processes. The lack of a physical quantity as an index is still a problem to measure the water content in sludge. A clear picture of moisture distribution in sludge and the force that bind water within the sludge itself can help to improve the dewatering performance. Specifically, an important indicator would be the fraction of water in sludge that tightly bound to the solid particles which is difficult and costly to be removed. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are the two methods used widely to measure the amount of free and bound water distributed in sludge (Guo et al., 2018).

1.2 Aim of the thesis

The aims of the thesis were:

- To investigate the efficiency of the EDW process for various types of sludge, in terms of final DS content and energy consumption, under different operating conditions, such as different initial cake thickness, voltage applied and time duration of the tests.
- To study the influence of conditioning with different polyelectrolyte dosages on the free and bound water content of sludge through DSC and TGA methods.
- To investigate the impact of different mechanical dewatering method on the removal of free and bound water by DSC method.
- To detect the influence of EDW process on different types of water, by measuring water content in sludge before and after the EDW process, through DSC and TGA methods.

- Finally, to establish a relation between sludge characteristic and bound water content in sludge.

1.3 Structure of the thesis

The general outline of this thesis is as follows:

- **Chapter 1** provides a general introduction to the problems associated with sludge disposal and treatment worldwide. It compares different kinds of treatment and the role of moisture distribution on sludge dewaterability. It also describes the goals of the thesis and its structure.
- **Chapter 2** provides a short description of sludge disposal problem in Europe; the emphasis is on mechanical dewatering, electrode-dewatering and different method to analyse water distribution in sludge, especially bound water.
- **Chapter 3** shows the materials and methods used for sludge characterization, EDW experiments and moisture distribution analysis.
- **Chapter 4** discusses the results obtained from the EDW experiments, DSC and TGA methods.
- **Chapter 5** summarizes the main findings of this work and points out the areas of interest for future investigation.

2. State of the art

2.1 The problem of sludge management and disposal in Europe

The amount of sewage sludge, which is discharged from wastewater treatment plants (WWTPs) has increased worldwide (Guo et al., 2018). The increase of the number of WWTPs will further increase the sludge production in the upcoming years. Therefore, it is required to find appropriate techniques to minimize treatment and management costs and, at the same time, to avoid negative impacts on the environment and pursue the recovery of the valuable material content in sludge (Bertanza et al., 2014).

Sewage sludge management is a crucial step in WWTPs since from 20 to 60% of the construction and operating costs of a wastewater treatment plant belong to sludge treatment and disposal (Feng et al., 2014). According to Pellegrini et al. (2016), annual DS production of sewage sludge in Europe is estimated to be about 10 million tons (2007-2011), considering both old and new member states (8.7 and 1.2 million tons, respectively). The amount of money spent on management of the treated sludge is about 1 billion €/year, while more than 150 million €/year is spent on control and handling of sludge digestion (Sánchez et al., 2006).

Moreover, the increased sludge production leads to higher level of contamination, which is a critical point in sludge management.

Different sewage sludge disposal routes include the following:

- Incineration of sludge to reduce its volume, destroying hazardous substances that can be released during incineration, and recovery of energy from the waste.
- Direct land use in agriculture or forestry as a fertilizer.
- Indirect application in agriculture to exploits phosphorus, nitrogen and organic substances to improve the physical and biological properties of the soil.
- Sanitary landfilling to provide environmental protection by the isolation of the waste from its surrounding environment, preventing water contamination and contact with air.

Some factors restricted each disposal routes. For example, landfilling has been decreased in the last decade, since it requires high costs to achieve a high level of isolation and limitation in space (Milieu Ltd. and WRc and RPA, 2010). Furthermore, landfilling leads to uncontrolled biogas production, leachate production and pollutants mobility in the subsoil. The *Landfill Directive* (EC Directive, 1991) enforced the member states to decrease the biodegradable waste disposal level in landfills (around 35% of 1995-levels by 2016) in Europe.

Application of sewage sludge to land as soil amendment or fertilizer is beneficial for the soil. However, it contains many organic compounds and pathogens that can be only partially degraded and killed by conventional treatment and heavy metals that cannot be removed from it. Therefore, the usage of sewage sludge after traditional treatment methods may increase the health risk because of passages of undesirable substances to food-chain (from soil to groundwater or plants) (Hanay et al., 2008). In Europe, the *Sewage Sludge Directive* (SSD, 278/86/EEC) set some regulations (e.g. limited values for seven heavy metals in soil and sludge that is disposed in agriculture) to protect human and environment from the harmful effects of uncontrolled spreading of sewage sludge (Milieu Ltd. and WRc and RPA, 2010). On the other hand, incineration is one of the most common disposal routes in some

European countries due to energy recovery and high volume reduction of sewage sludge. However, it requires high investment costs (Pellegrini et al., 2016).

The sludge management and transportation costs are highly dependent on the moisture content in raw sludge. In the other word, the higher water content in wastewater sludge means greater transportation and disposal costs. To facilitate the use of sludge as a fuel, or as an organic matter for composting and decrease the transportation and disposal costs, it is required to reduce the water content in sludge. To this aim, the dewatering process becomes interesting to mitigate the subsequent costs (Feng et al., 2014; Sharma and Sanghi, 2013).

2.2 Sludge dewatering

The dewatering of sludge is mainly performed to reduce the water content of the sludge because of the following reasons:

- Decrease the transportation and disposal costs;
- Reduce leachate production at the landfill;
- Enhance the handling properties of the sludge;
- Increase the calorific value of the sludge to make it suitable for incineration.

The conventional dewatering techniques such as gravitational settling, mechanical dewatering and thermal drying can thicken and concentrate the dilute suspension of solid particles. The advantage of the thermal drying process is to provide a dehydrated solid product at the cost of high-energy consumption. Among these techniques, mechanical dewatering devices are widely used due to less energy consumption and high solid content compared to thermal drying and gravitational settling, respectively (Mahmoud et al., 2010).

2.2.1 Mechanical dewatering

Mechanical dewatering (MD) techniques such as centrifugation or filtration/compression (belt filter presses, plate filter presses or vacuum filters) are commonly used for dewatering due to their simplicity, versatility and low costs. With mechanical dewatering, the amount of water removed depends on the technique, the sludge characteristics and the water status in sludge. In most of the MD processes, two stages are involved: filter cake formation followed by compression to squeeze more water out from the cake (Sharma and Sanghi, 2013).

Belt-filter press and centrifugation are continuous-feed sludge dewatering processes. In belt-filter presses, sludge is pressed within two moving filter belts close to each other, where three phases are involved. In the initial stage, sludge is fed into the belt press and a significant portion of free water is removed by gravity. Sludge needs to be flocculated to have a better performance in dewatering, since it avoids the blinding of the belts and facilitates the gravity drainage. The initial step is followed by a low-pressure phase and a high-pressure phase in which the sludge is subjected to squeezing and shear forces respectively.

Centrifugation is a process in which centrifugal force is exerted to the feed sludge to increase solid-liquid separation. Polymer conditioning of sludge is needed and can be directly added to the feed line. Polymer dosage depends on the type of sludge.

Sludge DS content is the main parameter used to give an indication on the efficiency of the dewatering process. The final DS content of sludge that can be achieved by belt presses is in the range 15-20% (max 25%) and by filter presses is in the range of 25-30% (max 35%). For centrifugation, a DS content of about 26-30% for anaerobically digested municipal sludge, or 20-25% for pre-thickened biological sludge, is considered as a good dewatering performance (Phuong To et al., 2016), but these figures make the sludge unsuitable for many applications, such as direct incineration. Furthermore, the excess water content of sludge increases the volume and the costs for sewage sludge (e.g. disposal, transport, storage) (Mahmoud et al., 2011b; Olivier et al., 2014).

To improve the dewatering efficiency, the intensification of the mechanical process can be carried out with different techniques, such as:

- Thermal mechanical dewatering
- Electrical mechanical dewatering
- Shear-force assisted mechanical dewatering
- Acoustic mechanical dewatering
- Magnetic mechanical dewatering
- Microwave mechanical dewatering

It is essential to have a proper choice of the combined field which leads to the lower moisture content in the sludge cake, higher product recovery, less energy consumption and environmental cost (Sharma and Sanghi, 2013).

2.3 Electro-dewatering

After mechanical dewatering, sludge cake contains a significant amount of water (around 80%) that is the main obstacle in disposal. Hence, in order to reduce sludge volumes and consequently decrease handling and disposal costs, electric field-assisted dewatering (also called electro-dewatering - EDW) has received considerable attention. Indeed, the EDW process leads to an increase of the final DS content in sludge and avoids filter media blockage, which are common issues in mechanical dewatering. Moreover, despite its high efficiency in terms of DS content, EDW entails lower energy consumption than thermal drying (Mahmoud et al., 2010).

Electro-dewatering consists in the application of an electric field during mechanical dewatering. The electric field can be applied during the mechanical dewatering stages (filtration and compression), or as a pre- or post-treatment of the dewatering process. Applying electrical current to the filter cake generates movement of charged particles and ions towards the electrode of opposite charge that can decrease the accumulation of particles on the filtering media and consequently increase the filtrate flow through the filter cake, thus accelerating the dewatering rate. After electric field implementation, the final water content can be reduced down to 40% (Citeau et al., 2015; Conardy; Olivier; Vaxelaire, 2016).

However, the passage of electric current through the sludge leads to several issues such as ohmic heating, high electrical energy consumption at final stages of dewatering, electrode corrosion, alkaline and acid contamination of filtrate and filter cake because of electrolysis reaction. Based on these problems electro-dewatering technology is not commonly used in industry (Citeau et al., 2015).

2.3.1 Electro-kinetic phenomena

The term "electro-kinetic" indicates motion induced by an electric field. It consists of six phenomena, but only four of them as listed below are involved in the sludge EDW process (Figure 2.1). The two phenomena of sedimentation potential (Dorn effect) and streaming potential are not involved.

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- Electrophoresis: movement of charged particles relative to a stationary liquid under the influence of the electric field.
  The importance of electrophoresis is evident at the beginning of the electro-dewatering process when the sludge particles are free to move. Particles move towards the anode because of their negative charge. As a result, the delay occurs in cake formation on the filter medium and increases water flow. When DS content of sludge becomes higher, sludge particles cannot move. In this case, only electro-osmosis acts on transporting water from the anode towards the cathode side.
- Electro-osmosis: induces the displacement of the bulk water molecules and takes place at the solid/liquid interface of the medium.

According to Tuan (2011), sewage sludge consists of charged particles having a double layer. By applying an electric field to the sludge through electrodes, the net charge in the electrical double layer move due to their electric charge. The electro-osmotic flow (Equation 2.1) is from the anode to the cathode (Lin et al., 2012) since the zeta potential of sludge is negative.

$$\frac{dV}{dt} = \mathrm{q} = \frac{\varepsilon_o \cdot \varepsilon_r \cdot \zeta}{\eta} EA \qquad (2.1)$$

In which:

V = Water volume (m^3)
t = Time (s)
q = Flow rate ($m^3 \cdot s^{-1}$)
ε_o = Dielectric permittivity of vacuum (8.854×10^{-12} $C \cdot V^{-1} \cdot m^{-1}$)
ε_r = Dielectric constant of the liquid
ζ = Zeta potential of sludge (V)
E = Electrical field strength across the cake ($V \cdot m^{-1}$)
A = Cross-sectional area (m^2)
η = Viscosity of the liquid medium ($kg \cdot m\text{-}1 \cdot s^{-1}$)

- Electromigration: transport of ions in solution according to their ionic mobility. Anions usually run towards the positively charged anode, while cations move towards negatively charge cathode under the application of electric field.
- Electrochemical reactions at electrodes guarantee the electrical transportation to be continuous. When electrodes are placed in an aqueous solution and voltage is applied, electrolysis of water occurs to maintain charge equilibrium by producing oxygen gas and protons, H^+, at the anode, and forming hydrogen gas and hydroxyl anions, OH^-, at the cathode. As a result, the pH near the anode decreases while the pH near the cathode increases. The electro-dewatering system acts as an electrochemical cell. Equations (2.2) and (2.3) show the reactions in the anode and cathode (Mahmoud et al., 2010).

Anode $$2H_2O \rightarrow 4H^+ + O_2 + 4e^-; \qquad (2.2)$$

Cathode $$2H_2O + 2e^- \rightarrow 2OH^- + H_2; \tag{2.3}$$

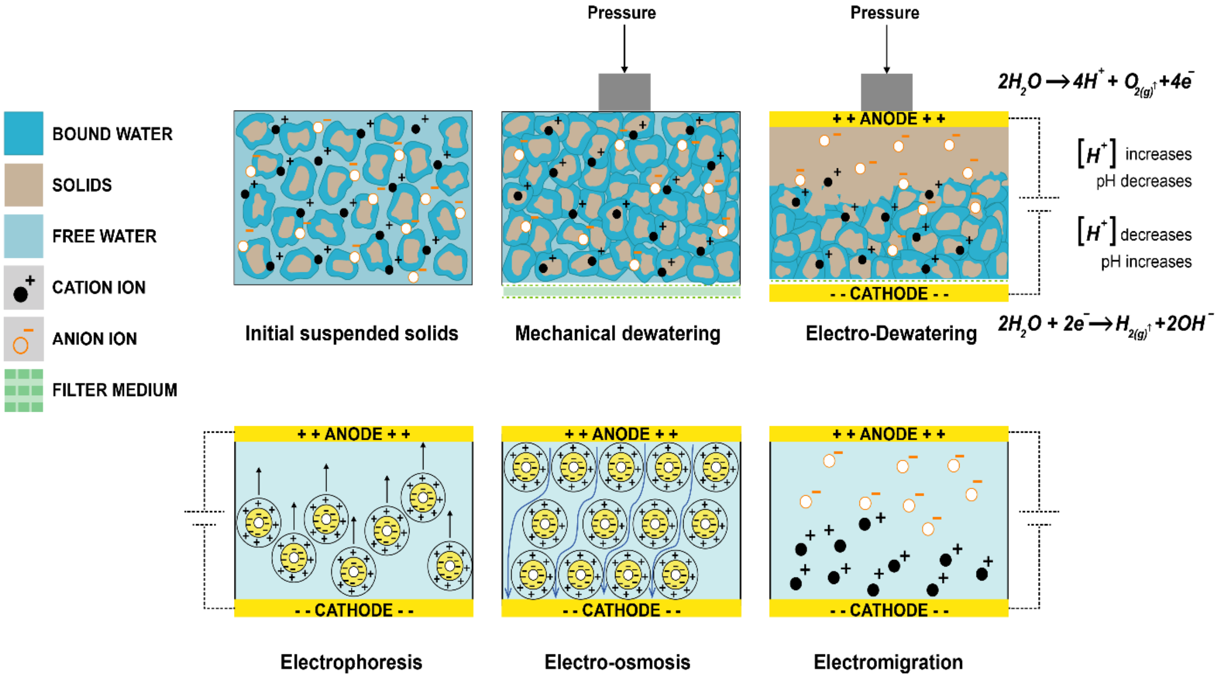

Figure 2.1 - Phenomena occurring during the pressure-driven electro-dewatering process (Mahmoud et al., 2010).

2.3.2 Pressure-driven electro-dewatering

The combination of mechanical dewatering technique with electro-kinetic phenomena (Figure 2.1) results in a reduction of water content through the following steps (Citeau et al., 2015; Mahmoud et al., 2010):

1. The volume of the pores decreases by mechanical dewatering, which squeezes the water out of the sludge cake;
2. By applying the electric field, the charged particles that are still free to move in the fluid suspension tend to migrate towards the anode;
3. When the cake has formed, the particles are unable to move and fixed in the position. Water containing ions is transported by vicious and/or molecular interactions and/or as a hydration sheath.

4. Electro-chemical reactions at the electrodes are required to restore charge equilibrium;
5. Finally, water ceases to be the continuous phase in the cake, and the electrical resistance increase leads to ohmic heating;
6. Joule effect decreases the viscosity of sludge and may accelerate the removal of some of the remaining water.

To summarize, EDW is consisting of three phases: the strength of the electric field controls the first phase, followed by a transition phase and a termination phase. At the beginning of the cake formation stage, the electro-dewatering rate is constant and then decreases by increasing the DS content. Then, the EDW process leads to an increase of the electrical resistance of the cake and reduces the developed electrical currents. In the end, electro-dewatering stops, and no water is furtherly removed. The continuous removal of the dry cake which is formed at the anode can be useful in increasing the efficiency of the electro-dewatering process (Tuan, 2011).

2.3.3 Factors affecting electro-dewatering efficiency

Many factors, such as voltage, time, pressure, polyelectrolyte dosage and floc size distribution, contributes to the water reduction and thus the efficiency of EDW (Citeau et al., 2012; Mahmoud et al., 2011b). Some of them may play a key role, more than others. Therefore, it is essential to study these parameters and their influence on EDW process yield.

2.3.3.1 Influence of voltage and pressure

During the EDW process, a dry layer with high electrical resistance may be formed at the anodic side, which causes loss of electrical contact between the electrodes and the sludge sample and also a drop in the electrical field. Thus, a minimum pressure, around 4-6 bar, is required to keep the contact between electrodes. The higher pressure application provides better contact, more efficient electro-osmotic flow and dryer sludge cake (Mahmoud et al., 2016; Tuan, 2011).

The electric potential value during EDW has a significant effect on the final DS content and the dewatering kinetics, which means that the higher applied voltage is leading to higher water removal rates (faster kinetics) and higher DS content of the final cake. According to Olivier et al. (2014), the increase in the applied voltage intensifies the field strength allowing the extraction of more water, so that water that is more tightly bound to the solid particles can be removed, thus leading to an increase in DS content.

Moreover, there is a linear correlation between applied voltage and energy consumption, since the process consumes more energy when a higher voltage is applied (Olivier et al., 2015, 2014).

According to Tuan (2011), to achieve the highest water removal rates a voltage of 15 V should be applied on sludge samples with initial DS contents of 3-7%. By applying electric potentials ranging from 10 to 30 V, EDW did not affect the DS content of the final sludge cake, while resulted in shorter dewatering times. Thus, high voltage applications are not economical from the energy consumption point of view.

In constant voltage mode (C.V.), there is a constant increase in the electric cake resistance based on Ohm's law and a decrease of electric current intensity with time (Citeau et al., 2012). The electric resistance, according to Yukawa and Shinkawa (1985), is not uniform inside the sludge cake throughout the dewatering process since it depends on the water distribution inside the cake and on the applied electric field itself. Under C.V. conditions, both anaerobically digested and activated sludge can achieve a DS content of more than 60% (Olivier et al., 2014).

2.3.3.2 Influence of cake thickness

The electro-dewatering rate is proportional to the electric field intensity (Citeau et al., 2012). The thinner sludge cake has a faster dewatering rate under C.V. condition, due to higher electric field intensity. Therefore, a dryer cake can be achieved for a thinner cake and thicker cakes lead to higher electrical resistance. An increase in the mass of the sludge for EDW process, which means higher cake thickness, increases the distance between electrodes and reduces the electric field strengths and the EDW efficiency (Tuan, 2011). However, for a cake dryness more than 20%, the electrical resistance does not depend on sludge loading amount (Conrardy et al., 2016).

2.3.3.3 Influence of electric current

Previous studies showed that the higher current intensity can improve the electro-osmotic dewatering rate, thus improving the water removal and the sludge dryness. However, ohmic losses play an essential role in the reduction of the energetic yield of the process. In other words, it is worthless to apply high electric field intensity to reduce the time of operation, since ohmic losses result in high energy consumption. An optimum point for the process time and the electric power applied has to be found (Larue et al., 2006). When a constant electric potential is used, there is a linear relation between the electric current and the filtrate flow rate (Equation 2.4):

$$Q_f = h(i_{meas}) \tag{2.4}$$

Where h is an empirical function, i_{meas} are the current values which are measured through the EDW tests. Olivier et al. (2015) stated that the filtrate flow rate depends only on the measured electric current, while it is independent of the applied voltage and the reached dryness. According to Citeau et al. (2012), for EDW at constant current (C.C.) and C.V., the filtrate flow rate is similar for the same electric field intensity. The selection of the current mode is important. In C.C. mode, the electrical resistance of the cake and voltage increase with time, and lead to a higher temperature by the ohmic effect, which can damage the filter cloth and the filter cell (Citeau et al., 2012).

2.3.3.4 Influence of time

The duration of the EDW process has ranged from several minutes to several hours. However, the selection of the optimum time is essential since a short electro-dewatering duration is not enough to induce a sufficient dewatering effect, while an extended time is not energy efficient. The EDW performance regarding final DS content and energy consumption directly depends on the electric field application times. To optimize the EDW process, in terms of energy consumption and high final DS, a good compromise between the electric potential applied and the duration of the test is required (Tuan, 2011).

