QATAR UNIVERSITY

COLLEGE OF ENGINEERING

INFLUENCE OF POLYELECTROLYTE'S ARCHITECTURE ON THE ELECTRO-KINETICS AND RHEOLOGICAL BEHAVIOR OF INDUSTRIAL MEMBRANE BIOREACTOR ACTIVATED SLUDGE

BY

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ABSTRACT

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Title: Influence of Polyelectrolyte's Architecture on the Electro-kinetics and Rheological behavior of Industrial Membrane Bioreactor Activated Sludge

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Membrane bioreactor (MBR) is a recent biological treatment process in many industrial and municipal industries that has been implemented to overcome the current difficulties of activated sludge (AS) processes for separation of biomass from the treated water and the sludge volume reduction. Improvement of MBR sludge dewaterability is greatly hindered by the presence of large amounts of interstitial wastewater molecules trapped in the sludge as a result of strong hydrophilic characteristics and high organic content.

Since, about 40-50% of the wastewater operating cost belongs to the sludge dewatering stage (i.e., filtration and centrifugation), sludge conditioning is required to effectively separate solid-liquid and enhance the efficiency of dewatering stage which has a real impact on the subsequent unit operations such as storage, pumping, transportation, and handling.

Organic polyelectrolytes such as polyacrylamide (PAM) are generally preferred for sludge conditioning and they are considered as the most efficient flocculating agents among the most important breakthroughs in solid-liquid separations. The flocs formed through charge neutralization and bridging mechanisms using organic polyelectrolyte are sufficiently large and strong and can be separated by physical means like sedimentation, and they are highly resistant to any breakage due to the hydrolysis stress. Therefore, this study aims to investigate the influence of polyelectrolyte-based flocculants (i.e., PAMs) with different molecular architecture (linear, slightly and highly branched), charge density (CD) and molecular weight (MW) on the electro-kinetics, dewatering, and rheological characteristics of highly stable industrial MBR sludge. The impact of PAM on flocculation is manifested in the supernatant turbidity, particle zeta potential, sludge capillary suction time (CST), floc size and settleability. Turbidity removal and reduction in zeta potential (ζ) are used to identify the optimum polymer dose. Overall, this work has been successful in establishing the relationship between electro-kinetic and rheological properties of MBR sludge and correlating these properties to the MBR sludge dewaterability and volume reduction.

Keywords: Activated sludge; Membrane bioreactor; Polyelectrolyte; Polyacrylamide; Organic coagulant Rheology; Electro-kinetics

DEDICATION

To my Father & Mother, the reason of what I became today

To my sisters & brothers

To my best friends & best supervisor.

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CHAPTER 1: INTRODUCTION

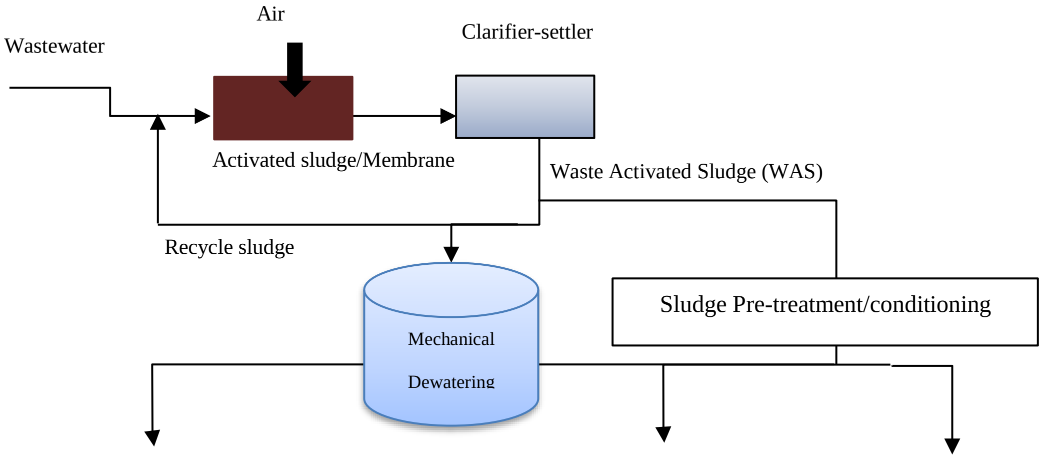
Research Overview

The expected population growth and high consumption of water have vitally impacted the wastewater treatment infrastructure. This has increased the pressure on the local wastewater treatment plant to handle a high amount of wastewater at high efficiency. Sludge treatment is one of the main sections of each wastewater treatment plant. Its efficiency and cost are strongly affected by the volume and properties of the sludge including the organic content, state of water, solid concentration, and rheological properties.