2.3.3.5 Influence of conditioning

The effect of polyelectrolyte conditioning on the performance of the EDW test has been studied by many researchers. The general idea is that adding the polyelectrolyte can improve the solid-liquid separation. According to Smollen and Kafaar (1994) polyelectrolyte addition improves the electro-osmotic water transport efficiency through charge neutralization of sludge particles. Moreover, Kondoh and Hiraoka (1993) found that adding poly aluminum chloride (PAC) improved the EDW treatment by 1.5-2 times, reducing energy consumption by about 50% and preventing the clogging of the filter media compared to EDW without PAC.

On the contrary, Citeau et al. (2011) reported that polyelectrolyte does not influence the EDW process rate and energy consumption. Laursen and Jensen (1993) found that there is no dependence of electro-osmotic flow on the polymer conditioning. This finding is in line with Saveyn et al. (2005), who pointed out that the polyelectrolyte addition dosage affects water removal during the pressure-driven phase, while there is no significant effect on the electro-osmotic flow efficiency. Moreover, Gingerich et al. (1999) stated that the higher DS content in the final sludge cake after EDW process is not related to the excessive addition of polymer dosage.

According to Saveyn et al. (2005), the negative surface charge is present in the sludge matrix even at pronounced overdosage of polyelectrolyte. The same hypothesis was expressed by Mikkelsen (2003), who stated that the number of charges present in the sludge could be magnitudes higher than those neutralized by the polyelectrolyte. Thus a large number of the surface charges are not affected by the polyelectrolyte (Citeau et al., 2011; Mikkelsen, 2003).

2.3.3.6 Influence of DS content

When the sludge has a low DS content at the early stage of the electro-dewatering process, sludge particles are free to move in the solution. Due to electrophoresis, the negatively charged particles move towards the cathode, and their concentration becomes lower at the cathode side. Moreover, electro-osmosis also contributes to transport water from anode to cathode. On the contrary, in the case of high initial DS loading, fine particles are entrapped within the sludge matrix and cannot move freely. So, electrophoresis becomes less effective compared to electro-osmosis.

Furthermore, the energy consumption due to applied voltage, is low at lower initial DS loading. According to Tuan (2011), energy consumption, when expressed as kWh/kg_{DS} depends on initial DS loading, while if expressed as kWh/m^3 of effluent it becomes independent of initial DS content in the sludge cake. Gingerich et al. (1999) showed that the energy consumption is not uniform during the electro-dewatering process, but it increases with the increasing of cake DS content because the last water fractions are hard to be removed due to their binding strength. This result is in line with Olivier et al. (2014) conclusion who stated that the energy consumption increases with DS content.

2.4 Sludge characteristics affecting dewaterability

Dewaterability of sludge can be affected by different factors, such as sludge treatment operation, extracellular polymeric substances (EPS), organic matter, metal ions, particle size, microbial population, cake porosity and water distribution in sludge that is considered as a leading factor (Zhang and Sun, 2012).

2.4.1 Sludge nature

Based on the treatment process, the sludge is classified as primary, secondary, tertiary and digested sludge and each type is different in physical, chemical and biological characteristics, which affect its dewaterability. Figure 2.2 shows the different types of sludge generated in a typical WWTP.

Primary sludge is the sludge formed during the primary treatment and consists of settable solids. It can be dewatered easily, due to its composition, mainly made of discrete particles.

The *secondary sludge* (activated sludge) includes micro-organisms, dead cells and their residues (cell walls), other absorbed and or adsorbed suspended solids and colloids and its dewaterability depends on many factors. In processes characterized by long solid retention time (SRT), the fraction of non-degraded, colloidal organics decreases, thus improving the dewaterability of sludge.

Stabilization of putrescible organic matter by transforming it in more stable organic substance is required for primary and secondary sludge, before dewatering process and final disposal, to avoid odours and unwanted or uncontrolled biogas production and to decrease the number of solids. Biological stabilization is performed by biological digestion under anaerobic and aerobic conditions. Aerobic digestion is a bacterial process that converts organic matter into carbon dioxide, water and stabilized organic debris in the presence of oxygen. On the other hand, anaerobic digestion is carried out in the absence of oxygen. In this case, biodegradation of organics leads to the production of methane and carbon dioxide. Dewaterability of unconditioned sludge after aerobic and anaerobic digestion reduces compared to primary sludge because of the increase of the fine particles (Tuan, 2011).

According to Citeau et al. (2012), the type of sludge affects the dewatering efficiency. The DS content of conditioned digested sludge increases from 10.5% to 35% while it ranges from 9.0% to about 20% for activated sludge, after two hours of mechanical dewatering. Therefore, the dewatering rate of stabilized and conditioned sludge is higher than the dewatering rate of the activated sludge. The reason can be related to the existence of higher content of microbial EPS in activated sludge.

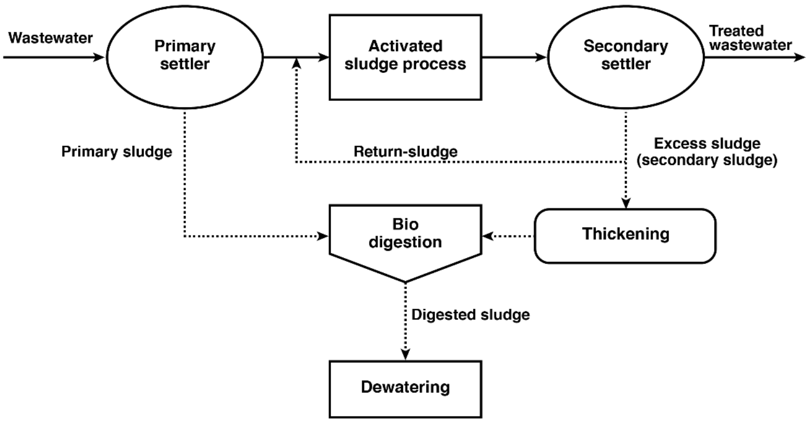

Figure 2.2 - Wastewater treatment process (Tuan, 2011).

2.4.2 Extracellular polymeric substances

The high molecular weight biopolymers, from bacterial secretion, hydrolysis and cell lysis are called extracellular polymeric substances (EPSs), which contain different organic compounds such as proteins, nucleic acid, polysaccharides and humic acid. Among all, proteins (EPSp) are playing a key role in sludge floc stability, settling and dewatering.

EPSs includes two categories;

- Loosely bound EPS (LB-EPS)
- Tightly bound EPS (TB-EPS)

The content and distribution of EPS can affect the water content and its delivery in sludge which is the main issue in the dewatering process. According to Tuan (2011) the higher EPSs in sludge means a reduction in sludge dewaterability. Mikkelsen and Keiding (2002) indicated that sludge with high EPS content has lower shear sensitivity and degree of dispersion which means better filterability of sludge. However, Chen et al. (2001) stated that the presence of EPS in sludge leads to more interstitial bound water and poor settleability due to its enormous size. However, the effect of EPS on sludge dewatering is not well documented yet. The reason might be the dependence of sludge and EPSs nature to process variables (e.g. type of wastewater, SRT, dissolved oxygen, nutrient level) (Tuan, 2011; Yin et al., 2004).

2.4.3 Water distribution in sludge

Sewage sludge is hydrophilic and contains a large amount of water (around 98-99%) that is hard to remove. The reason of non-homogeneity of water in sludge is the presence of solid particles. Therefore, different types of water distributed in sludge have different properties such as density, viscosity, vapour pressure, enthalpy and entropy. The behaviour of the molecules of water is widely dependent on its proximity to the solids during the dewatering process. The efficiency of dewatering methods can be improved by understanding the water distribution in sludge. The representation of the water distribution within activated sludge may be an effective method to characterize its dewatering ability (Phuong To et al., 2016; Vaxelaire and Cézac, 2004).

2.4.3.1 Water classification in sludge

Many models have been proposed to classify the different types of water. Even though each model differs at some extent, they all have common categories based on the intensity of the water binding forces to particles.

The simplest classification divides water into two main types, according to the binding strength with solid particles: free water and bound water. *Free water* is defined as the most considerable portion of water in sludge which is not affected by solid particles. *Bound water* includes a small proportion of the total water in sludge and its properties change due to the presence of solid particles. Sludge dewatering efficiency is mainly based on bound water content since a significant amount of energy is required to remove it, if compared to free water. However, a simple classification of water is not enough to understand the mechanism of dewatering and the pre-treatments which are associated with it, such as flocculation and coagulation.

A more detailed classification considers additional types of water. Generally, four kinds of water are proposed within activated sludge, with some differences in their definition. The most popular categorization of water in sludge is the one proposed by Smith and Vesilind, (1995) and Vesilind and Hsu (1997), which is usually used as a reference and is generally sufficient for dewatering considerations (Figure 2.3) (Colin and Gazbar, 1995; Mahmoud et al., 2010; Phuong To et al., 2016; Smith and Vesilind, 1995; Vaxelaire and Cézac, 2004).

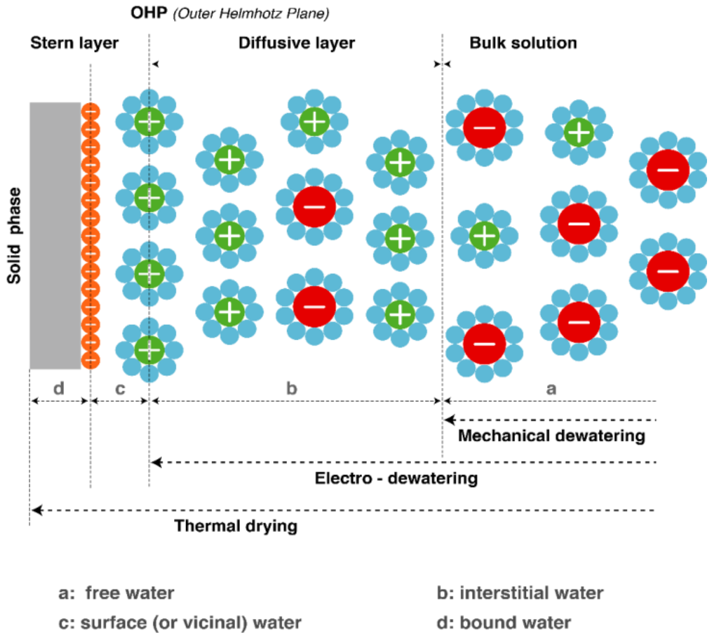

Figure 2.3 - Distribution of water in sludge and dewatering technologies (Tsang and Vesilind, 1990).

The types of water considered are:

- Free water (FW) – water not attached to the particles, including void water that is not affected by capillary forces and can be easily separated mechanically (through filtration/compression, gravitational settling and centrifugation).
- Interstitial water – water trapped inside the floc structure or a cell. This water might be removed partially by mechanical dewatering devices.

- Surface (vicinal) water – multilayers of water held tightly on solid particle surface by adsorption and adhesion. This type of water cannot be removed by mechanical methods.
- Intracellular or chemically bound water (BW) – a portion of water bound within the particle structure that cannot be removed by mechanical means.

It is generally admitted that mechanical dewatering technologies are only efficient to remove parts of free and interstitial water, while to remove all types of water thermal drying is required (Mahmoud et al., 2010).

However, the classification reported above does not fully consider water entrapped in proteins and polymer in sludge. Moreover, the nature of intracellular water is not clear yet.

Mikkelsen and Keiding (2002) considered surface water, osmotic water and water trapped within polymer matrix under the term ‘’water holding’, but no data about dewatering are available associated to these new types of water.

According to the previous studies, many researchers classified different types of water based on the measurement techniques (Table 2.1). Smollen (1988), Vesilind and Tsang (1990) had classified the moisture content based on the transition points on the drying curve as a result of drying test. The portion of moisture content that evaporates at a lower rate under a constant temperature bound more tightly to the solid particles. Therefore, a discrete classification was obtained according to the tightness of water-solid binding. To have a continuous classification the drying rate should be used as an index (Chen et al., 1997).

Colin and Gazbar (1995) found three types of bound water as a function of mechanical dewatering strain applied to the sludge by using dilatometry method. They employed centrifugal force to the sludge sample and measured the moisture content that remained in the sludge cake after applying increasing shear strains (Chen et al., 1997).

Table 2.1 - Classification of moisture in sludge according to different researchers.

Vesilind and Tsang	Smollen	Colin and Gazbar
Free water (gravity thickening)	Free moisture (gravity thickening)	Free water
Floc water (high-speed centrifugation)	Immobilized moisture (mechanical dewatering)	Water not removable mechanically
Capillary water (very high-speed centrifugation)	Bound moisture (thermal drying)	Bound water not removable under a realistic mechanical strain
Bound water (not removed by centrifugation)	Chemically bound moisture (high temperature - 105°C)	Bound water removable by the maximum applied mechanical strain (60,000 g)

2.4.3.2 Measurement techniques of water distribution in sludge

The distribution of water within sludge is not well-defined yet, thus choosing the best-adapted method is difficult. Many techniques have been proposed to measure the moisture distribution considering different properties of water. The most common methods are listed below (Phuong To et al., 2016; Vaxelaire and Cézac, 2004).

- Drying test: this method assumes that the water evaporation rate depends on the type of bond between water and solid particles. The analysis is performed based on thermal drying curve which describes evaporation rate versus average moisture content (*W*). This curve consists of 4 stages (Figure 2.4). In the initial period, the temperature rises, followed by a constant rate stage, which corresponds to the free water evaporation. Then there is a first falling rate period, which is typical of the drying boundary progressing into materials. As the drying boundary progresses into the sample, the mass and heat transfer resistance increase, thus evaporation rate decreases. The second falling rate stage happens due to the slow evaporation of hardly bound water in sludge.
- Techniques based on freezing properties: the assumption is that bound water freezes below a given threshold, which is typical -20 °C.

- In dilatometry, the free water content (frozen part) is measured by using dilatometer set at -20 °C. The bound water portion is obtained from the difference between total water content and free water content. A widely accepted definition is that the free water is freezing at the frozen point, but bound water remains unfrozen at this point.
- Differential scanning calorimetry (DSC) measures the variations in heat flow between the sample and the reference material (thermally inert material).
- Differential thermal analysis (DTA) measures the differences in temperature between the sample and the reference. This difference can be plotted against fixed temperatures. Increasing or decreasing, respectively, show the exothermic or endothermic transformations in the sample.
- Mechanical strain: bound water is considered as the final moisture content of sludge after the application of a mechanical force.
- Centrifugal settling test is based on the assumption that a sample centrifuged under infinite rotational speed tends toward an equilibrium height that corresponds to the formation of a sludge sediment, whose water content is reported as bound water.
- In expression test, the bound water content is defined as the final water content of sludge by applying very high constant pressure (around 31 MPa).
- Filtration test measures the moisture content of the sludge after vacuum filtration.

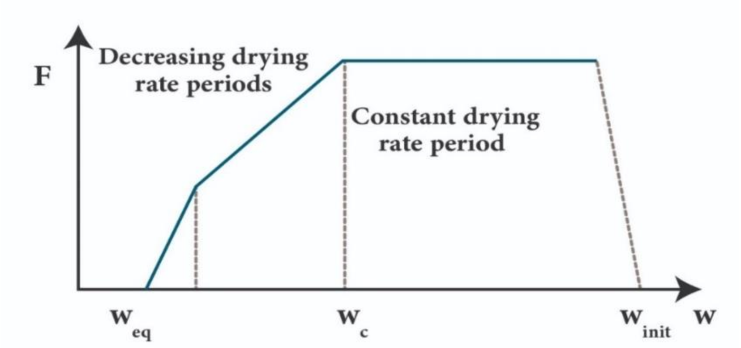

Figure 2.4 - Standard drying curve (Kopp and Dichtl, 2001a).

Between the above methods, DTA and DSC are considered as quick and valuable tools for bound water measurement (Katsiris and Kouzeli-Katsiri, 1987). It is essential to select the threshold temperature to differentiate the bound and free water (Lee and Lee, 1995). To this goal, G. W. Chen et al. (1997) and Ferrasse and Lecomte (2004) proposed to perform DTA or DSC simultaneously with thermogravimetric analysis (TG-DTA or TG-DSC). However, different methods follow various assumptions and basis which result in some difficulties to get a clear idea of moisture distribution within sludge and comparing the results of different techniques (Phuong To et al., 2016).

Furthermore, no method can be preferred to another based on the discussion of the measurement technique. Drying test is not favoured due to two reasons: it depends on operating conditions and it is not able to measure the water distribution as an intrinsic parameter of sludge. About mechanical strain methods, centrifugal force seems to not be efficient for viscoelastic and compressible materials like activated sludge (Vaxelaire and Cézac, 2004). However, the final limits of mechanical dewatering device can be obtained by performing the mechanical test under very high strain.

Many studies have investigated water distribution in sludge through TGA and DSC. Kopp and Dichtl (2001b) studied the water distribution in both anaerobically and aerobically sludge through TGA. The analysis pointed out two critical points on the drying curve as the ending points of free and interstitial water. Bound water content was determined by dilatometric test. For anaerobically and aerobically digested sludge, the interstitial water content was found to be 7.5% and 9.6%, while the bound water content was found to be 0.8% and 1.1%, respectively. Furthermore, they stated that the binding energy was less than 0.28 kJ/kg$_{water}$ for free water and higher than 5 kJ/ kg$_{water}$ for bound water content

Wu et al. (1998) conducted free and bound water measurement by using dilatometric test, with the same assumption that bound water remains unfrozen up to -20°C. At this temperature, the bound water bonding strength was calculated as 24.5 kJ/kg, which is close to the normal physical-adsorption process, so that the unfrozen moisture was considered as bound water content. Moreover, they concluded that the differences in bound water content due to the different DS content was not significant when the binding strength was equal to 24.5 kJ/kg, while for binding strength lower than this value, less bound water content corresponded to higher solid concentration, since the expelling strength became higher than the binding strength and resulted in higher release of interstitial water, and the moisture with lower binding strength (E_B close to zero) could easily transfer to free water.

Table 2.2 at the end of this chapter, summarizes the methods and the results obtained for free and bound water content in the previous works.

2.4.3.3 Influence of polyelectrolyte dosage on water content within the sludge

There is some discrepancy among previous studies about the influence of polyelectrolyte on bound water content. Katsiris and Kouzeli-Katsiri (1987) concluded that a reduction in bound water content could be achieved by increasing the polymer dosage. According to Robinson and Knocke (1992), bound water content decreases due to the replacement of water molecules by the polymer molecules on the solid surface which leads to stronger water release. On the contrary, Smollen (1990) found an opposite trend, with increasing bound water content by increasing the polymer dosage because of water molecules adsorption onto the polymer molecules. Wu et al. (1997) reported a different trend for alum sludge: bound water content decreased until a minimum point and then increased with polymer dosage. Based on his idea, interparticle squeezing is dominant at the beginning of the conditioning (lower dosage of polymer) then at a higher dose, the effect of water molecules adsorption becomes important. Chu and Lee (1999) stated that the moisture with high bond strength is not influenced by the presence of polymer molecules, while the conditioning affects physi/chemi-sorbed moisture. The bound water content decreases with the increase of polymer dosages, at low polymer dosage levels, due to the replacement of the surface water with polymer molecules, while in the overdosed regime, moisture absorption onto polymer molecules might be responsible for the raise in bound water content.

Kopp and Dichtl (2000) examined the influence of polyelectrolyte dosage on the water distribution for different digested sludge samples and various polymer products. The results confirmed that the free water content does not change from one dosage to the other for each sludge. On the contrary, Guo et al. (2018) found that conditioning of raw activated sludge can reduce the bound water content (around 2.15 g/g_{DS}) and increase the free water content, due to the movement of bound water to free water under the effect of magnetic micro-particle conditioning

2.4.3.4 Influence of MD and EDW process on water content in sludge

According to Mahmoud et al. (2013) only free water can be removed by chemical and mechanical methods. Vesilind (1994) stated that mechanical dewatering could be efficient in removing free water and a portion of interstitial water, which result in a higher water content (65-80%).

Mahmoud et al. (2010) stated that EDW could reduce interstitial and some vicinal water in sludge. Guo et al. (2018) studied the effect of the EDW process on activated sludge and found that the application of 50 V and 400 kPa can decrease the water content to 44%. However, Tuan and Mika (2010) found a water content reduction of 60% by applying 50 kPa and 20 V for 150 min and claimed that EDW not only increases the dewatering rate but may also remove both free and bound water content from the sludge. Feng et al. (2014) stated that a pressure of 600 kPa could remove only a small amount of free and bound water in activated sludge, while the application of both pressure and electric potential (50 V) leads to a further decrease in free and bound water content, 0.24 g/g_{DS} and 0.25 g/g_{DS} respectively

According to Guo and Wang (2017), magnetic micro-particle conditioning and EDW process of activated sludge can reduce the total and bound water content by 98.9% and 83.0% respectively compared to the raw sludge, which implied that reduction of bound water mainly occurs in conditioning and electrical compression stages.

Table 2.2 - Summary of the previous studies on measurement of moisture distribution by TGA and DSC.

Reference	Method	Temp (°C)	Type of sludge	DS (%)	Type of water	Water content (g/g_{DS})	Bonding energy (kJ/kg)
Chen, W., Hung, W.T., Chang, I.L., Lee, S.F., Lee, D.J., 1997	TGA/DTA	80	Activated sludge Unconditioned + Vacuum filtration	10.0	Bound water (W_{FIL})	5.9 – 10.2 Vacuum filtration-53.3 kPa	1.0
					Bound water (W_{DRY})	4.2 Drying-TGA	20.0 – 40.0
					Bound water (W_{EXP})	3.7 Expression-31,026.4 kPa	70.0 (limit for MD)
			Activated sludge + Freeze thaw + Vacuum filtration	10.0	Bound water (W_{DRY})	3.7 Drying-TGA	NA
					Bound water (W_{EXP})	2.5 Expression-31,026.4 kPa	60.0 – 70.0 (limit for MD)
Chu, O., Lee, D.J., 1999	TGA/DTA	80	Activated sludge Unconditioned + Vacuum filtration	9.7 – 14.8	Bound water (W_{DRY})	4.3 Drying-TGA	<40.0
			Activated sludge + Conditioning (20 ppm) + Vacuum filtration		Bound water (W_{DRY})	4.0 Drying-TGA	
			Activated sludge + Conditioning (40 ppm) + Vacuum filtration		Bound water (W_{DRY})	3.2 Drying-TGA	
			Activated sludge + Conditioning (120 ppm) + Vacuum filtration		Bound water (W_{DRY})	4.0 Drying-TGA	
			Activated sludge Unconditioned + Vacuum filtration		Bound water (W_{EXP})	3.6 Expression-20,684.2 kPa	~110.0
			Activated sludge + Conditioning (20 ppm) + Vacuum filtration		Bound water (W_{EXP})	2.9 Expression-20,684.2 kPa	~80.0
			Activated sludge + Conditioning (40 ppm) + Vacuum filtration		Bound water (W_{EXP})	1.8 Expression-20,684.2 kPa	~40.0
			Activated sludge + Conditioning (120 ppm) + Vacuum filtration		Bound water (W_{EXP})	2.9 Expression-20,684.2 kPa	~60.0

Reference	Method	Temp (°C)	Type of sludge	DS (%)	Type of water	Water content (g/g_{DS})	Bonding energy (kJ/kg)
Chu, C.P., Lee, D.J., Chang, C.Y., 2005	TGA/DTA	80	Activated sludge Unconditioned + Vacuum filtration		Bound water	At 4.0 At 2.0	~60.0 ~140.0
			Activated sludge + Conditioning (25 ppm) + Vacuum filtration	2.43	Bound water	At 4.0 At 2.0	~4.0 ~20.0
Lee, D.J., Lai, J.Y., Mujumdar, A.S., 2006	TGA/DTA	80	Activated sludge + Conditioning (25 ppm) + Vacuum filtration		Bound water	3.7	70 Dewatering filters
					Bound water	3.1	30 Screw press at high stress
Deng, W., Li, X., Yan, J., Wang, F., Chi, Y., Cen, K., 2011	Drying test	30	Mechanically dewatered	21.7	Free water	0.0	
					Interstitial water	2.1	
					Surface water	1.5	
					Bound water	0.1	
	TGA/DTA	80			Interstitial water	>1.0	38.2
					Surface water	<1.0	366.4
	Water activity test				Bound water	<0.2	Marked increase of H_b
Kopp, J., Dichtl, N., 2001	TGA	35	Anaerobically stabilised + Centrifugation at lab	~14.0	Interstitial (7.5%) + bound (0.8%) water	2.6	Free water: <0.28 Bound water: >5.0
			Aerobically stabilised + Centrifugation at lab	~14.0	Interstitial (9.6%) + bound (1.1%) water	3.4	
Xu, H., Ding, T., 2016	TGA/DTA	40	Drinking water treatment sludge	2.2 – 3.7	Free water	4.13	
					Pore water	19.83	
					Surface adhesion water	5.35	
					Internal adhesion water	0.64	
			Drinking water treatment sludge + Vacuum filtration (-0.06 MPa)	40.6	Free water	-	
					Pore water	1.44	
					Surface adhesion water	0.33	
					Internal adhesion water	0.63	
			Drinking water treatment sludge + EDW (-0.06 MPa – 2.5 V/cm)	40.6	Free water	-	
					Pore water	0.41	
					Surface adhesion water	0.18	
					Internal adhesion water	0.62	

Reference	Method	Temp (°C)	Type of sludge	DS (%)	Type of water	Water content (g/g_{DS})	Bonding energy (kJ/kg)
Wang, W., Li, A., Zhang, X., 2011	DSC	-30	Thickened	4.13	Bound water	1.90	
			Belt pressed	12.8	Bound water	1.31	
			Hot-pressed	28.2	Bound water	1.21	
Feng, J., Wang, Y.L., Ji, X.Y., 2014	DSC	-50	Activated sludge	0.9	Free water	98.60	
					Bound water	11.52	
			Activated sludge + Conditioning (4 g kg_{DS}) + Drainage under gravity	8.7	Free water	6.25	
					Bound water	3.23	
			Activated sludge + Conditioning (4 g kg_{DS}) + Compression (600 kPa)	10.0	Free water	3.78	
					Bound water	2.07	
			Activated sludge + Conditioning (4 g kg_{DS}) + EDW (600 kPa – 50 V)	62.4	Free water	0.24	
					Bound water	0.25	
Zhang, H., Yang, J., Yu, W., Luo, S., Peng, L., Shen, X., Shi, Y., Zhang, S., Song, J., Ye, N., Li, Y., Yang, C., Liang, S., 2014	DSC	-20	Primary + secondary Unconditioned	2.8 – 3.6	Bound water	1.5	
			Primary + secondary + Fenton's reagent		Bound water	0.9	
			Primary + secondary + Red mud		Bound water	1.4	
			Primary + secondary + Fenton's reagent + red mud		Bound water	0.9	
Hong, C., Si, Y., Xing, Y., Wang, Z., Qiao, Q., Liu, M., 2015	DSC	-30	Activated	5.0	Bound water	3.2	
			Activated + 75 mg/g_{DS} dodecyl dimethyl benzyl ammonium chloride		Bound water	1.6	
			Activated + 150 mg/g_{DS} dodecyl dimethyl benzyl ammonium chloride		Bound water	1.3	

Reference	Method	Temp (°C)	Type of sludge	DS (%)	Type of water	Water content (g/g_{DS})	Bonding energy (kJ/kg)
Wang, W., Liu, W., Wang, L., Yang, T., Li, R., 2016	DSC	-40	Thickened	12.4	Bound water	6.3	
			Thickened + Sodium dodecyl sulfate		Bound water	5.7	
			Belt pressed	15.1	Bound water	4.7	
			Belt pressed + Sodium dodecyl sulfate		Bound water	4.1	
					Mechanically bound water	24.86	
					Free water	1.33	
			Secondary + Centrifugation at lab	9.7	Bound water	0.63	
					Mechanically bound water	8.55	
					Free water	0.18	
			Secondary + Centrifugation at lab + thermal dried (40°C x 30 min)	12.4	Bound water	0.43	
					Mechanically bound water	6.43	
					Free water	0.19	
			Secondary + Centrifugation at lab + thermal dried (40°C x 60 min)	17.8	Bound water	0.27	
					Mechanically bound water	4.14	
					Free water	0.19	
			Secondary + Centrifugation at lab + thermal dried (40°C x 120 min)	25.3	Bound water	0.22	
					Mechanically bound water	2.55	
					Free water	0.17	
			Secondary sludge + Centrifugation at lab + thermal dried (40°C x 180 min)	34.7	Bound water	0.20	
					Mechanically bound water	0.25	
					Free water	0.09	
			Secondary + Centrifugation at lab + thermal dried (40°C x 240 min)	96.2	Bound water	0.01	
					Mechanically bound water	-	
					Free water	0.01	

Reference	Method	Temp (°C)	Type of sludge	DS (%)	Type of water	Water content (g/g_{DS})	Bonding energy (kJ/kg)
Qian, X., Wang, Y., Zheng, H., 2016	DSC	-60	Activated sludge	0.52	Free water	188.23	
					Bound water	2.32	
			Activated sludge + Conditioning with magnetic micro particles (MMP)	0.52	Free water	188.96	
					Bound water	1.59	
			Activated sludge + MMP + Conditioning with magnetic field (MF)	0.52	Free water	189.01	
					Bound water	1.54	
			Activated sludge + MMP + MF + Drainage under gravity (DG)	4.77	Free water	18.70	
					Bound water	1.22	
			Activated sludge + MMP + MF + DG + Horizontal electric field -HEF	11.43 ANODE	Free water	6.79	
					Bound water	0.96	
			Activated sludge + MMP + MF + DG + Horizontal electric field -HEF	7.17 CATHODE	Free water	11.86	
					Bound water	1.08	
He, D.-Q., Zhang, Y.-J., He, C.-S., Yu, H.-Q., 2017	DSC	-20	Activated Unconditioned	1.1	Bound water	1.0	
			Activated Unconditioned – NaCl 0.15 M		Bound water	1.0	
			Activated Unconditioned – NaCl 0.3 M		Bound water	1.0	
			Activated Unconditioned – NaOH 1 M		Bound water	2.7	
			Activated Unconditioned – H_2SO_4 1 M		Bound water	0.2	
Hu, Y., Wang, Y., 2017	DSC	-60	Water treatment residuals	1.7	Free water	47.58	
					Bound water	5.95	
			Water treatment residuals + Freeze-thaw		Free water	52.09	
					Bound water	0.83	
			Water treatment residuals + Freeze-thaw + Gravity filtration	29.1	Free water	1.7	
					Bound water	0.9	
			Water treatment residuals + Freeze-thaw + Compression (811 kPa)	44.5	Free water	0.6	
					Bound water	0.7	
			Water treatment residuals + Freeze-thaw + EDW (811 kPa – 30 V)	46.9	Free water	0.27	
					Bound water	0.9	

Reference	Method	Temp (°C)	Type of sludge	DS (%)	Type of water	Water content (g/g_{DS})	Bonding energy (kJ/kg)
Guo, X., Qian, X., Wang, Y., Zheng, H., 2018	DSC	-60	Activated sludge	0.82	Free water	115.43	
					Bound water	5.52	
			Activated sludge + Conditioning with magnetic micro particles (MMP)	0.82	Free water	117.58	
					Bound water	3.37	
			Activated sludge + MMP + Drainage under gravity (DG)	6.18	Free water	13.08	
					Bound water	2.11	
			Activated sludge + MMP + DG + Mechanical compression (MC)	7.89	Free water	9.80	
					Bound water	1.86	
			Activated sludge + MMP + DG + MC + EDW	43.10	Free water	0.38	
					Bound water	0.94	

3. Materials and methods

In this chapter materials, methods and operations used for the experiments are described in detail. Sludge characterization and conditioning are carried out to improve the understanding of the sludge properties and increase the separation of solid and liquid phase. Moreover, electro-dewatering is performed at different voltages and time durations to study the EDW efficiency. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) methods are described in detail to measure free and bound water content in the sludge samples. The framework model (Figure 3.1) below shows all the operations carried out during this work.

3.1 The sludge samples

Sludge samples have been taken from five different WWTPs located in the Milan metropolitan (Italy). Aerobically stabilized sludge is taken from WWTPs 1, 2, 3 and 4 while WWTP 5 provides an anaerobically digested sample which serves the highest population equivalent and produces the highest amount of sludge per year. Table 3.1 shows some details of the sludge samples in the five different WWTPs.

Two different types of samples have been taken from each WWTP: (i) mechanically dewatered (MD) sludge by belt press or centrifugation based on the dewatering treatment in the WWTPs and (ii) thickened sludge before conditioning (TU). To perform further operations such as EDW, TGA and DSC, the sludge samples have been conditioned with different polyelectrolyte dosage to find a dosage to be used for EDW test. TC is referred to the thickened sludge after conditioning.

To reduce biochemical changes of the sludge, the samples have been stored for a maximum of five days at 4 °C, before the experiments. All experiments were performed within a week from the date of sampling.

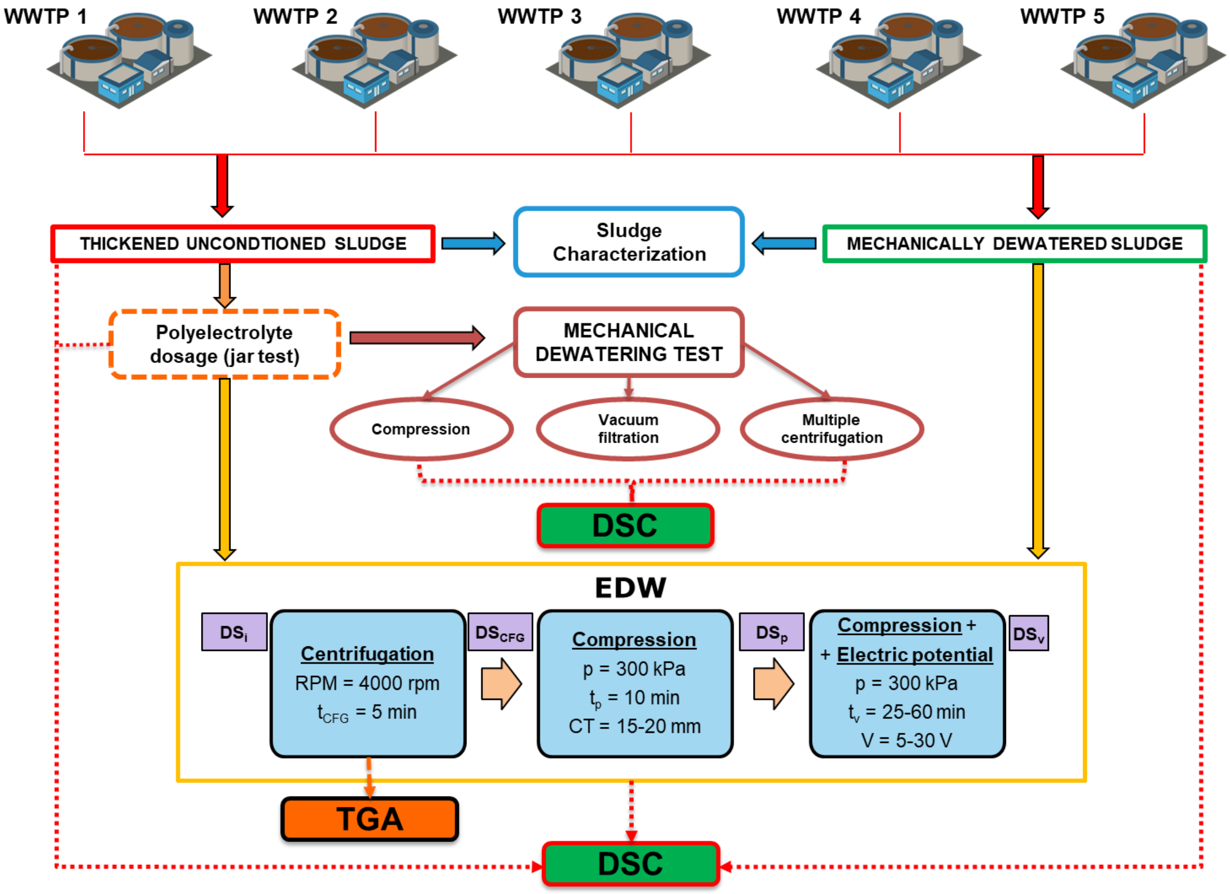

Figure 3.1 - Framework of the procedures used for the experiments.

Table 3.1 - Main characteristics of the sludge samples taken from the five WWTPs.

WWTP No.	Population equivalent served	Polymer dosage	Mechanical dewatering treatment	DS	VS/DS	SEEC	Mass of dewatered sludge produced	Disposal route
	PE	g/kg$_{DS}$		%	%	Wh/kg$_{H_2O}$	t/year	
1	59,312	11.2 TILLFLOCK CL1480	Centrifuge	19.5	72.0	1.7	6041	Agriculture
2	33,722	15.0 TILLFLOCK CL1480	Centrifuge	19.0	80.0	3.8	1674	Agriculture
3	6,653	PREASTOL 853BS	Belt press	14.3	80.0	NA	993	Agriculture
4	47,080	5.3 PREASTOL 645BC	Belt press	18.1	76.0	1.7	2458	Incineration Landfilling
5	308,646	15.4 TILLFLOCK CL1480	Centrifuge	24.1	60.0	0.4	13,808	Agriculture

3.2 Sludge characterization

To have a better insight into sludge dewatering properties, sludge characterization is required. Sludge characterization in the laboratory consisted in preliminary tests (e.g. initial DS content, volatile to dry solid ratio – VS/DS, pH and conductivity), capillary suction time (CST) test and zeta potential measurement.

3.2.1 Preliminary characterization

Preliminary characterization tests, such as initial dry solid (DS), dry solid to volatile solid ratio (VS/DS), pH and conductivity of the sludge have been carried out in the laboratory.

3.2.1.1 Initial DS content and VS/DS ratio

DS content and VS/DS ratio of the sludge samples have been determined according to the Standard Methods (APHA/AWWA/WEF, 2012). The mass of an empty crucible is weighed, then sludge is put in the empty crucible, and the mass of the sludge is recorded. The crucible with the sludge is inserted in the oven at 105 °C for 12 h in order to evaporate all the water in sludge samples. The mass of the crucible with the sludge in, after drying in the oven is recorded. Prior to measuring, the crucible is put in the desiccator to prevent errors in weighing by providing a 0% humidity atmosphere when the crucible cools down to room temperature. The DS content is calculated from Equation 3.1:

$$DS = \left(\frac{m\mathrm{A} - mB}{mC}\right) * 100 \tag{3.1}$$

Where: mA: mass of the crucible and sludge after drying

mB: mass of the empty crucible

mC: mass of the sludge before drying

After that, the crucible filled with the dried sludge sample is ignited in the muffle furnace at 550 °C for 6 hours. The mass of the crucible and sludge after incineration in the muffle is recorded after one hour of cooling in a desiccator. The ratio between volatile solid and dry solid is computed with Equation 3.2:

$$\frac{VS}{DS} = \left(\frac{mA - mD}{mA - mB}\right) * 100 \tag{3.2}$$

Where: mA: mass of the dish and sludge after drying

mB: mass of the empty dish

mD: mass of the plate and sludge after incineration at 550°C for 6 hours

3.2.1.2 pH and conductivity

The electrical conductivity and pH were measured both on thickened unconditioned (TU) sludge thickened conditioned (TC) samples, after polymer dosing in the lab. Conductivity was measured by using a conductivity meter (B&C Electronics-C 125.2) and pH by a pH-meter Metrohm 827 pH. The probes of pH and conductivity meter were inserted in a 250 ml beaker where

150 ml of liquid sludge (unconditioned or conditioned) was poured. A preliminary dilution with distilled water (1:10 w/w) has been performed in case of mechanically dewatered (MD) sludge.

3.2.2 Capillary Suction Time (CST)

Sludge filterability and dewaterability can be determined by capillary suction time (CST), which consists in timing the movement of water from the sludge sample through a filter paper (APHA/AWWA/WEF, 2012).
The apparatus consists of two main components (Figure 3.2): (a) an automatic time counter and (b) a filtration unit.

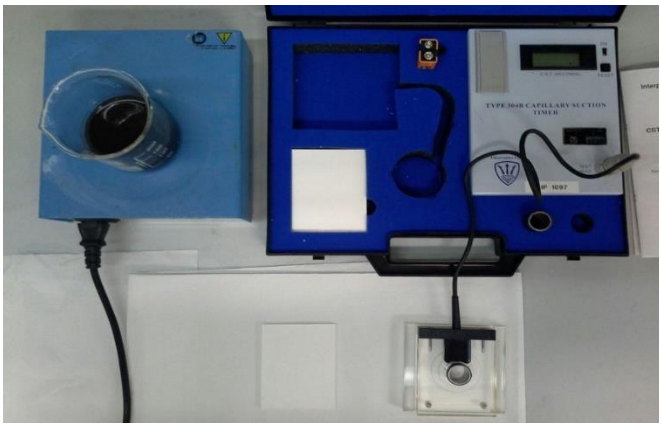

Figure 3.2 - The standard CST apparatus.