The activated-sludge process is the most widely used biological treatment in the wastewater treatment process. Recently in many industrial and municipal applications, MBR technology is used instead of the activated-sludge (AS) process as a treatment unit in the wastewater treatment process. MBR has a smaller footprint and minimizes the sludge production compare to the AS process [1]. This process utilizes the conventional AS process and membrane filtration and effectively separates solid-liquid without the secondary settler [2]. One of the main drawbacks of all the AS processes including MBR process is the production of a large amount of waste activated sludge (WAS). As the name applies, the technology provides biological treatment utilizing membrane separation [3]. Biological treatment normally produces excess sludge with more than 99% of water at the bottom of thickeners [4]. The produced sludge has a poor dewaterability due to the presence of extracellular polymeric substances (EPS) [5]. These large quantities of WAS need to be handled effectively as it causes serious environmental problems [6]. In a wastewater treatment process, about 40-50% of the operating cost and 30-40% of capital cost belong to the sludge management disposal, and it is a significant challenge in the global wastewater treatment industry [7]. Waste activated sludge has a complex and unstable nature. It composes of water and dissolved wastewater as a continuous phase and sludge flocs, particulate

wastewater, and biological products, organic content and micro-organism are the dispersed phases [8]. Due to its hydrophilicity nature, it traps a large amount of water molecules within the networked sludge flocs and makes it difficult to be dewatered. Therefore, mechanical dewatering is required to reduce the sludge volume. However, before mechanical dewatering, it is essential to condition the WAS using chemical, physical and/or biological methods to fasten the dewatering step, improve sludge quality and reduce the sludge volume and consequently reduce the cost of transportation and ultimate disposal [9].

Sludge contains colloidal particles which form a stable suspension. The high stability of the colloidal particles of sludge for a long period can be explained through the mechanisms of repulsion effect of electrostatic surface charges, hydrogen bonding, hydrophobic and ionic interactions, and physical enmeshment which make them difficult to settle and consolidate [4,10]. Aggregation of these fine particles into larger flocs, through destabilization of the suspension, is commonly practiced to provide efficient solid-liquid separation [11,12]. Therefore, the selection of an appropriate pretreatment method is necessary prior to mechanical dewatering. Among the variety of alternatives for the pretreatment of WAS which is shown in Figure 1-1, coagulation/flocculation process is found to be one of the costs effective, user-friendly and well-known technology and has been used widely and for a long period of time for pre-treatment/conditioning of sludge [13,14]. Reagents used for this purpose comprise chemical conditioners such as organic flocculants (i.e. polyelectrolytes), inorganic coagulants (ferric and aluminum sulfate, lime and iron chloride, etc.) and organic coagulants (polymers with high CD) and low MW such as polydiallyldimethylammonium chloride (polyDADMAC) and polyamine [15–17]. The use of these flocculants and coagulants lead to agglomerating the colloidal particles and forming compact flocs that typically range in size from a few microns to several hundred microns or larger. However, optimizing the type of coagulant/flocculant and dosing is challenged by the heterogeneous and complex nature of WAS [18,19]. Organic polyelectrolytes, especially cationic polyacrylamide (CPAM) are generally preferred for this duty if the ultimate end disposal route is incineration since these materials are combustible. On the other hand, they showed a significant enhancement in the separation processes [6,10,14,20].