The filtration unit includes a thick filter paper (usually Whatman n° 17), inserted between two plastic rectangular blocks. A hollow cylinder as a sludge reservoir is placed on top of the paper filter at the centre of the upper plastic block. 1A and 1B are the sensors placed on the first concentric circle around the sludge reservoir (diameter of 32 mm). Sensor 2 is positioned on a second concentric circle (diameter of 45 mm). These three sensors are connected to a counter. The reservoir (diameter of 18 mm) is filled with the sludge sample. As soon as the sludge reaches the filter paper in the bottom, it starts to wet the filter paper due to capillary suction phenomena through the spaces between the hydrophilic fibres of the filter paper and the water proceeds rapidly. When the water in the sludge-paper interface is absorbed by the paper, the sludge that contacts directly with paper becomes compact and acts as a barrier for further water loss. When the filtrate reaches the first two sensors (1A and 1B), the counter is automatically activated. When the filtrate reaches sensor 2, the counter stops and shows the value of CST. The rate at which the filtrate spreads concentrically on the filter paper points out the filterability and dewaterability of the sludge sample.

CST is mainly used to investigate the optimal polymer dosage for the conditioning step. The lower CST value indicates, the better sludge filtration properties.

The procedure for CST tests can be summarized as follows:

1. 100 ml of unconditioned sludge sample is poured in a 250 ml beaker on a magnetic stirrer;
2. 20 ml of water is added into the sludge and, after 10 s of stirring, the beaker is removed, and the CST is measured;
3. The beaker is replaced onto the stirrer and sludge is stirred for further 10 s, then CST is measured;
4. The stirring procedure is repeated for further 30 s and 60 s and CST is recorded;
5. The average CST of four values is computed.

For conditioned sludge, the same steps are repeated but with a known amount of conditioner instead of 20 ml of water in step 2.

3.2.3 Zeta potential

Zeta potential (ζ) is the electric potential and a key indicator of the stability of colloidal dispersions. The magnitude of zeta potential determines the capability of microbial flocs to aggregate. The closer the magnitude of zeta potential to zero the lower the repulsive forces between flocs and the higher the opportunity to form larger flocs. In other words, the higher the absolute value of zeta potential indicates a more stable colloidal system. To separate the particles and remove easily the surrounding fluid, the lower magnitude of zeta potential is needed.

Sludge samples were filtered under vacuum with a Whatman 42 filter paper (2.5 µm pores size) and the zeta potential of the filtrate was determined by the instrument Malvern Zetameter ZS90. The cuvette was rinsed with methanol and deionized water and filled with the filtrate. Then the sample was placed in the zetameter viewing chamber where an electric field is activated. This leads to movement of colloids with a velocity proportional to their zeta potential, and positive or negative charge can be determined from the direction of colloids movement. Five to ten repetitions were carried out and average values with standard deviations of the zeta potential were obtained for each sludge sample.

Zeta potential was measured for both conditioned and unconditioned sludge samples. The sludge samples from WWTPs have a negative value for zeta potential which means no aggregation due to electrostatic repulsion between sludge particles. Zeta potential for conditioned sludge was generally expected to be lower than the unconditioned one. When polyelectrolyte is added the repulsive forces are decreased and zeta potential approaches zero, thus allowing aggregation due to short-range attractive forces.

3.3 Sludge conditioning

The conditioning of sludge provides positively charged organic or inorganic polymers (polyelectrolyte) to neutralize the negatively charged polymer network of EPSs and improves solid-liquid separation. Conditioning decreases the stabilizing effect of EPS and increases the co-aggregation of particles and EPSs in the sludge.

The polyelectrolyte Praestol 645 BC (1-Propanaminium, N, N, N-Trimethyl-3-[(1-Oxo-2-Propenyl)Amino]-, Chloride, Polymer With 2-Propenamide) was used for conditioning through a jar test device. 1,000 ml of sludge sample was poured into a 2,000 ml beaker, the desired concentration of polymer was dosed in each backer and the solution was stirred at 200 rpm for the first 30 seconds, for rapid and complete mixing, followed by 15 minutes at 20 rpm, to enhance the formation of aggregates. Figure 3.3 shows the jar test device used during sludge conditioning in the laboratory.

Figure 3.3 - Conditioning of the sludge by jar test in the laboratory.

The effect of different polyelectrolyte dosages was studied. Polyelectrolyte solution was prepared and mixed with 1,000 ml of thickened unconditioned (TU) sludge with different dosages (2, 4, 6, 8, 10, 12 g/kg$_{DS}$), to determine the optimal polyelectrolyte dosage by using CST and zeta potential.

3.4 Mechanical dewatering methods

Different mechanical dewatering methods were carried out in the lab on conditioned sludge samples taken from WWTPs 4 and 5 in order to evaluate the maximum achievable DS content. Moreover, to study the influence of these methods on free and bound water content, the sludge cake at the end of process was examined through DSC test. The techniques studied in this work were (i) sludge compression at constant pressure, (ii) vacuum filtration and (iii) centrifugation.

3.4.1 Multiple centrifugation (MCFG)

200 ml of TC sludge sample was centrifuged in the lab at 4,000 rpm for 5 min. Afterwards, the collected supernatant was removed, and the sludge cake was furtherly centrifuged at 4,000rpm for 5 min. The test was repeated until no more supernatant could be collected.

3.4.2 Vacuum filtration (FIL)

The TC sludge sample (50 ml) was poured on a filter paper (Whatman Grade 589, Black Ribbon), placed on a Buchner funnel, fixed by a rubber funnel adaptor. By using the vacuum pump, the filtrate was collected in the flask until no more than two drops were collected in 5 minutes. After this process, the DS content of the sludge cake was measured, and DSC was carried out to measure free and bound water content.

3.4.3 Compression at constant pressure (PRS)

The compression of TC sludge was carried out in the same lab-scale device used for EDW tests (described in Section 3.5.1). The sludge was preliminarily centrifuged in the lab at 4,000 rpm for 5 min, to achieve a DS content of 8-9%. The cylindrical glass vessel was filled with centrifugated sludge sample (90 g). Constant pressure (300 kPa) was applied by a piston to compress the sludge and remove the water through the filter, placed at the bottom of the cell. The duration of the test was considered around 2 hours, when no more than two drops of water were removed from the sample in 5 minutes, meaning that the pressure application was not effective anymore in removing water from the sample. After this process, the DS content of the sludge cake was measured, and DSC was carried out to measure free and bound water content.

3.5 EDW tests

3.5.1 The lab-scale device

The laboratory scale set-up used for the study is described in Visigalli (2015). This lab scale device (Figures 3.4 and 3.5) consists of a cylindrical filtration/compression cell made of glass (176 mm high, with a diameter of 80 mm) with a double effect piston (SMC-CP96SDB32-200). The upper dimensionally stable anode DSA® (manufactured by Industrie De Nora, Milan, Italy) made of titanium coated with mixed metal oxide (Ti/MMO) is fixed to the bottom of the piston, on a support made of polytetrafluoroethylene (PTFE). At the bottom of the cell, there is a cathode made of stainless steel mesh (AISI 304), covered by a poly-trimethylene terephthalate (PTT) filter cloth to keep the sludge and let water flow through it.

Both cathode and anode are disc-shaped and are connected to the negative and the positive pole of the direct current (DC) power supply (GBC-34121070 bench scale generator, maximum 30 V/5 A). The laboratory pressurized air system was connected to the piston, equipped with a manometer and valves to set the chosen value for pressure (max 450 kPa). The filtrate water is collected in a beaker, put on a precision scale balance. The mass of collected water in a beaker against time were recorded at regular intervals of 1 minute to calculate the dewatering rate.

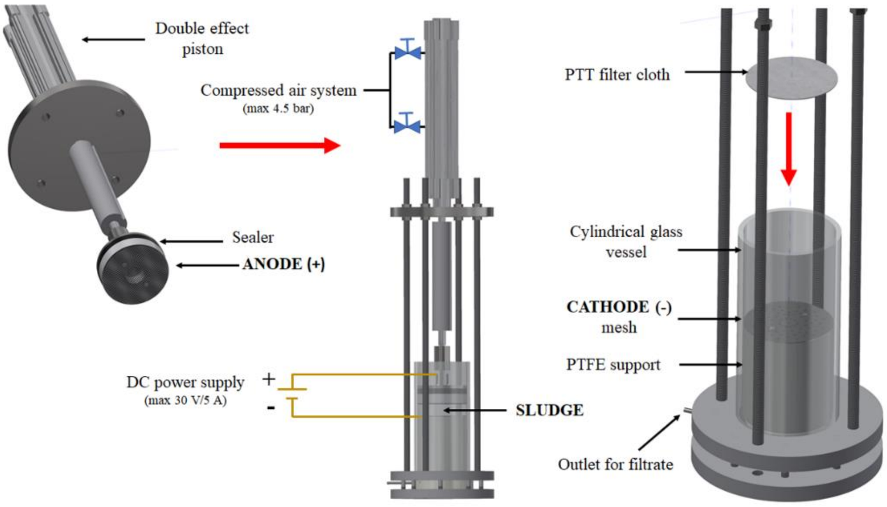

Figure 3.4 - A schematic of the lab-scale device used for EDW test.

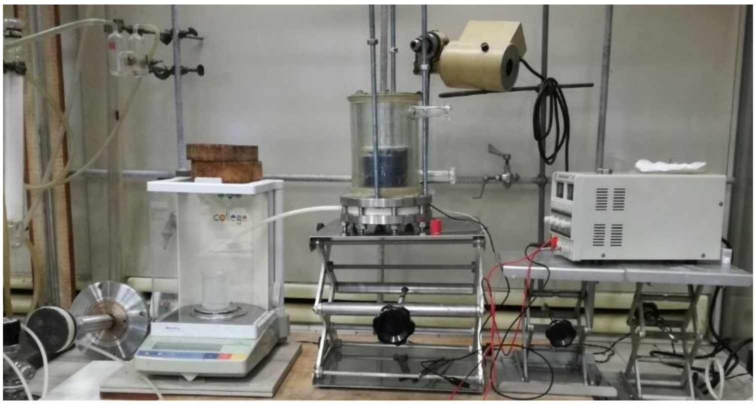

Figure 3.5 - The lab-scale device for EDW test.

3.5.2 The procedure for EDW test

Sludge samples from WWTPs 4 and 5 were used for EDW test under different operating conditions. For each sludge, the TC samples, after conditioning in the lab with an EDW test dosage of polyelectrolyte, and the MD samples were. The lab scale device provided mechanical pressure and an electric field to increase the dewatering rate and final DS in the sludge cake.

The procedure can be summarized as follows:

1. Centrifugation of the unconditioned (TU) or conditioned (TC) sludge samples in the laboratory (4,000 rpm for 5 minutes) to achieve a DS content around 8-9%. In case of mechanically dewatered sludge (MD), this step was not performed, since the initial DS content was 16-18% and directly used for EDW test.
2. Measuring 90-120 g of centrifuged sludge for the pressure-driven EDW test. These amounts correspond to about 15-20 mm of cake thickness on the 80-mm diameter supporting plate. 55 g of mechanically dewatered (MD) sludge was used, which corresponds to about 15 mm of cake thickness.

Table 3.2 – Sample weight with the corresponding cake thickness for EDW tests.

Sludge sample	Sample weight (g)	Cake thickness (mm)
TU or TC	90	15
TU or TC	120	20
MD	55	15

3. Filling the glass cell with the sludge weighed in step 2.
4. Filtration of the sludge sample by applying mechanical pressure (P=300 kPa) by means of the piston for the first 10 min.
5. Application of a constant electric potential to the sludge cake by means of the DC power supply. This step was carried out with different applied voltages ranging from 5 to 30 V, and different time duration (25 or 60 min). The pressure was kept constant at 300 kPa until the end of the EDW test. The total length of the EDW test was varied from 35 min (10 min pressure + 25 min EDW) to 70 min (10 min pressure + 60 min EDW).
6. From the beginning until the end of the EDW test, the mass of filtrate (water removed) and current values were recorded manually at regular intervals of 1 min.

7. Measuring the final DS content: at the end of EDW test, a sludge cake sample was put in oven (at 105 °C for 18 hours) in order to compute final DS content (Equation 3.1). The values of DS content ranged from 16% to 56%, depending on the voltage applied and the duration of the tests. To get a reliable result, each experiment was repeated twice.

3.5.3 Specific energy consumption (SEC)

As mentioned before, during the EDW test, the mass of water removed, and the electrical current value were recorded at intervals of 1 min. By using these data, DS content vs. time and current density against time were plotted. The specific energy consumption (Wh/kg$_{H2O}$) was computed from Equation 3.3 (Mahmoud et al., 2016):

$$\text{Specefic Energy Consumption} = \text{SEC} = \frac{V \cdot \sum_{j=1}^{n} I_j \cdot \Delta t}{m_{H_2O}} \tag{3.3}$$

Where:

V = Applied electric potential (V)
n = Number of recorded measures
I_j = Measured current (A)
Δt = Time interval between two recorded measures (hours)
m_{H2O} = Total mass of water removed (kg) during the polarization phase.

The total equivalent thermal energy consumption can be computed by taking into account the national electrical energy conversion efficiency (Italy) equal to 0.47 (Caputo and Sarti, 2015).

3.6 Water content measurement

To evaluate the different types of water in sludge, DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis) techniques were used. TGA was performed on TU and TC sample after centrifugation for sludge taken from WWTPs 4 and 5 to evaluate the influence of the type of sludge and the polyelectrolyte dosage on the binding energy of water with the sludge particles. DSC test was carried out using the TU, TC with different dosage of polyelectrolyte and MD samples, in order to study the influence of conditioning, mechanical dewatering techniques and EDW process under different operating conditions on free and bound water.

3.6.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a technique in which the variation in mass of the sample is measured as a function of time when it is cooled or heated in a furnace in a controlled atmosphere. This variation can be a loss of mass (liquid to gas phase) or a gain of mass (gas to liquid phase) (Figure 3.6).

On the other hand, differential thermal analysis (DTA) measures the difference in temperature between the sample and the reference as a function of time or temperature (Figure 3.7). TGA and DTA can perform simultaneously to record both variations in mass of sample and temperature as a function of time.

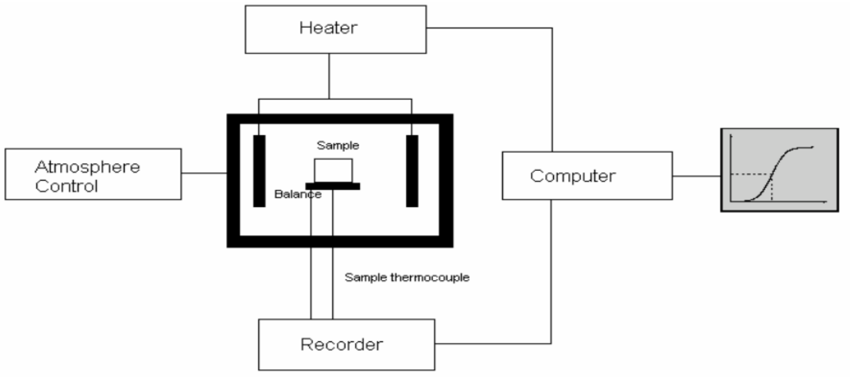

Figure 3.6 - Scheme of Thermogravimetric Analysis process (TGA).

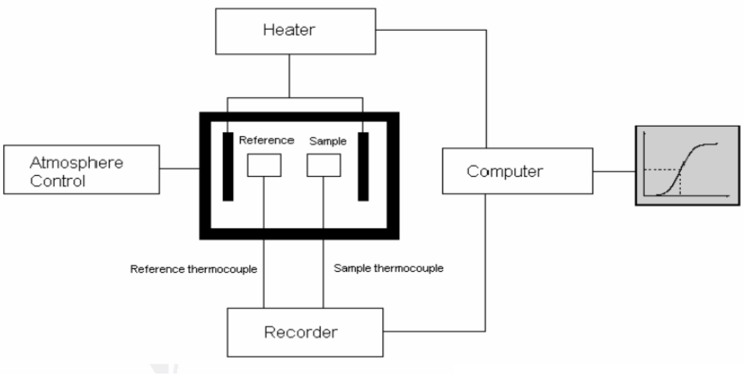

Figure 3.7 - Scheme of differential thermal analysis (DTA).

3.6.1.1 TG/DTA instrument

The measurement was carried out by using a SII EXSTAR6000 TG/DTA 6300 instrument in the lab which is designed to perform the TG and DTA measurement simultaneously (Figure 3.8). TGA utilizes a horizontal differential type balance beam which provides the highest sensitivity and stability. Some details of the instrument are listed below:

- Temperature Range: room temperature to 1500 °C;
- Balance Method: horizontal differential type;
- Maximal sample weight: 200 mg;
- Program rate: 0.01 to 100 °C/min;
- TG measurement Range/Sensitivity: 200 mg / 0.2µg;
- DTA measurement / Sensitivity: +1000 µV / 0.06µV;
- Automatic Cooling unit: forced air cooling;
- Gas flow rate: 0 to 1000 ml/min;
- Cooling rate: less than 15 min from 1000 to 50 °C;
- Atmosphere: air, inert gas;
- Sample pan material: platinum, alumina and aluminum;

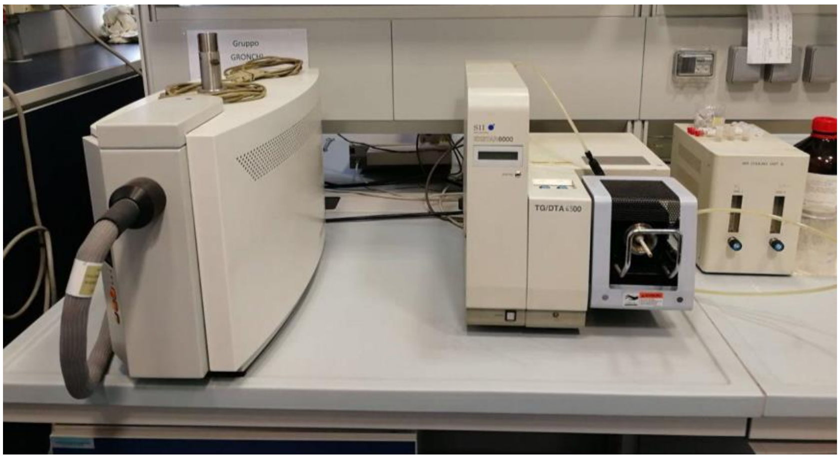

Figure 3.8 - TG/DTA instrument in the lab.

3.6.1.2 TG/DTA sample preparation and measurement procedure

The procedure for the preparation of the samples and the TGA measurement of different sludges is summarized below:

1. Centrifugation of the thickened sludge sample (unconditioned or conditioned with different dosage) to get initial DS content between 6-10%. It is important to note that a low DS content (less than 5%) leads to some errors in TGA measurement since the bound water content is too low with respect to free water. On the contrary, a high DS content (higher than 15%) means that the free water content in the sludge sample has been mostly lost during the test, according to G. W. Chen et al. (1997). Therefore, centrifugation of the sludge samples aims at getting a DS content of about 10%.
2. Weighing the sludge sample before starting the experiment.
3. Usually, the maximum sample weight for TG/DTA instrument is 200 mg since a considerable sample weight can increase the heat and mass transfer resistance within the sludge sample. Furthermore, moisture evaporation from an oversized sample results in higher substantial latent heat of water which may exceed the heater capacity of the analyzer. The mass of samples during the experiment were ranging from 20 to 30 mg.

4. Place the weighed sample in a pan (crucible dish) positioned in a furnace on a quartz beam attached to an automatic recording balance.
5. Drying the sample at constant conditions (heating rate of 1 °C/min, temperature 20 °C to 80 °C, 70 min). First, the cell temperature (T-cell) heated up from 20 °C; then the surroundings reach the set temperature. By increasing the cell temperature, the sample mass is reduced due to water evaporation (moisture loss).
6. The balance records the sample weight versus time during the drying procedure. The thermocouple is positioned in direct contact with the sample holder, to measure the precise temperature variation between the sample cell and the reference cell.
7. The drying rate curve is monitored in the computer through the instrument software, from which the water distribution can be derived.
8. Plotting the combined TGA/DTA test based on the recorded values of time, temperature, DTA and TGA. Excel sheet of recorded values and the curve for the interpretation of results were provided by the instrument.

3.6.1.3 TGA measurement of bound water

TGA method is commonly used to determine the composition of materials and to predict their thermal stability, by measuring their weight loss or gain due to sorption/oxidation or desorption/reduction of volatiles.