Physical	Chemical	Biological
Addition of skeleton builders [21]	Addition of acid and alkali [26]	
Thermal approach [22]	Addition of surfactant [27]	
Freeze-thaw approach [23]	Addition of oxidant [28]	
Use of Microwave [24]	Addition of coagulants/flocculants [28]	
Ultrasonic conditioning [25]	Bio-chemical agents [28]	

Figure 1-1. Various conditioning methods for sludge dewatering

Flocculation of sludge fine particles using organic flocculants (i.e., polyelectrolytes) may occur by a combination of mechanisms including polymer bridging, charge neutralization, particle-particle surface complex formation and depletion flocculation [29]. Charge neutralization occurs through electrostatic attraction of the unlike charges between the negative surface charge of the sludge particles and the positive amide group of the PAM. Charge neutralization is reflected in a reduction and reversal of zeta potential. In the bridging mechanism, the polyelectrolyte chains are required to be adsorbed onto a few regions of the particle surface, with the bulk of the polyelectrolyte chains being projected into the surrounding solution for contact and adsorption onto other particles [30]. Strong adsorption in the flocculation process causes surface saturation and prevents effective bridging and re-stabilizing the fine particles [29]. The flocs formed through charge neutralization and bridging mechanisms are sufficiently large and strong and can be separated by physical means like sedimentation, and they are highly resistant to any breakage due to the hydrolysis stress [31,32]. In order to improve the quality of the produced sludge flocs (i.e., floc size, structure, strength, and dewater-ability), a combination of coagulation and flocculation seems to be a good option and simple that need further investigation [13,32]. The presence of coagulant in tandem with flocculent helps with the formation of stronger flocs and reduces the optimum dosage of the flocculant [32].

Moreover, PAM can be partially hydrolyzed into toxic monomers such as acrylic acid and an organic amine that lead to producing secondary pollution in sludge treatment process [33]. Thus, it is essential to reduce its environmental impact by lowering the dosage through its combination with an appropriate coagulant [34]. The two most widely used organic coagulants; polyDADMAC and polyamine are preferred over other organic and inorganic coagulants due to their exceptional properties as shown in Table 1-1 [16].

Table 1-1**.** *Comparison of PolyDADMAC and Polyamine with Other Organic and Inorganic* Coagulants [16]

Compared to inorganic coagulants	Compared to organic coagulants
Effective at a lower dosage	Less sensitive to an overdose
Lower sludge volume produced	Better optimization of organics removal
pH and alkalinity correction are reduced	More suitable for enhanced coagulation
Less corrosive	
Flocs are more resistant to shearing	

The degree of flocculation and the strength of the produced flocs can be examined through the rheological measurements. The characteristics obtained from the rheological measurements can be used as design parameters in transporting, storing, pumping, landfill and spreading operations, and as controlling parameters in treatment processes such as stabilization and dewatering [35–37]. For example, the magnitude of the Bingham yield stress, $\tau_{B,}$ is used to assess the strength of the floc in a flocculated suspension such as those existing during the pumping and filtration processing. Bingham yield stress also measures the amount of stress needed to break the flocculated suspension to a suspension containing smaller assembled flocs or primary particles [38]. On the other hand, viscoelastic properties such as elastic modulus (G'), viscous modulus (G''), and complex viscosity (η^*), obtained from dynamic oscillatory measurements are indicative parameters for assessing the strength of the flocs and provide more information on flocculation kinetics of the networked suspension [11,29,39].

Tangible Objectives

The ultimate objectives of this study are to:

i. Investigate the influence of PAM's architecture, MW and CD on the electro-kinetic properties, particle size, and consequent dewaterability and volume reduction of a highly stable industrial MBR sludge. The architecture explored encompassed linear, slightly branched and highly branched molecular structures. This was achieved through measuring the zeta potential, residual turbidity, capillary suction time (CST), flocs size and settleability.

ii. Examine the effect of organic coagulants; polydiallyldimethylammonium chloride (polyDADMAC) and polyamine of low MW and high CD on the degree of flocculation of highly stabilized MBR sludge.

iii. Study the effect of the hybrid coagulation-flocculation system on the flocculation and dewaterability efficiencies. The impact was examined by adding two organic coagulants; polyDADMAC and/or polyamine before PAM's addition and measuring residual turbidity, zeta potential (ζ), flocs size and capillary suction time (CST).

iv. Investigate the influence of polyelectrolytes architecture and type on the degree of flocculation and rheological behavior of industrial MBR sludge. This has been achieved through the dynamic and oscillatory measurements of the flow behavior and viscoelastic components of the suspensions, primarily governed by the PAM's charge type, density, and MW.

v. Study the influence PAMs, polyDADMAC and polyamine structure and type on the combined degree of flocculation and rheological behavior of industrial MBR sludge.