Although this method is not commonly used to measure enthalpies, our aim is to use TGA to evaluate the enthalpies of water in the sludge sample by comparing it with pure water as a reference (Chen et al., 1997). Differential thermogravimetry (DTG) numerically evaluates the mass loss as a function of time (mg/min), which is known as a derivation of TGA ($DTG = \dot{m} = d(TGA)/dt$). DTA data corresponds to the difference in temperature between the sample cell and the reference, which is recorded as the difference in voltage of the thermocouple.

Since TGA and DTA tests are conducted simultaneously, the specific enthalpy for moisture evaporation can be calculated by division ($\Delta H = Q/\dot{m}$, J/g) if the enthalpy flow is entirely used in moisture evaporation. When $\Delta H = \Delta H_{bw}$, that is the standard enthalpy change for the bulk water, water in the sludge sample exhibits the same energy level as the bulk water and is considered as free water, since it has the same physical and chemical properties of bulk water (Tsang and Vesilind, 1990). If, on the other hand, $\Delta H > \Delta H_{bw}$, the difference, $\Delta H - \Delta H_{bw}$, which is called water bond strength, should be attributed to the existence of a solid phase (the sludge particles). A larger bond strength corresponds to a lower water energy level, which requires more enthalpy to evaporate water (Chen et al., 1997).

Figure 3.9 shows TGA (g or %), DTG (mg/min), DTA (µV) and T_{cell} (°C) in the same plot as a function of time (s) for pure water (a) and a sludge sample (b).

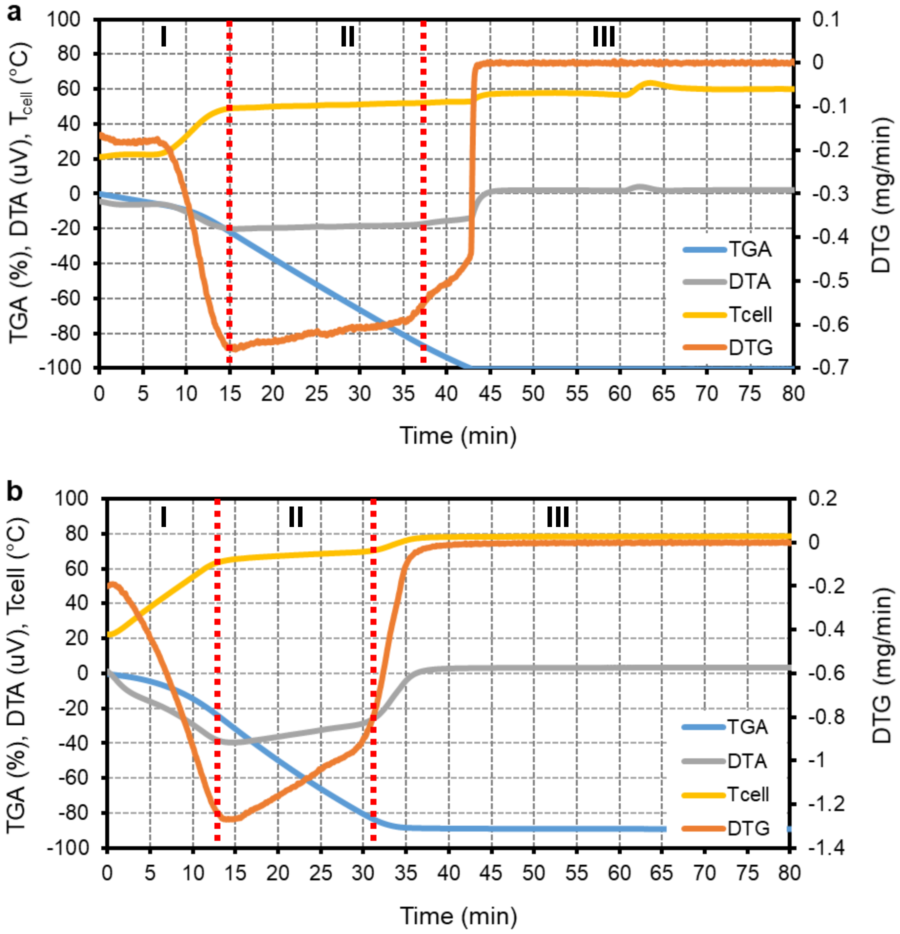

Figure 3.9 - Examples of TGA/DTG/DTA and T_{cell} diagrams for pure water (a) and sludge sample (b).

The sample mass decreases as the cell temperature increases, due to water evaporation. The phase II of the TGA test for pure water yield a nearly constant evaporation rate (DTG), and the corresponding DTA data are also constant (constant temperature difference between the sample cell and the surroundings). Therefore, the heat flow into the cell is entirely used for water evaporation.

For the test on sludge, the “constant” DTG period is rather short and lower in value when compared with the pure water test, due to the presence of impurity or dissolved electrolytes, which results in vapor pressure reduction.

At the end of stage II, when the DTG values fall down rapidly (falling rate period), water exhibits a higher resistance to evaporation and is bound more tightly than free water.

When all removable water is exhausted, the process enters stage III. In contrast to the pure water test, there exists the residue solid phase in the final sludge sample (Chen et al., 1997).

In order to measure the bound water content through this method, the time which shows the end point of DTG falling rate is recorded. DS content, bound water content (g/g_{DS}), bond strength (J/g), evaporation heat of sludge (J/g) and heat flow rate corresponding to the recorded time are calculated.

The water-solid bond strength can be useful as a valid index for a continuous classification, by providing an upper energy level to classify the type of water: as a result, the water with a bond strength lower than the upper energy level can be classified as free water.

The heat flow to the sample cell is calculated by using Equation 3.4. The effective heat transfer area of the sludge has a small contribution in heat transfer due to slight changes with time during the test. Moreover, the parameters $A{\cdot}h$ and a are difficult to measure precisely. So, the group $A{\cdot}h{\cdot}a$ is calculated by experimental data (Equation 3.6) in which Q is obtained from Equation 3.5. For the sludge sample the group $A{\cdot}h{\cdot}a$ is assumed to be constant in both pure water and sludge sample.

Based on Equation 3.5, the evaporation heat of moisture at 25 °C can be obtained through DTG results.

$$Q = A{\cdot}h{\cdot}\left(T_{ref} - T_{cell}\right) = A{\cdot}h{\cdot}a{\cdot}V \tag{3.4}$$

When the heat flows to the cell is wholly utilized for moisture evaporation:

$$Q = \dot{m}[H_0 - (C_{PW} - C_{PV})(T_{cell} - 25)] \tag{3.5}$$

$$A \cdot h \cdot a = \frac{\dot{m}[H_0 - (C_{PW} - C_{PV})(T_{cell} - 25)]}{V} = k_w[H_0 - (C_{PW} - C_{PV})(T_{cell} - 25)] = k_w H_{Tev} \quad (3.6)$$

Where:

Q = Heat flow into the sample cell (J/g)
A = Effective heat transfer area (m^2)
h = Average heat transfer coefficient ($W/m^2 \cdot K$)
T_{ref} = Reference temperature (K)
T_{cell} = Cell temperature (K)
a = proportionality constant between ΔT and DTA
V = DTA (V)
$\dot{m}$ = Mass flow rate, or DTG (g/s)
H_0 = Heat of evaporation of water at 25 °C
C_{PW}, C_{PV} = Heat capacities for liquid phase and vapour-phase of water (J/gK)

For pure water, a linear correlation is observed between DTG ($\dot{m}$) and DTA (V) which is called K_W (proportionality constant) and can be calculated from the slope (angular coefficient) of the curve in Figure 3.10.

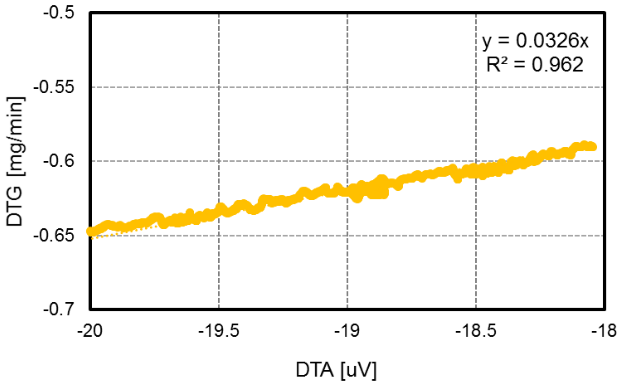

Figure 3.10 - Calculation of K_W (proportionality constant).

The measure of the bound water content consists in the calculation of the bond strength (H_B) between the moisture and the solid phase (Equation 3.7).

$$H_B = H_{0,\ sludge} - H_{0,\ water} \quad (3.7)$$

Where:

H_0= heat of evaporation at 25 °C, kJ/kg
H_B = bond strength

When bond strength is approaching zero, the heat of evaporation for moisture in the sludge is equal to the heat of vaporization for bulk water, which corresponds to the same energy level. This portion of moisture in the sludge is considered as free water content. The bond strength increases when the remaining moisture content decreases.

3.6.2 Differential scanning calorimetry (DSC)

DSC is a technique in which the differences in heat flow between sample and reference is measured during its cooling or heating. In other words, DSC measures the electrical power (heat) required to keep the sample and the reference at the same temperature (Figure 3.9).

The peak area directly corresponds to the heat consumed or produced by the sample.

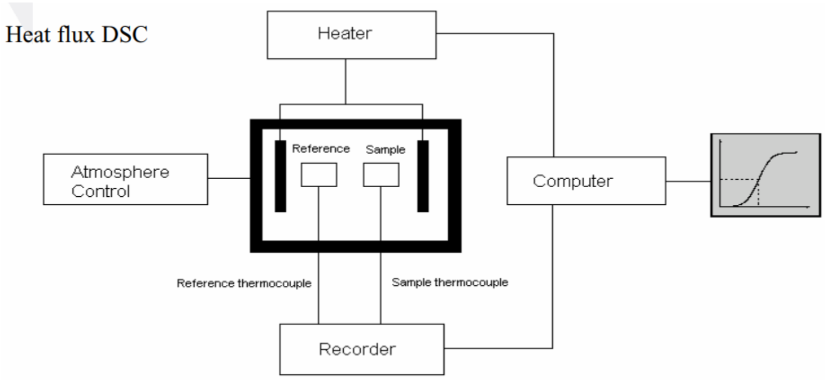

Figure 3.11 - Scheme of differential scanning calorimetry (DSC).

3.6.2.1 DSC instrument

The measurement was performed by using the SII EXSTAR6000 DSC instrument (Figure 3.10).

Figure 3.12 - DSC instrument in the lab.

3.6.2.2 DSC sample preparation and measurement procedure

The assumption for this method is that the bound water remains unfrozen to up to a threshold temperature, assumed to be -20/-30°C for sludge samples (Deng et al., 2011; Erdincler and Vesilind, 2003; Hong et al., 2015)
The procedure used for DSC measure is listed below:

1. TU, TC sludge with different polyelectrolyte dosages, MD sludge samples were studied by DSC. Furthermore, the sludge cake after EDW test under different voltages and time durations were also included.
2. Weighing the sample. The sample weight was in the range 10-20 mg.
3. The sludge sample temperature decreases at the constant rate of 1 °C/min down to -20 °C, then increases up to 20 °C at the same rate. The analyser is equipped with nitrogen cooling system.
4. The endothermic or exothermic curve is monitored by a computer.

3.6.2.3 DSC measurement of bound water

The integration of the peak area of the endothermic curve corresponds to the heat absorbed during the process while the exothermic curve is related to the amount of heat released. To calculate the free water content in sludge, the area of the endothermic peak below the baselines is calculated. Since this area corresponds to the amount of heat that is required to melt the frozen water (free water), the heat uptake during the phase transition of free water can be calculated with Equation 3.8:

$$W_{free} = \frac{\Delta H}{\Delta H_0} \tag{3.8}$$

Where:

ΔH: the amount of heat absorbed in the melting process (J/g_{DS})
ΔH_0: water heat of melting (J/g water)
W_{free}: free water content (g/g_{DS})

Therefore, the amount of bound water was determined as a difference between total water content and free water content of the sludge (Equation 3.9).

$$W_B = W_{tot} - \frac{\Delta H}{\Delta H_0} \tag{3.9}$$

Where:

W_B = Bound water content (g/g_{DS})
W_{tot} = Total water content (g/g_{DS})
ΔH = Heat absorbed in the heating stage (J/g_{DS}) (DSC enthalpy of the sludge sample)
ΔH_0 = Standardized melting heat of ice (J/g water) = 334.7 kJ/kg

4. Results and discussion

In this Chapter, the results of preliminary characterization tests of the sludge samples from different WWTPs and the pressure-driven EDW experiments are described in details. The EDW tests have been carried out on unconditioned, conditioned and mechanically dewatered sludge samples taken from different WWTPs, at different operating conditions, such as the applied electric potential, the initial cake thickness and the duration of the tests. The results, in terms of final DS content and specific energy consumption, highlighted the efficiency and feasibility of EDW. Furthermore, in order to study the EDW operating conditions that are affecting the free and bound water content, results of DSC method are reported. The influence of different polyelectrolyte dosage and different mechanical techniques on free and bound water content in sludge are described through DSC and TGA results.

4.1 Sludge characterization and conditioning

In this section, in order to investigate the dewatering properties of sludge, the results of characterization tests on unconditioned, conditioned and mechanically dewatered sludge belonging to different WWTPs is reported. Table 4.1 lists the average and standard deviation values of main characteristics of sludge samples collected from five different WWTPs. DS_i and VS/DS indicate the dry solid content and the ratio between volatile solid and dry solid respectively.

Table 4.1 - Main characteristics of samples from different WWTPs.

WWTP No.	ID	Polymer dosage	pH	Conductivity	CST	Zeta potential	DS$_i$	VS/DS
		g/kg$_{DS}$	-	mS/cm	s	mV	wt%	wt%
1	**TU**	0.0	7.2 ± 0.23	1.2 ± 0.10	17.8 ± 0.03	-9.4 ± 0.38	2.0	61.9
	TC	6.0	7.0 ± 0.29	1.3 ± 0.12	9.5 ± 1.56	-7.4 ± 0.55	1.9 ± 0.01	61.9
2	**TU**	0.0	6.9 ± 0.17	2.3 ± 0.11	53.0 ± 4.30	-13.9 ± 0.81	3.6	61.8
	TC	8.0	6.9 ± 0.12	2.3 ± 0.09	10.1 ± 1.16	-10.2 ± 0.53	3.2 ± 0.01	61.8
3	**TU**	0.0	6.9 ± 0.10	1.4 ± 0.03	15.5 ± 0.15	-11.0 ± 0.53	2.2	70.7
	TC	6.0	6.7 ± 0.12	1.4 ± 0.11	8.8 ± 1.30	- 8.8 ± 0.38	2.3 ± 0.02	70.7
4	**TU**	0.0	6.8 ± 0.26	1.4 ± 0.11	23.6 ± 5.40	-12.1 ± 0.63	3.1 ± 0.65	63.4 ± 6.05
	TC	6.0	6.7 ± 0.17	1.4 ± 0.13	10.7 ± 1.06	-7.8 ± 1.30	3.0 ± 0.54	66.6 ± 6.70
	MD	5.3*	6.8 ± 0.10	0.2 ± 0.03	NA	NA	17.3 ± 0.93	67.3 ± 7.65
5	**TU**	0.0	7.1 ± 0.15	5.5 ± 0.66	188.6 ± 6.92	-10.2 ± 0.91	3.4 ± 0.14	62.9 ± 2.64
	TC	10.0	7.3 ± 0.18	5.5 ± 0.97	10.9 ± 2.36	-7.5 ± 0.86	3.4 ± 0.19	64.1 ± 1.47
	MD	15.4**	7.0± 0.02	0.7 ± 0.02	NA	NA	22.9 ± 0.69	59.8

* Conditioning at WWTP with TILLFLOCK CL1480
** Conditioning at WWTP with PRAESTOL 645BC

Thickened unconditioned (TU) sludge and mechanically dewatered (MD) sludge were taken directly from the corresponding WWTPs. Thickened conditioned (TC) samples refer to sludge conditioned with polyelectrolyte Praestol 645 BC through jar test in the laboratory. The reported polymer dosages correspond to the dosage of polyelectrolyte used in EDW test, studied in preliminary tests by CST and zeta potential measurements.

A key requirement for any WWTPs is to obtain an optimal dosage of polyelectrolyte in sludge, since the addition of an excess of polyelectrolyte leads to waste of money without an effective increase in sludge dewaterability. As already explained in Chapter 3, an optimal polymer dosage usually refers to the dosage at which the electrostatic repulsive forces are sufficiently reduced and the value of the zeta potential is closer to ± 0 mV.

Table 4.2 summarizes pH, conductivity, CST and zeta potential values of the sludge samples from WWTP 4 before (0 g/kg$_{DS}$) and after conditioning with different dosages.

Table 4.2 - Characteristics of the sludge sample from WWTP 4 before and after conditioning with different polymer dosages by jar test in the lab.

Polymer dosage	pH	Conductivity	CST	Zeta Potential
	-	mS/cm	s	mV
0 g/kg$_{DS}$	6.7	1.5	22.9	-12.6 ± 0.31
2 g/kg$_{DS}$	7.1	1.4	11.7	-12.1 ± 0.15
4 g/kg$_{DS}$	7.2	1.4	11.2	-10.9 ± 0.26
6 g/kg$_{DS}$	7.2	1.4	7.1	-9.9 ± 0.28
8 g/kg$_{DS}$	7.2	1.5	6.3	-8.4 ± 0.01
10 g/kg$_{DS}$	7.1	1.5	6.9	-9.3 ± 0.28
12 g/kg$_{DS}$	7.2	1.5	6.3	-8.5 ± 0.35

It is clear from Table 4.2 that adding a higher dosage of polyelectrolyte leads to a reduction in both CST and absolute value of zeta potential, which implies that a good flocculation of sludge particles is achieved. Indeed, aggregation of particles promotes filterability of the sludge (lower CST value compared to original sludge) and leads to a decrease in zeta potential value, which approaches to zero. There is an evident reduction in CST values from 22.9 s to 11.7 s before and after conditioning with a polyelectrolyte dosage of 2 g/kg$_{DS}$. On the contrary, the zeta potential value does not change significantly at this dosage with respect to the TU sample. Moreover, at high dosages (8-12 g/kg$_{DS}$) CST values do not decrease to less than 6.3 s. Zeta potential follows the same trend and does not decrease to less than -8.4 mV. CST and zeta potential values corresponding to a polymer dosage of 6 and 10 g/kg$_{DS}$ are close to each other, which means that the addition of high polyelectrolyte doses is not effective in reducing CST and zeta potential. Conductivity and pH values remain approximately constant from one dosage to another, so that these two parameters seem to not have any correlation with polyelectrolyte dosage. From the economic point of view, a trade-off must be reached between the reduction of CST and zeta potential on the one hand and minimum dosage of polyelectrolyte on the other. As a result, we set 6 g/kg$_{DS}$ as a polyelectrolyte dosage in sludge sample used in EDW test for sludge from WWTP 4.

For sludge from WWTP 5, we did not apply the minimum and maximum dosage of polyelectrolyte (2 and 12 g/kg$_{DS}$), as we know that the former is not enough to be effective and the latter maybe excessive. Table 4.3 summarizes the characteristics of the sludge sample from WWTP 5 before and after conditioning with different dosages of polyelectrolyte.

Table 4.3 - Characteristics of the sludge sample from WWTP 5 before and after conditioning with different polymer dosages by jar test in the lab.

Polymer dosage	pH	Conductivity	CST	Zeta Potential
	-	mS/cm	s	mV
0 g/kg$_{DS}$	6.9	3.9	114.4	-10.2 ± 0.91
4 g/kg$_{DS}$	6.9	3.7	57.3	-9.5 ± 0.46
6 g/kg$_{DS}$	7.0	3.7	54.5	-7.6 ± 0.27
8 g/kg$_{DS}$	7.1	3.7	45.0	-8.9 ± 0.74
10 g/kg$_{DS}$	7.1	3.8	13.7	-7.5 ± 0.86

A similar trend to samples from WWTP 4 was found for sludge from WWTP 5. According to Table 4.3, CST values significantly reduce by increasing the polyelectrolyte dosage. Also in this case, at polymer dosages of 6 and 10 g/kg$_{DS}$, the values of the zeta potential are close to each other, but a dosage of 10 g/kg$_{DS}$ provides better filterability due to the considerabily lower value of CST. Therefore, we set 10 g/kg$_{DS}$ as the dosage to be used in the EDW tests. The pH and conductivity values did not change considerably by adding a higher polyelectrolyte dosage in this range.

For the sludge samples from WWTPs 1, 2 and 3, we tested the polymer doses in the same range of the previous sludge samples (6, 8, 10 g/kg$_{DS}$). A sufficient reduction in CST and zeta potential values were obtained at dosage of 6 g/kg$_{DS}$ for WWTPs 1 and 3, and 8 g/kg$_{DS}$ for WWTP 2 (Table 4.1).