Research Contribution

There are some studies available on the chemical flocculation/conditioning of the activated sludge. These studies have tended to focus on the following:

- The impact of sludge chemical quality in general and specifically the extracellular polymeric substances, or EPS
- Examination of synergistic effects through combination with inorganic and oxidative chemicals or technologies
- Rheological impacts

Organic flocculants studied and used for WAS conditioning have predominantly been cationic in nature [4,6,14,40–44] and with polyacrylamide polymers featuring prominently [6,14,44]. This is a consequence of the inherent affinity of the positively-charged ionogenic for the negatively charged suspended particles, thereby affecting charge neutralization of the latter [45].

However, while their application to inorganic suspensions has encompassed optimization of the polyelectrolyte architecture [45], this aspect appears to have received much less attention for their application to biological sludge from wastewater treatment. As a result, there remains a scarcity of information and knowledge regarding polyelectrolyte efficacy and characteristics for the specific duty of AS conditioning and consolidation. This gap is especially evident for MBR sludge which is known to be more challenging to dewater than classically AS due to their generally smaller floc size and higher EPS content [43,46]. Despite this, the limited work conducted in polyelectrolyte dosing of MBR sludge appears to have been primarily directed at membrane fouling inhibition [47,48]. The current study addresses the abovementioned gap in knowledge. Specifically, the work presented provides a comprehensive investigation of the influence of the PAM's architecture, MW and CD on the electro-kinetic properties, particle size, and consequent dewaterability and volume reduction of a real highly stable MBR sludge. The architecture explored encompassed linear, slightly branched and highly branched molecular structures and the sludge samples have been extracted from an MBR treating industrial effluent which is highly challenging in terms of its settleability and dewaterability.

On the other hand, several studies on hybrid coagulation-flocculation process have looked at improving the flocculation of suspended sludge particles and investigated the dewatering ability and performance efficiency of the hybrid systems yet little is known in the open literature on the influence of PAM's architecture, MW and CD on electro-kinetic properties and dewaterability of sludge when combined with strong or weak polyelectrolyte organic coagulants [31]. Combination of PAM with strong and weak polyelectrolytes such as polyDADMAC and polyamine, respectively is expected to have an influence on the electro-kinetics of flocs size and consequently the dewaterability of a real highly stable MBR sludge. Therefore, this study investigates the synergistic influence of organic coagulants; polyDADMAC (FL 4440) and polyamine (FL 2949) combined with six different PAMs (with different architecture, MW and CD) on the flocculation and dewatering enhancement of the MBR sludge.

Additionally, studying the rheological characteristics of AS is crucial for AS management in the wastewater treatment plant and sludge handling [8]. The concentrated sludge frequently consists of polymer flocculants, which is used to improve its settleability and filterability; hence, understanding the influence of flocculation on the rheological properties of the AS is essential. The information collected from such measurements may provide valuable information on floc strength and the flocculation mechanism of colloidal dispersions.

Few researchers have shown the effect of conditioning on the rheological properties of sludge which is essential for the cost and selection of proper equipment and sizing, handling of the sludge and transportation [37,49,50], and limited researches have been conducted on correlating the sludge dewatering (i.e., CST) [37,51], electro-kinetics (i.e., zeta potential, ζ, and turbidity) and flocs size parameters to the rheological characterizations [52,53]. In the past, the characterization of solid-liquid separation of flocculated suspensions was common to either focus on the free settling region of the suspension through ζ, turbidity and floc size measurements, or on the behavior of networked suspension either in the form of sediment or a filter cake through rheological measurements. A combination of results from these regimes for the same system is rarely investigated and, if complete knowledge of the characterization from individual suspended particles of sludge to a fully networked sludge is required, it is necessary to correlate the degree of flocculation of the sludge with its rheological behavior. Therefore, in addition to the influence of PAM's structure and type on the degree of flocculation of industrial MBR sludge, this study investigates the impact of organic flocculants and coagulants structure and type on the combined degree of flocculation and rheological behavior of industrial MBR sludge which is either rare or not available in the open literature. It focusses on the rheological characteristics of the polyelectrolytes flocculated MBR sludge and correlate them to their degree of flocculation and dewatering.