It should be noted that for all the sludge samples, the dosage used in the lab was lower compared to the one used in the corresponding WWTPs.

4.2 Pressure-driven EDW tests

The results of the pressure-driven EDW tests, in terms of final DS content achieved and the specific energy consumption (SEC) are discussed in this section. The main aim of this research was to assess the feasibility of the EDW process on different types of sludge under different operating conditions. EDW process was carried out on sludge samples taken from WWTP 4 (aerobically stabilized sludge) and 5 (anaerobically digested sludge).

4.2.1 Influence of electric potential and cake thickness

As a first step, the TU sludge sample from WWTP 4 was tested to study the influence of the cake thickness on the EDW process efficiency. Table 4.4 summarizes the main characteristics of the sludge sample before EDW. The initial DS content of the sludge after centrifugation was 8.5%. 90 and 120 g of centrifuged sludge, corresponding to a cake thickness of about 15 and 20 mm respectively, were tested

1) under pressure application only (constant pressure at 300 kPa for 35 min) and
2) pressure-driven EDW process to compare the final DS achieved by the two dewatering processes. Pressure-driven EDW tests were carried out by applying constant pressure (3 bar) for 10 min, followed by a constant potential (10, 15 and 20 V) for 25 min to evaluate the best cake thickness at different voltages.

Table 4.4 - Characteristics of the TU sludge sample taken from WWTP 4 used in EDW tests.

WWTP No.	Sample ID	pH	Conductivity	CST	Zeta Potential	DS_i	DS_{CFG}*	VS/DS
		-	mS/cm	s	mV	%	%	%
4	TU	6.7	1.5	8.6	-12.6	2.3	8.5	70.4

*CFG = centrifuged sludge

Figure 4.1 shows the current density over time of the EDW test at 10, 15 and 20 V for two initial cake thicknesses (15 mm and 20 mm). In general, at the beginning of the cake formation stage, the electrical resistance of the cake is lower which leads to an increase in the current density. By continuing the process over time, the cake is dryer and increases the electrical resistance, thus reducing the measured electrical current (Tuan, 2011). The current density increases by applying greater voltages for both the sludge masses. Plots of EDW tests at 10 V show a slight growth towards the end of the test, while, at 20 V they show a significant up and down in current density over time. The lines corresponding to 15 V reveal a trend between the two.

The current density values are higher for the test with a cake thickness of 15 mm (90 g) with respect to the test with a cake thickness of 20 mm (120 g), at equal electric potential applied.

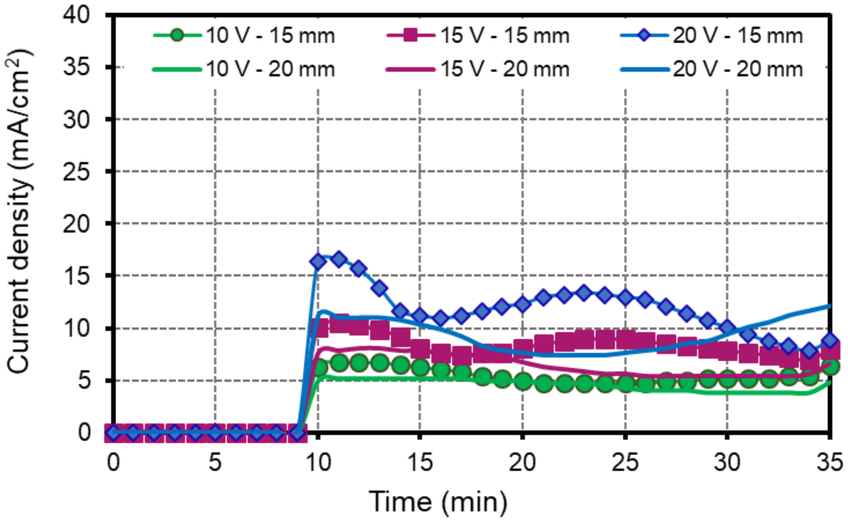

Figure 4.1 - Current density of EDW test at 10, 15, 20 V for sludge sample 3-TU with initial thicknesses of 90 g (15 mm) and 120 g (20 mm).

Figure 4.2 shows the final DS and SEC values achieved during the EDW test. According to the chart, there is an upward trend in final DS content by increasing the applied electric potential for both the cake thicknesses and this increase is faster for a sludge mass of 90 g. As an example, the final DS achieved after EDW at 15 V was 35.0% for the test with a cake thickness of 15 mm and 19.8% with a cake thickness of 20 mm, respectively. Therefore, the thicker cake provides lower final DS content for all the electric potentials. This result was confirmed by Conrardy et al. (2016), who showed that the thinner sludge cake has a faster dewatering rate under the constant potential condition, because of higher electric field intensity and can get achieve a dryer cake.

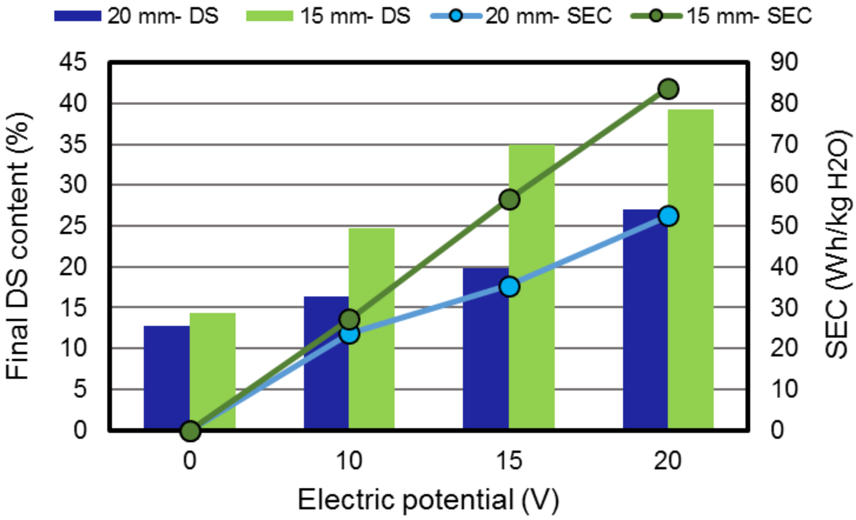

Figure 4.2 - Final DS content and SEC of EDW tests conducted at 0, 10, 15, 20 V and with a cake thickness of 15 mm (90 g) and 20 mm (120 g).

Energy consumption follows the same trend as final DS content in both cases. An increase in energy consumption by increasing the electric potential. The energy consumption is lower in thicker cake compare to a thinner one since lower electric current developed in thicker cake due to the higher distance between electrodes. Similarly, Citeau et al. (2012) reached the same conclusion .Based on the chart, the maximum energy consumption value was around 84 Wh/kg$_{H2O}$ belonging to the 90gr mass of sludge under 20 V which is lower than the energy consumption by thermal drying. The typical value of energy consumption of dryers is around 1000 Wh/kg$_{H2O}$ (Mahmoud et al., 2011a). Therefore, EDW process is economically feasible rather than thermal drying. To sum up, we can state that by increasing the voltage, the final DS content increased, but at the expense of higher energy consumption and the thinner cake shows better results under all the voltages during EDW process. For the following tests, 90 g (15 mm) of sludge masses were chosen for unconditioned and conditioned sludges. 55 g of mechanically dewatered sludge provides the same thickness (15 mm).

4.2.2 Influence of electric potential and types of sludge

To evaluate the feasibility of EDW process on different types of sludge, two sludge samples, aerobically and anaerobically digested (taken from WWTPs 4 and 5 respectively), were tested after conditioning by applying a constant potential (5, 15 and 25 V) for 25 min to assess the best compromise between final DS content and energy consumption. The same operating conditions were applied to MD sludge from the same WWTPs, after belt pressing and centrifugation respectively. Centrifugation provides higher DS content (5-MD) compared to belt press in WWTP 4 (4-MD). Table 4.5 reports the initial DS content, DS after centrifugation for conditioned sludge and the ratio between VS and DS of the sludge samples.

Table 4.5 - Summarized initial DS content, DS after centrifugation and VS/DS ratio for the sludge sample under EDW test at 5, 15 and 25 V.

Sample ID	DSi	DS_{CFG}	VS/DS
	%	%	%
4-TC	3.30	9.5	60.0
4-MD	17.8	-	57.6
5-TC	3.28	10.57	64.08
5-MD	22.43	-	59.84

Figures 4.3 and 4.4 show the current density over time plots corresponding to the EDW tests on the TC and MD samples. As mentioned above, the higher voltage application implies a greater value of current density. Both the two sludge samples show the same behaviour under EDW process at a constant voltage. At the same voltage, 5-TC and 5-MD sample shows greater starting

point with respect to samples from WWTP 4. Even though current densities for EDW tests on samples from WWTP 5 are higher at the beginning of the polarization phase, they reached nearly the same value of aerobically digested samples at the end of the tests (around 8 mA/cm^2).

According to Figure 4.3, there is a significant up and down in the lines for 25 V related to 4-TC. On the contrary, Figure 4.4 shows a sharp decrease of current density values for anaerobically digested sludge samples.

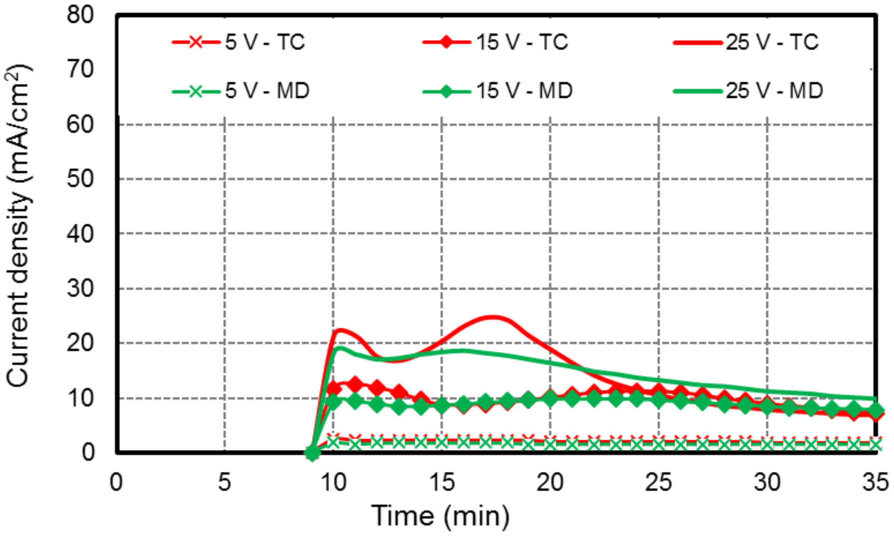

Figure 4.3 - Current density vs. time of EDW tests at 5, 15, 25 V for TC and MD sludge from WWTP 4.

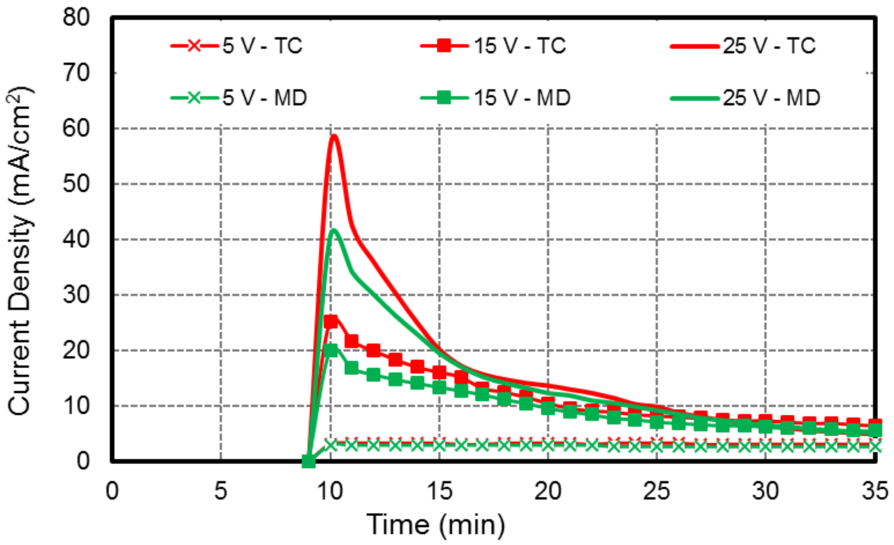

Figure 4.4 - Current density vs. time of EDW tests at 5, 15, 25 V for TC and MD sludge from WWTP 5.

According to Table 4.1, the electric conductivity of 5-TC is around 3 times higher if compared to 4-TC, which leads to higher current density values and higher specific energy consumption, in spite of a similar final DS content. The influence of different electrical conductivity values is more pronounced at 15 and 25 V, in terms of current density and energy consumption, while at 5 V there is not any remarkable change between the two sludge samples.

Figure 4.5 displays the corresponding specific energy consumption and DS content after EDW at different electric potentials (5, 15, 25 V) for TC and MD sludge samples from WWTP 4 and 5.

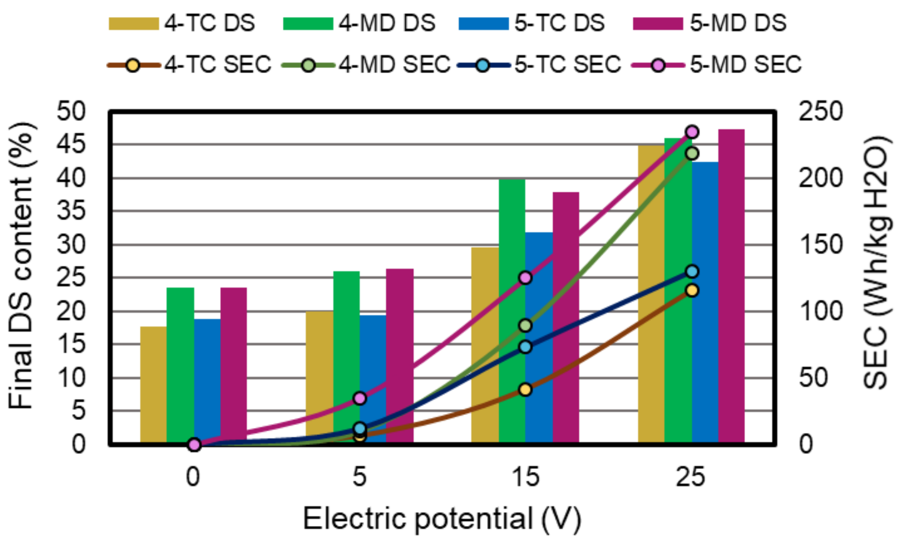

Figure 4.5 - Final DS content and specific energy consumption of EDW test for anaerobically and aerobically digested sludge at 0, 5, 15 and 25 V for both TC and MD sludge samples.

In all the sludge samples, by applying higher voltage, there is an increase in terms of final DS and SEC, since the application of greater voltage leads to an increase in the strength for water extraction.

In absence of electric potential, pressure play the main role in the dewatering process, which can be improved by adding the polyelectrolyte. In general, the DS content achieved for MD samples after the application of mechanical pressure only is higher than the DS achieved after belt pressing and centrifugation, which means that the mechanical dewatering efficiency in the two WWTP could be furtherly improved. At 15 and 25 V the influence of the pressure-driven phase becomes lower and the final DS contents are not too much different between the sludge samples.

The SEC is similar at 5 V for aerobically digested sludge samples (less than 10 Wh/kg$_{H2O}$). However, greater SEC values are entailed for anaerobically digested sludge due to the higher electrical conductivity (12.33 and 30.84 Wh/kg$_{H2O}$ for 4-TC and 5-TC respectively). At 15 and 25 V, there is a huge increase in the energy consumption value, especially for MD samples which have higher DS$_i$ content and dissipate electric energy in heat due to Joule effect. Indeed, the SEC value for MD samples is around twice of TC samples at 15 V and 25 V. As an example, SEC for MD sample from WWTP 4 at 15 and 25 V was 89.6 Wh/kg$_{H2O}$ and 219 Wh/kg$_{H2O}$, which is twice the SEC of TC sample, namely 57.1 Wh/kg$_{H2O}$ and 109.7 Wh/kg$_{H2O}$, respectively.

According to Olivier et al. (2014) and (Mahmoud et al., 2016), free water content can be removed by chemical and mechanical methods, while removing bound water content with higher binding strength requires more energy (Guo et al., 2018).

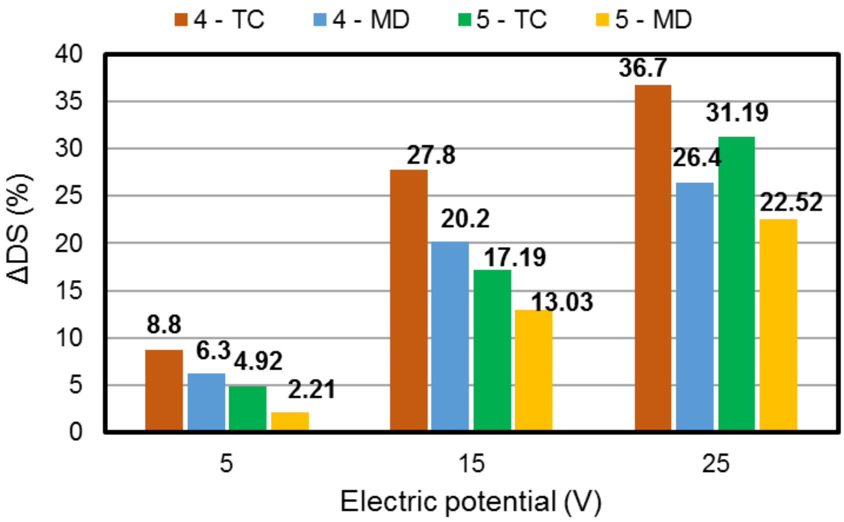

Figure 4.6 - Difference between final DS content after EDW test and DS content achieved after 10 min of pressure-driven phase.

Figure 4.6 shows the difference between the final DS content achieved after the EDW test and the DS content achieved after 10 min of pressure-driven phase (DS$_P$). The DS$_P$ was 11.2%,19.6%,14.0% and 23.5% for sludge sample 4-TC, 4-MD, 5-TC and 5-MD respectively.

Even though the final DS content was approximately the same at 25 V for all the sludge samples (Figure 4.5), the changes in DS content during EDW test is higher in aerobically digested sludge samples (4-TC and 4-MD) that started with a lower DS$_P$ compared to the anaerobically digested samples. As an example, sample 4-TC had a DS$_P$ equal to 11.2% for the first 10 min, and, by applying an electric potential of 5, 15 and 25 V, the corresponding final DS was

20.0%,30.0% and 45.0%. On the other hand, sample 5-TC started from a DSP of 14.0% and achieved a final DS of 19.3%, 31.8% and 42.4%, by increasing the voltage.

To sum up, the EDW process is more efficient on aerobically stabilized sludge, since the developed current densities are lower, due to the lower conductivity and the lower energy entailed by the process, if compared to anaerobically digested sludge. Indeed, mechanical dewatering on anaerobically digested sludge, due to its lower organic fraction, is more efficient than on aerobically stabilized sludge and EDW leads to a lower DS content increase.

4.2.3 Influence of electric potential and the test duration

To evaluate the influence of test duration at different applied electric potentials on the EDW efficiency, tests, as described in the previous section, were carried out on both aerobically and anaerobically digested and conditioned sludge, by increasing the time duration up to 70 min (10 min of compression + 60 min of electric potential at 5, 15 and 25 V). Figure 4.7 shows the results achieved in terms of final DS content and energy consumption for conditioned sludge in the two different time durations of the test.

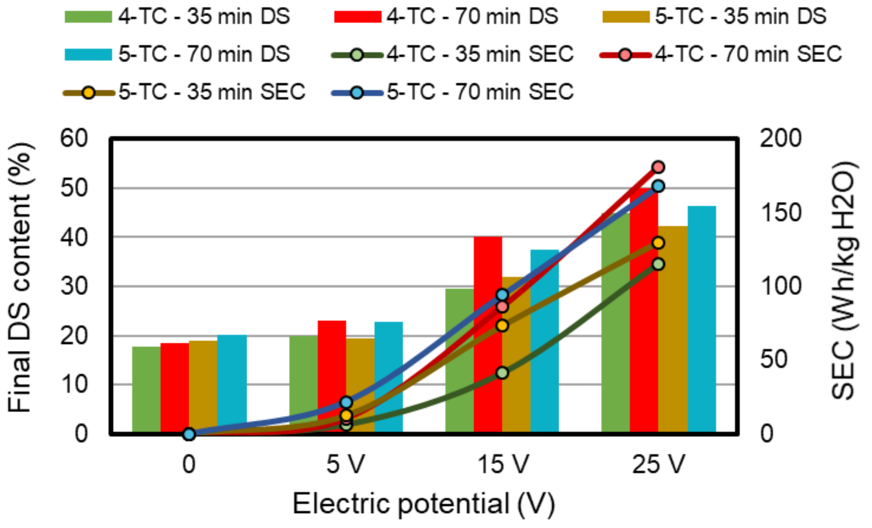

Figure 4.7 - Final DS content and SEC of EDW tests, on aerobically and anaerobically digested TC sludge sample, with a total duration of 35 min and 70 min.