Research Outcome (Publications)

i. S.A. Yousefi, M.S. Nasser, I.A. Hussein, S. Judd, Influence of polyelectrolyte architecture on the electrokinetics and dewaterability of industrial membrane bioreactor activated sludge, *J. Environ. Manage*. 233 (2019) 410–416. doi:https://doi.org/10.1016/j.jenvman.2018.12.067

ii. S.A. Yousefi, M.S. Nasser, I.A. Hussein, Abdelbaki Benamor, Enhancement of Flocculation and Dewaterability of MBR Activated Sludge Using a Hybrid System of Organic Coagulants and Polyelectrolytes, *J. Environ. Manage*. (2019). *Under review*

iii. S.A. Yousefi, M.S. Nasser, I.A. Hussein, Abdelbaki Benamor, Influence of Polyelectrolye Structure and Type on the Degree of Flocculation and Rheological Behavior of Industrial MBR Sludge, *Sep. Purif. Technol.* (2019). *Under review*

iv. S.A. Yousefi, M.S. Nasser, I.A. Hussein, Abdelbaki Benamor, Muftah El-Naas, Optimizing the Flocculation Effeciency of MBR Sludge Using Response Surface Methodoly. *Under preparation*

CHAPTER 2: LITERATURE REVIEW

The Wastewater Treatment Process

A general wastewater treatment plant consists of three main stages; primary or pre-treatment step by using mechanical or physical, secondary treatment using chemical or biological techniques and sludge treatment step. In some plant, tertiary treatment is also involved for removing the remaining contaminants such as removing salts produced due to the mineralization of organic matter [54].

Characteristics of Water in the Sludge

In the wastewater treatment plant sludge will be produced from different units with different characteristics. Sludge components are highly complicated [55]. They are mainly water with various types of solids. The presence of various types of solids in sludge resulted in different forms of sludge with different properties (i.e., vapor pressure, enthalpy, entropy, viscosity, and density). For better understanding the pretreatment approaches for improving the sludge dewatering, it is essential to classify the moisture in sludge [13]. In any water-solid system such as WAS, there is an interaction energy binding or some structural binding between the water molecule and solid particles [13,56]. The water in sludge can be classified as “free water,” “interstitial water” “surface water” and “hydration or internal water” [13,56]. Free water accounts for approximately 70% of the total water and can be easily separated by gravitational settling as it is not attached to the solid particles [56]. Interstitial water is the water, which is trapped within the crevice’s spaces of the flocs and organisms, mechanical dewatering such as centrifugation or vacuum filtration can separate the only small amount of interstitial water and to completely release the water, it is required to break up the flocs or disrupt the cell. Vicinal or surface water is the third classification of water, which is physically adsorbed on the surface of the particles and cannot be separated by any mechanical dewatering. And the last classification is hydration water where water molecules are attached chemically to the solid particles and will be separated only by thermochemical destruction of the particles [56,57]. One of the major limiting factors that affect the dewatering efficiency of sludge is bound water [58,59]. Bound water is the sum of the interstitial, vicinal and hydration water that cannot be easily separated from the sludge particles due to the high binding energy between the water molecules and solid particles [56,60].

Sludge Type and Characteristics

Primary Sludge

Primary sludge is a product of physical or mechanical processes in the pre-/primary treatment of a wastewater treatment plant. It contains about 2-7% solids, and it can be easily dewatered due to the consistency of the particles [61].