The DS content after centrifugation was 9.1% and 10.5%, respectively. It is clear that the final DS content and SEC increased by applying higher voltages and extending the durations of the EDW test. The aerobically digested sample shows better results in terms of final DS content and SEC for both durations at 25 V. The difference in the SEC value for 4-TC sample after a duration of 35 and 70 min was 50 Wh/kg$_{H2O}$, while the final DS content differed of no more than 3%. The same happened for TC samples from WWTP 5, whose DS content increase of about 2% with EDW tests conducted for 70 min, but entailing 30 Wh/kg$_{H2O}$ more than tests conducted for 35 min.

As a conclusion, it should not be convenient to extend the duration of the EDW tests above 35 minutes, as the increase in SEC exceeds the gain in final DS values. This result can be seen in both anaerobically and aerobically digested sludge samples. However, a detailed economic analysis should be carried out to investigate if savings in the disposal costs, due to the lower volumes of sludge, can compensate the higher energy costs.

4.3 Types of water

This section presents a discussion of the results obtained from differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to measure the free and bound water content in sludge. Moreover, the influence of different processes such as conditioning, mechanical dewatering techniques and electro-dewatering under different operating conditions on free and bound water content in the sludge samples was examined.

4.3.1 Influence of conditioning

4.3.1.1 DSC – Bound water content

In order to identify the effect of conditioning on water content within the sludge, samples were taken from five different WWTPs and examined before and after conditioning with polymer dosage used in EDW test, using DSC method. The main characteristics of the sludge samples is summarized in Table 4.1.

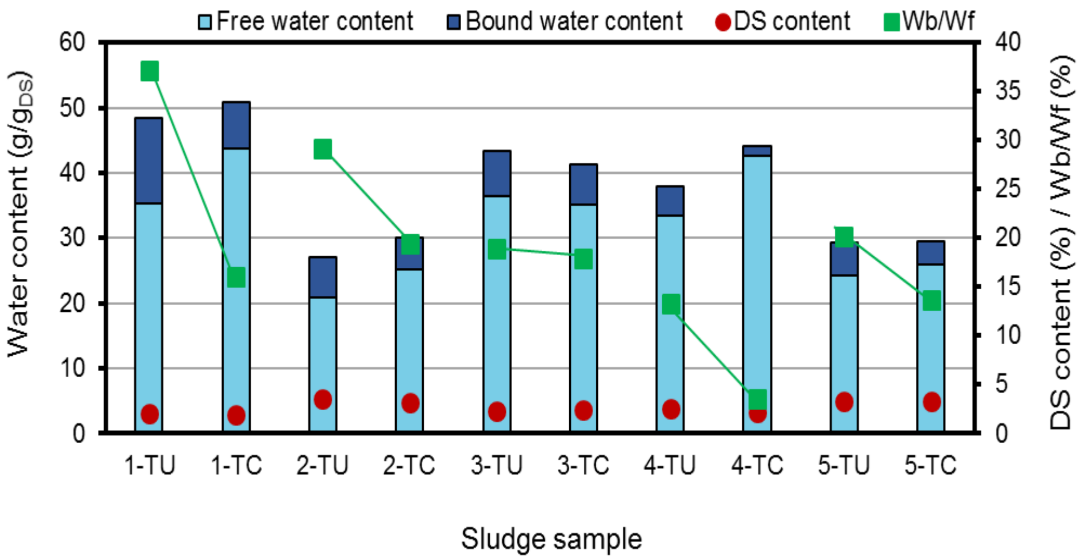

Figure 4.8 - Free and bound water content in TU and TC sludge samples taken from five different WWTPs.

Figure 4.8 shows the amount of free water (FW) and bound water (BW) content within the sludge samples before and after conditioning. The DS content of the TU and TC sludge samples and the ratio between BW and FW (Wb/Wf, %) is reported too.

In general, the FW content increases while the BW content decreases for all the sludge samples after conditioning. Addition of water during the conditioning step leads to an increase in the FW content while BW content decreases due to the migration of water, which is bound to the particles, outside the flocs. This result was confirmed by Robinson and Knocke (1992) and Katsiris and Kouzeli-Katsiri (1987). They found a reduction in BW content due to the replacement of water molecules by the polymer molecules on the solid surface, which improves the release of water. However, for sample from WWTP 3, not only the BW content decreases after conditioning, but also the FW amount decreases. This can be explained by considering the DS content of the TC sample, which was unexpectedly higher than the TU sample.

According to these results, the FW content in TU sludge samples is in the range 20.9-36.5 g/g_{DS} and the BW content is in the range 4.4-13.1 g/g_{DS}. After conditioning, the FW content ranges between 25.2 and 43.8 g/g_{DS}, while the BW content is between 1.5-7.0 g/g_{DS}. It must be considered that the sludge samples with initial DS content lower than 3% shows wider ranges in FW and BW content.

The ratio between BW and FW (Wb/Wf, %) content decreases after conditioning due to the BW content reduction and the FW content increase. A lower decrease in Wb/Wf ratio (from 18.9% to 17.9%) can be observed in sludge from WWTP 3 due to the reduction in FW content with respect to the total water content. The Wb/Wf ratio in TC samples from different WWTPs 1, 3 and 4 is not similar despite of the same dosage of polyelectrolyte used for conditioning. This means that the effect of polyelectrolyte on bound and free water is not the same for different WWTPs and that the type of polymer and its dosage need to be studied in detail to improve the dewatering efficiency.

Therefore, DSC method evidenced its reliability in the determination of the bound water content to improve the conditioning step and the following dewatering processes. The conditioning step, which can be studied by considering the sludge characteristics such as CST and zeta potential, may be improved also considering the amount of bound water content released after the addition of polymer at different dosages.

The influence of conditioning with different polyelectrolyte dosages on FW and BW was tested with sludge samples from WWTPs 4 and 5, through DSC and TGA test. Figure 4.9 displays the DSC results in terms of FW and BW with the corresponding DS content in both TU and TC sludge samples, with polyelectrolyte dosages of 4, 6, 8 and 10 g/kg_{DS}.

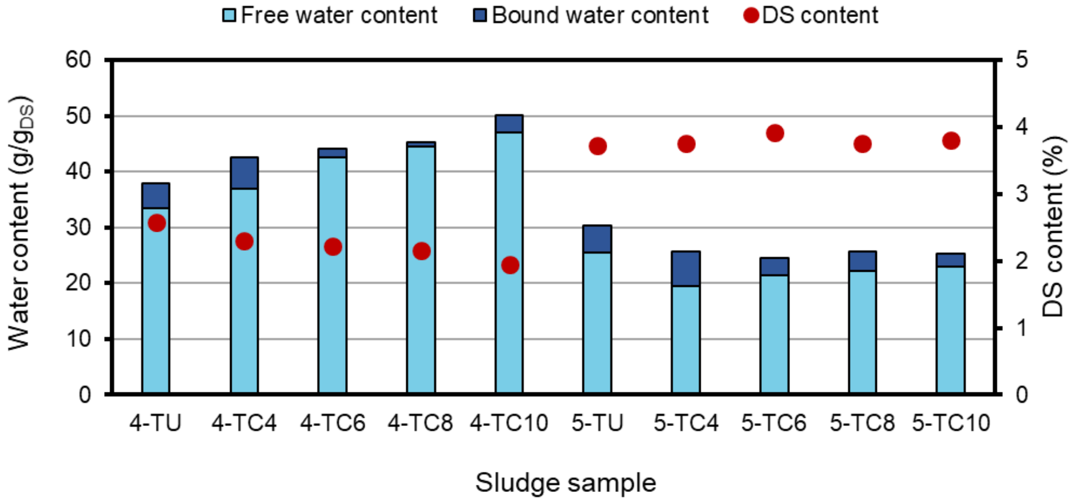

Figure 4.9 - Free and bound water content within the sludge samples taken from WWTPs 4 and 5, before and after conditioning with four different dosages.

By increasing the polyelectrolyte dosage, the FW content increases in the sludge sample taken from WWTP 4, whose total water amount tends to increase with conditioning. On the contrary, the DS content of sludge samples from WWTP 5 before and after conditioning is almost constant and the FW content is reduced after conditioning, especially with a dosage of 4 g/kg_{DS}.

In terms of BW content, both anaerobically and aerobically digested sludge samples show the same behavior. From TU to TC4, there is an increase in BW content, while, at higher polyelectrolyte dosages, it decreases until a minimum point and then increases again. The minimum value of BW content is achieved with a polymer dosage of 8 g/kg_{DS} for sludge from WWTP 4 and with 10 g/kg_{DS} for the sludge from WWTP 5. This trend was confirmed by Wu et al. (1997): at low polymer dosage, interparticle squeezing is prevalent which becomes less effective compared to water molecules adsorption at higher dosage of polymer.

It is interesting to mention that, there is a relation between zeta potential and bound water content within TC sludge samples (Figure 4.10). According to Table 4.2 and 4.3, zeta potential decreases by increasing the polymer dosage in TC sludge sample from WWTPs 4 and 5. The same trend occurred in corresponding bound water content. The dosage at which zeta potential does not follow the decreasing trend, the bound water content increases (green circles in Figure 4.10).

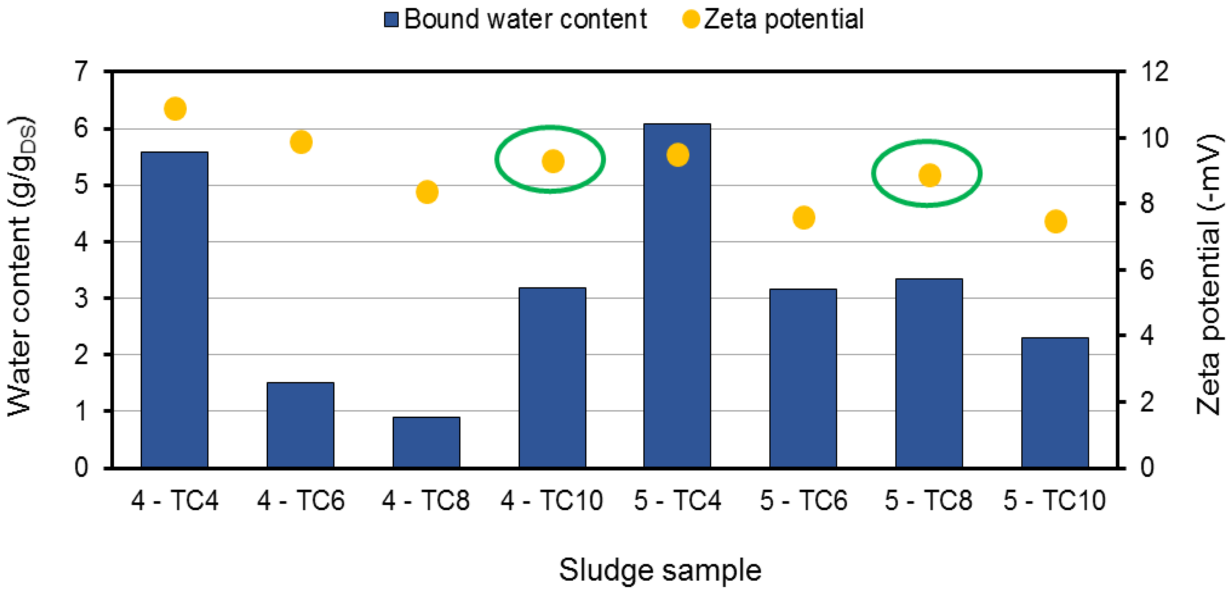

Figure 4.10 - Relation between zeta potential and bound water content in sludge sample from WWTPs 4 and 5 after conditioning with different polyelectrolyte dosages.

In general, despite of a lower DS content and a higher total water amount, the BW content of sludge from WWTP 5 is higher than sludge from WWTP 4. Only samples TC10 have the opposite trend. A higher BW content would lead to a greater energy for its removal from sludge, so the choice of the dewatering method becomes essential.

4.3.1.2 TGA – Bound water content and bond strength (H_B)

For TGA test, the thickened sludge sample (TC) was centrifuged to get initial DS content between 6-10%.

When H_B is approaching zero the heat of moisture evaporation within the sludge is equal to heat of bulk water evaporation. This point corresponds to FW content: when all FW content is removed, only BW is present in sludge. Moreover, by decreasing the total water content in sludge, the bond strength increases.

Figures 4.11 and 4.12 show the results obtained from TGA tests on sludge from WWTPs 4 and 5, after conditioning at different polyelectrolyte dosages, based on bond strength interpretation. The BW content and the corresponding DS content for different polymer dosages is marked.

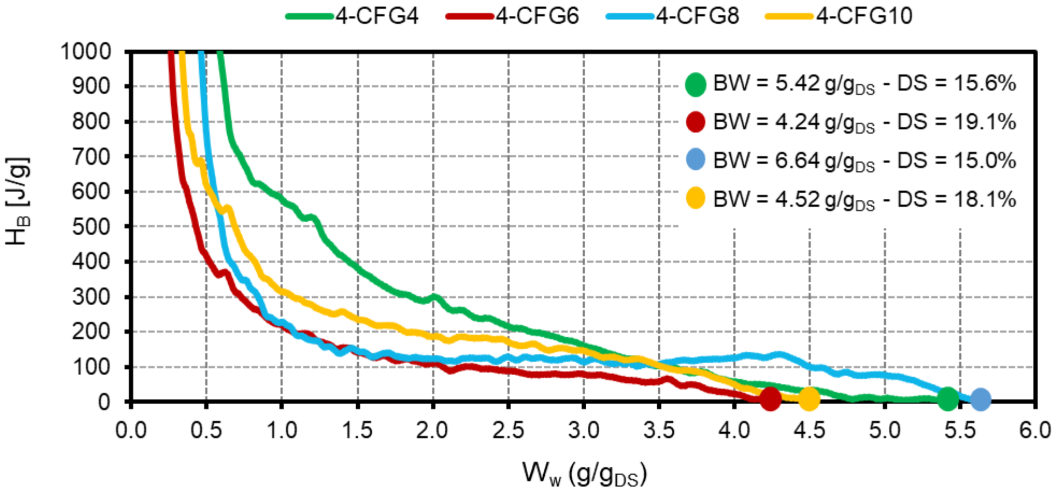

Figure 4.11 - Bound water content obtained from TGA test for different polymer dosage in sludge sample from WWTP 4.

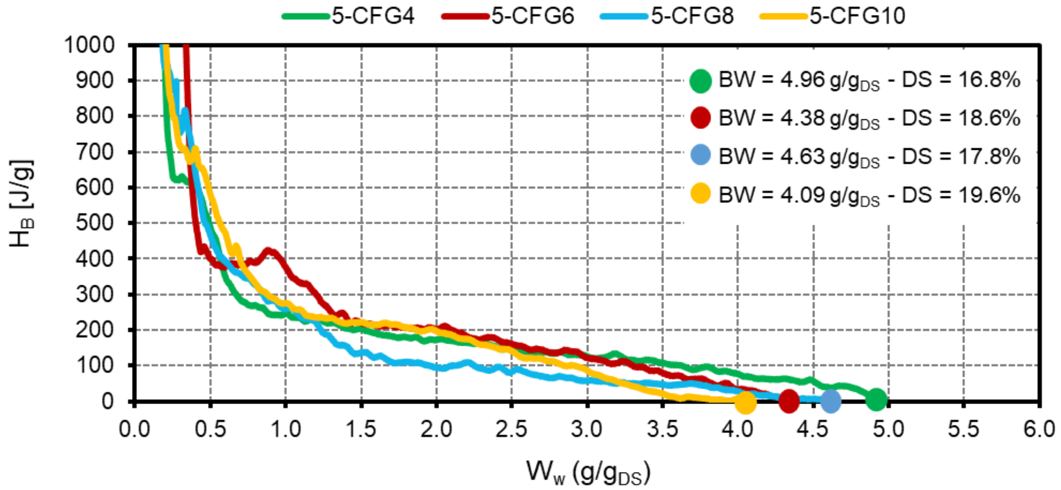

Figure 4.12 - Bound water content obtained from TGA test for different polymer dosage in sludge sample from WWTP 5.

By increasing the polymer dosage, the BW content of centrifuged sludge (CF) tends to decrease with respect to the TU samples. However, in this case, BW means the water that has higher energy then the bulk water and may include part of the water that is commonly classified as interstitial and surface water. Therefore, from TGA, an important data is the continuous classification of the types of water in the sludge samples: the bond strengths increase as the total water content decreases, as there are bonds with different strength between water and particles. Generally, the bond strength is nearly constant (0-150 J/g) until the water content is lower than 2.0-2.5 g/g$_{DS}$, and then rapidly increases until values higher than 800-1000 J/g, which corresponds to the energy of physisorption and chemisorption/chemical reactions (Chen et al., 1997). One question raises when considering the constant values of bond strength at higher water amounts: why the dewatering process is harder at higher DS content, if the bond strength is constant? A possible explanation is the fact that the bond strength value is taking into account the types of bonds between sludge and water, but it’s not taking into account other factors, such as the viscoelastic properties of sludge and its rheology.

The importance of the bond strength is evident when considering the case of TU sludge from WWTP 4: the energy required for water removal is considerably higher than TC samples. However, this behaviour is not shown by sludge from WWTP 5, where TU and TC curves are almost superimposed. Generally, the BW content of sludge from WWTP 4 is higher than that of WWTP 5, which is the opposite result of data from DSC tests.

4.3.2 Influence of mechanical dewatering techniques (at lab-scale) on free and bound water in sludge

The sludge samples taken from WWTPs 4 and 5 have been used to study the influence of different mechanical dewatering techniques on free and bound water content within the sludge sample. To this aim, five lab-scale mechanical dewatering techniques have been investigated on sludge conditioned with polymer dosage used for EDW test, that is the dosage at which zeta potential reaches a minimum. These techniques are:

- Centrifugation at 4,000 rpm for 5 min (CFG);
- Centrifugation at 4,000 rpm for 5 min with multiple repetition (MCFG);
- Vacuum filtration (FIL);
- Compression (PRS) at 350 kPa for three different durations: 35, 70 and 145 min;
- Mechanical dewatering (MD) directly in the WWTPs (belt press and centrifugation for WWTPs 4 and 5 respectively).

Overall, seven different dewatering runs have been applied.

Figures 4.13 and 4.14 show the free and bound water content obtained from DSC tests after the lab-scale dewatering runs with the corresponding DS content and the ratio between bound and free water. TC sludge sample is considered as reference.

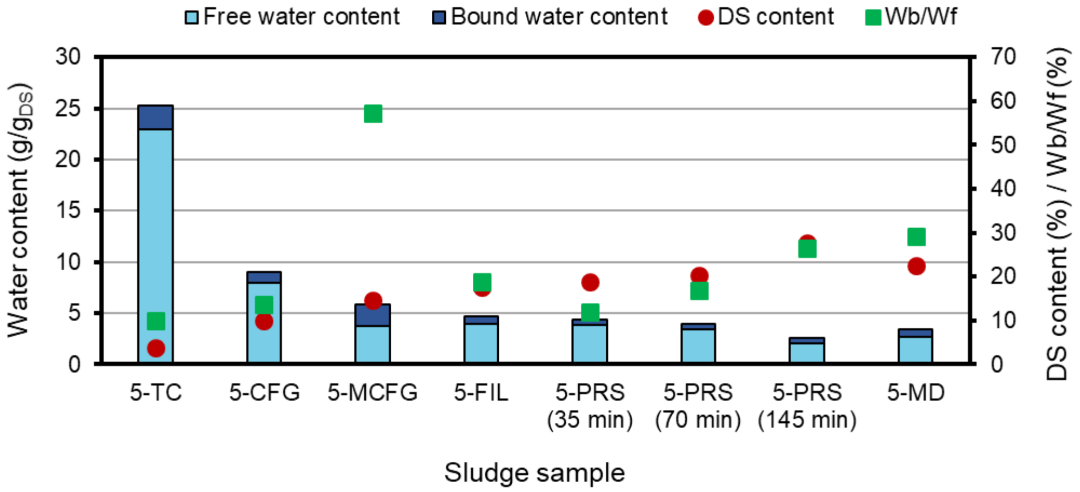

Figure 4.13 - Free and bound water content with the corresponding DS content after different lab-scale mechanical dewatering procedures for the sludge sample from WWTP 4.

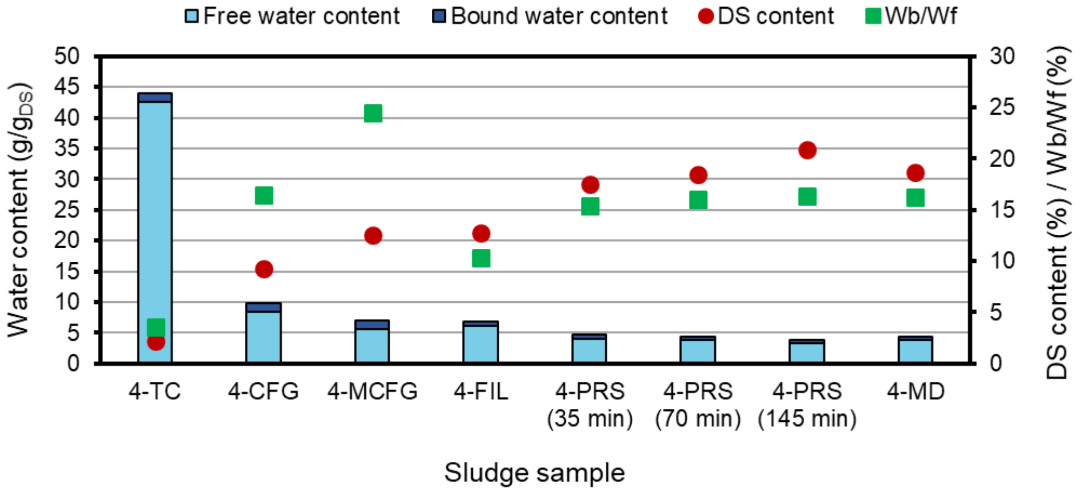

Figure 4.14 - Free and bound water content with the corresponding DS content after different lab-scale mechanical dewatering procedures for the sludge sample from WWTP 5.

It is clear that FW and BW content decrease by using any of the tested mechanical dewatering methods. Compression for 145 min is the most effective technique to remove both free and bound water content from the two sludge samples: FW content is reduced of 92.4% for TC-4 and 91.0% for TC-5, while BW content is decreased of 64.7% and 76.1%. This is consistent with common practice results, as long-duration filter pressing is the dewatering method that allows to achieve the highest final DS values by pure mechanical means.

However, in spite of a similar efficiency in dewatering and similar final DS content, vacuum filtration is more effective in removing BW compared to multiple centrifugation. Indeed, the BW content is reduced of 7.8-8.6% after multiple centrifugation with respect to TC samples from WWTP 4 and 5, while it is reduced of 67.8-57.3% after filtration. Wb/Wf ratio confirms that multiple centrifugation is the less effective in removing BW. This result highlights that lab-scale centrifugation is not efficient enough in removing BW from sludge, in spite of a similar DS content.

On the other hand, FW content, after multiple centrifugation, vacuum filtration, compression (for different durations) and mechanical dewatering in the WWTPs, is reduced of about 80.1-92.3% for both the sludge samples. Therefore, mechanical methods, in spite of a different dewatering efficiency, for DS contents higher than 10%, have a similar effect on free water removal, but lead to different BW contents.

Considering the mechanical dewatering in the two WWTPs (4-MD and 5-MD), in spite of a higher DS content achieved by centrifugation in the WWTP 5 (around 22.43% compare to 18.62% for MD-4), BW content is higher than that of sludge dewatered by belt press in the WWTP 4. Therefore, application of pressure in a belt press is more effective in removing BW content compared to centrifugation. This result, together with the data of compression tests carried out in the lab, highlights that centrifugation (even at high speed) has lower efficiency in BW removal.

Figure 4.15 shows the comparison between BW content and the corresponding DS of the two sludge samples after application of different mechanical dewatering processes.

In spite of higher DS content in the sludge samples from WWTP 5 after vacuum filtration, multiple centrifugation and mechanical dewatering in the WWTPs, BW content is higher compared to that of sludge from WWTP 4. Therefore, these techniques are capable to remove BW content from sludge 4 more efficiently than in sludge 5.

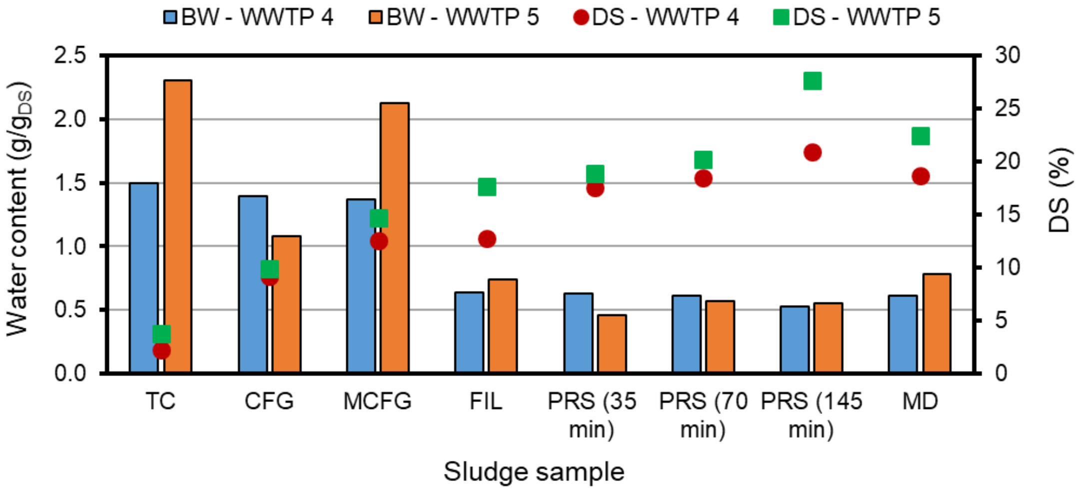

Figure 4.15 - Bound water content with the corresponding DS content after different lab-scale mechanical dewatering procedures for the sludge sample from WWTP 4 and WWTP 5.

Even though the anaerobically stabilized sludge shows better dewaterability under pressure for 70 min and 145 min, there is no significant difference in BW content in the two sludge samples. In conclusion, BW removal efficiency in aerobically digested sludge under different mechanical dewatering techniques is higher or similar to that in anaerobically stabilized sludge, except for centrifugation and compression for 35 min.

These results confirm that dewatering efficiency, in terms of DS content and energy consumption, not only depends on the types of water in sludge and the bond strength between water and particles, but also on other factors (e.g. sludge rheology, VS content, dosage and type of polyelectrolyte, EPS) are affecting the water removal. Therefore, in spite of a higher BW content, anaerobically stabilized sludge has usually a higher dewatering efficiency due to the lower organic fraction (Skinner et al., 2015). The choice of the dewatering method (centrifuge, belt press, filter press) needs to take into account both the BW removal efficiency and the characteristics of the sludge.

This study should be broadened to other WWTPs, with different stabilization treatments, different dewatering methods and efficiencies.

4.3.3 Influence of EDW on free and bound water

In order to study the influence of EDW process on free and bound water content, TC and MD sludge samples taken from WWTPs 4 and 5 were tested under different operating conditions. Figures 4.16 and 4.17 show free and bound water contents of the TC sludge sample examined after EDW at 5, 15 and 25 V for 35 and 70 min test duration. The TC-CFG sludge corresponds to the sludge centrifuged in the lab.

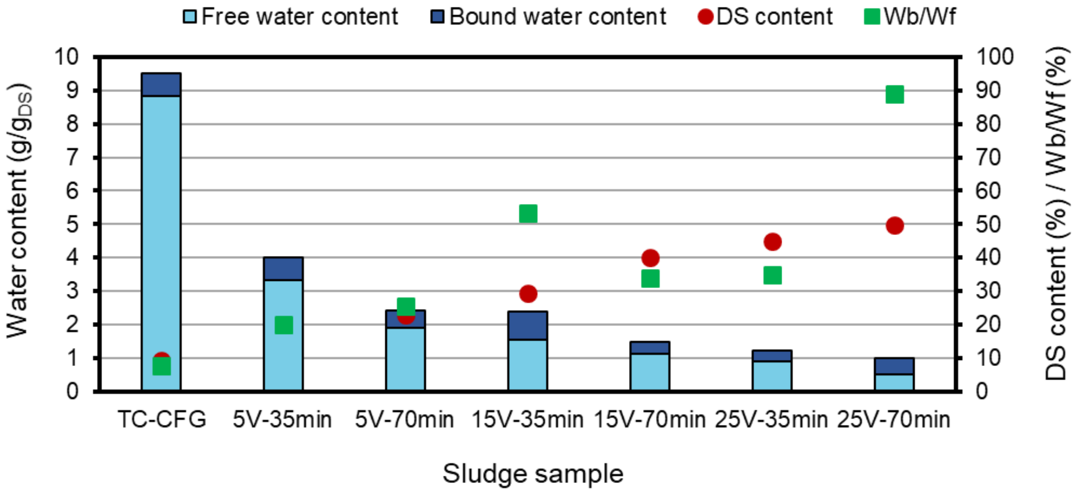

Figure 4.16 - FW, BW content with the corresponding ratio and DS content for sludge from WWTP 4 under different electrical potential for 35 and 70 min test duration.

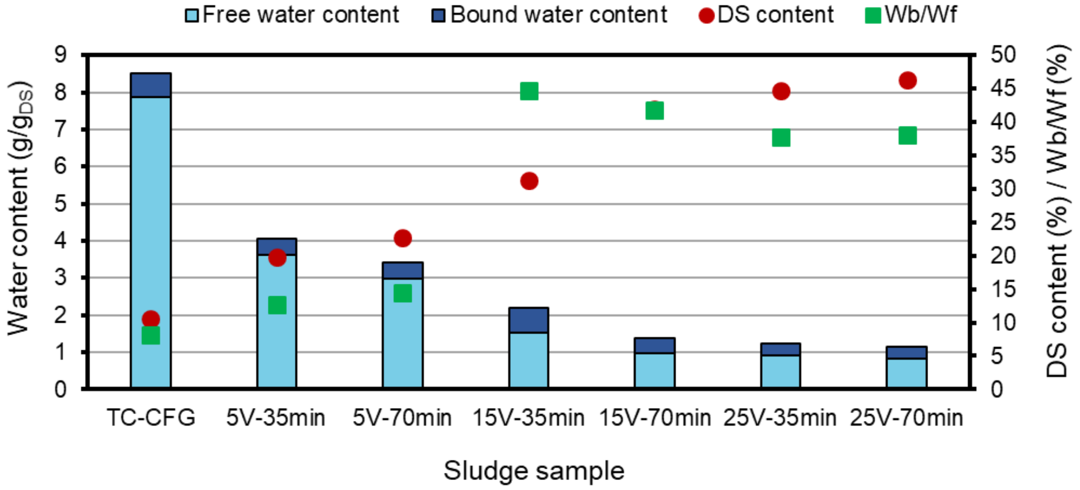

Figure 4.17 - FW, BW content with the corresponding ratio and DS content for sludge from WWTP 5 under different electrical potential for 35 and 70 min test duration.

In general, by applying higher voltage and increasing the test duration, FW content decreases and higher DS content is achieved for sludge from either WWTP. Therefore, both voltage and test duration have a positive effect in removing FW. The FW removal efficiency increases by applying higher potential and extending test duration. The maximum reduction in FW content for sludge from WWTP 4 and 5 occurs at 25 V for 70 min, where reductions of 94.0% and 89.3% with respect to the centrifuged sludge in the lab are achieved. In terms of BW content, reduction can be seen by increasing the applied voltage and the time duration of the tests, except for the case at 15 V for 35 min in sludge coming from either WWTPs and at 25 V for 70 min in sludge from WWTP 4. The reduction in BW content reaches 22.4% by increasing the electric potential from 5 V to 15 V for 70 min, but at the expense of the SEC, which is eight times higher (Figure 4.7). The same behaviour is shown by sludge from WWTP 5, in which the BW content is reduced by 4.6%, at the expense of the SEC, which is four times higher. However, it is worthwhile to consider that the corresponding DS increases to around 45% by increasing the voltage from 5 to 15 V.

There is an obvious increase in the Wb/Wf ratio (from 35% to 88%) by extending the duration of EDW test at 25 V, which indicates that BW content is reduced much less than FW content after 70 min of test duration.

According to Figure 4.7, sludge from WWTP 4 shows better results in terms of final DS content and SEC for both durations at 25 V. For sludge 4, EDW test at 25 V leads to a difference in the SEC value of 50 Wh/kg$_{H2O}$ after a duration of 35 and 70 min, with a 3% increase in the corresponding DS. For sludge from WWTP 5, the DS content increases of about 2% by extending the test duration to 70 min, at the expense of the SEC, which is 30 Wh/kg$_{H2O}$ higher with respect to tests conducted for 35 min, for only 5% reduction in BW content.

In terms of DS content, there is no significant difference between sludge from these two WWTPs under the same operating conditions. For example, the DS achieved after applying 5, 15 and 25 V for 35 min is 20.1%, 29.5% and 44.8% for sludge 4, which are not far from DS contents of 19.7%, 31.3% and 44.7% for sludge 5. On the other hand, DS content after EDW tests at 25 V for 70 min is different between sludge 4 and 5 (49.9% and 46.3% respectively). In spite of higher DS content achieved for sludge of WWTP 4, the BW content is higher of that from WWTP 5.

In conclusion, the test at 25 V for 35 min shows higher efficiency in terms of BW reduction, corresponding DS content and SEC for both aerobically and anaerobically digested sludge. The EDW test duration effect is not significant in BW reduction and final DS content in comparison to the higher SEC.

Figure 4.18 shows free and bound water content on MD sludge sample before and after EDW tests at 5, 15 and 25 V for 35 min. The effect of EDW under different voltages is similar to what achieved for TC sludge samples.

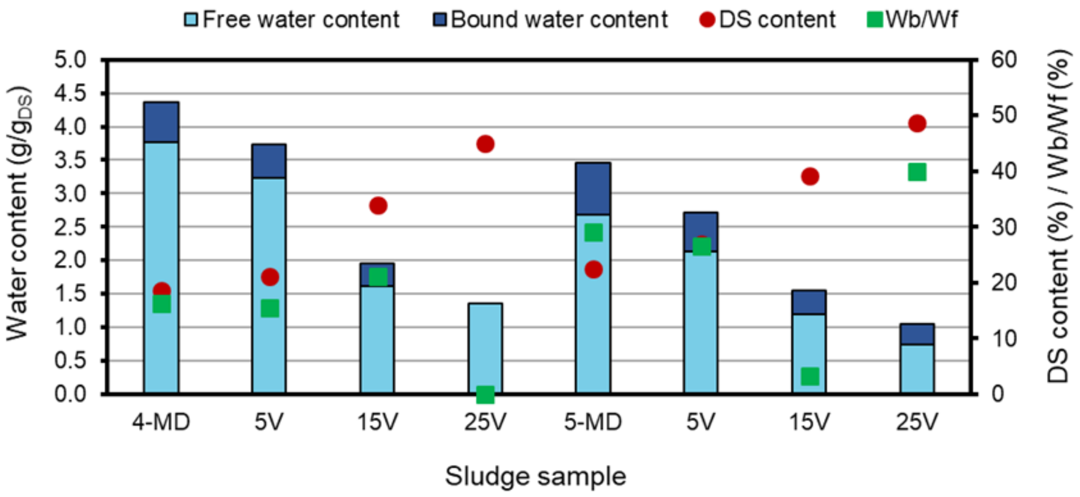

Figure 4.18 - FW and BW content with the corresponding ratio and DS content for MD sludge from WWTP 4 and 5 under different electrical potential for 35 min test duration.

By applying higher voltages, FW and BW contents decrease. The maximum reduction in FW and BW content is 63.8% and 100.0% in WWTP 4, 72.0% and 61.5% in WWTP 5 by applying 25 V. As mentioned before, the MD sludge sample from WWTP 4 shows better result in FW and BW reduction, despite of a lower DS content. The belt press used in WWTP 4, can improve the dewatering rate of the sludge sample in a better way compared to centrifugation used in WWTP 5.

According to Figure 4.5, the difference in SEC value for 5-MD after applying 25 V was 16 Wh/kg$_{H2O}$ with 8% increase in final DS, in comparison with 4-MD. On the other hand, the reduction in BW content is 30% lower in 5-MD sludge sample with respect to 4-MD after EDW at 25 V.

Sludge 4 shows a better BW reduction with lower energy consumption. While FW removal efficiency is more evident in sludge 5 (around two times more than 4-MD sludge sample) under 25 V.

In conclusion, the anaerobically and aerobically digested sludge samples tested, both in TC and MD forms, show a more efficient BW content removal after EDW at 25 V for 35 min duration of the test with respect to other voltages and time durations. As a comparison, aerobically stabilized sludge shows better results in terms of BW removal efficiency, final DS achieved and corresponding SEC compared to anaerobically digested sludge. The belt press used in WWTP 4 is more efficient compared to centrifugation in WWTP 5 in terms of BW content removal and corresponding SEC.

5. Conclusions

The pressure driven EDW process efficiently decreases the water content in the final sludge cake, so that final DS content of as much as 48% can be achieved, much higher than in conventional MD devices.

Initial DS content, applied voltage and initial cake thickness are the main operation parameters that affect EDW performance.

By increasing the voltage from 5 V to 25 V, the final DS content increased from 16.0% to 48.0% for all types of sludge, regardless of the initial DS content. An increase in voltage generates higher current densities and leads to higher energy consumption. The thinner cake (15 mm) showed better results in terms of SEC and final DS content under EDW. The specific energy consumption highly depends on the initial DS content, therefore it was considerably higher for mechanically dewatered sludge than conditioned and unconditioned sludge. The time duration of the EDW test from 35 to 70 min, increased the final DS content by 2-3% for different types of sludge at the expense of a higher energy consumption.

Further economic analysis must be carried out to investigate whether cost saving of disposal can compensate the higher energy cost. Aerobically stabilized sludge has shown a better compromise between final DS content and SEC due to the lower energy consumption compared to anaerobically digested sludge. On the other hand, anaerobically digested sludge showed better results in terms of DS content under mechanical dewatering due to its lower organic fraction.

The effect of polyelectrolyte on BW and FW content need to be studied in detail to improve the dewatering efficiency. The conditioning step, by considering the sludge characteristics such as CST and zeta potential, may be improved also considering the amount of bound water content released after the addition of polymer at different dosages. This step improves dewatering during the pressure-driven phase and save energy before applying the electric field. Sludge characterization before and after conditioning is an important step to select the dosage of polyelectrolyte to be used in EDW test. CST values could predict the efficiency of the pressure-driven phase after the polyelectrolyte dosage, while zeta potential is related to dewaterability of EDW process.

DSC and TGA are important means to analyze the types of water in sludge and give important indications. DSC method evidenced its reliability in the determination of the bound water content to improve the conditioning step and the following dewatering processes. TGA showed information on the bond strength between water and particles.

Lab-scale mechanical dewatering methods used in this work, in spite of a different dewatering efficiency, have a similar effect on free water removal for DS contents higher than 10%, but lead to different BW contents. Compression for long duration (145 min) showed greater FW and BW removal efficiency in aerobically and anaerobically digested sludge (91-93% and 65-76% reduction in FW and BW respectively). Moreover, application of pressure in a belt press is more effective in removing BW content compared to centrifugation. This result, together with the data of compression tests carried out in the lab, highlights that centrifugation (even at high speed) has lower efficiency in BW removal.

The anaerobically and aerobically digested sludge samples tested, both in TC and MD forms, show a more efficient BW content removal after EDW at 25 V for 35 min duration of the test with respect to other voltages and time durations. As a comparison, aerobically stabilized sludge shows better results in terms of BW removal efficiency, final DS achieved and corresponding SEC compared to anaerobically digested sludge.

TGA at water amounts lower than 2.5 g/g_{DS} may relate to bond strength, which looks constant. However, experience shows that the release of water to lower values is more and more difficult and energy expensive. This might be explained by considering other factors, such as viscosity or other rheological properties of the sludge, which can reduce the water flow, even if the strength of static bonds is constant.

As a matter of fact, another research topic that is currently under investigation is the evaluation of the influence of rheological parameters and of EPS on electro-dewatering of the sludge.

This work is a preliminary study performed mainly to make sure that the procedures we adopted for characterizing sludge and the EDW process were reliable and repeatable.

One of the next steps will be to extend the number of sludge samples both from the same and from different WWTPs, to get a wider statistical series of data, on which one can draw more solid conclusions.

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