Secondary/Activated Sludge

Biological treatment processes such as trickling filter, MBR, and AS produce a secondary or biological sludge. This type of sludge is challenging to dewater due to the presence of high organic content and biological flocs [62]. Table 2-1 shows the comparison of physical parameters of sludge produced from primary and AS treatment processes. According to this table, about 90% of AS particles are less than 0.2 mm.

Chemical Sludge

Chemical sludge is produced from the chemical precipitation and filtration processes, and it contains chemical precipitates and some heavy metals [62].

Table 2-1. *The Physical Parameters of the Primary and Activated Sludge* [62]

Sludge type	Density (g.cm^{-3})	Particles size (mm)
Primary sludge	1.0-1.03	• Less than 1 mm for 50 to 80% of the sludge. • Between 1-7 mm for 9-33% of the sludge. • Larger than 7 mm for 5-7% of the sludge.
Activated sludge	1.0	• Less than 0.2 mm for 90% of the sludge. • Between 0.2- 1 mm for 8% of the sludge. • 1 mm for 1.6% of the sludge. 3 mm for 0.4% of the sludge.

Activated Sludge Process

Increasing the demand for the protection of water sources has let to treating more industrial and municipal wastewater in the wastewater treatment plant and production of a high amount of WAS [63].

In the wastewater treatment, biological treatment including AS or MBR process is used to reduce the organic contaminant of the wastewater effectively. The AS process is part of the secondary treatment and is the most widely used biological treatment in the wastewater treatment process. In this process, the contaminants are digested by bacteria and metabolized into cellular structures and intermediate products. Bacteria grow up and reproduce and this constant bacterial population which is referred to as “mixed liquor suspended solids” is required in such reactor. The treated stream is sent to the clarifier where the digested contaminants and AS will be separated from the decontaminated stream by gravity. A portion of the bacterial solids is recycled to the aeration tank, referred to as “return activated sludge,” while some have to be wasted referred to as “WAS.” WAS is sent to the sludge treatment process to process the highly contaminated waste stream. Figure 2-1 shows the process of AS in the wastewater treatment plant [46].

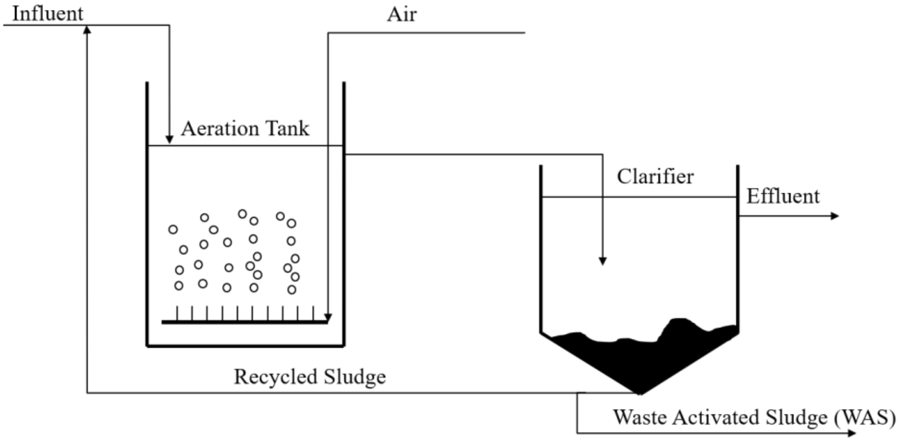


Figure 2-1. Activated sludge process

The AS process produces a large amount of sludge which contains more than 90% of water [5,13,14]. Recently in many industrial and municipal applications, MBR technology is used as a treatment unit in the wastewater treatment process. As the name applies, the technology provides biological treatment utilizing membrane separation [3]. Table 2-2 summarizes the most significant advantages of the MBR over conventional AS process. This process utilizes the conventional AS process and membrane filtration and effectively separates solid-liquid without the secondary settler [2,46]. However, it produces a large amount of WAS. These large quantities of WAS need to be handled effectively as it causes serious environmental problems [6]. In a wastewater treatment process, a majority of the operating cost belongs to the sludge disposal and management [13,61]. WAS has a complex and unstable nature. It composes of water and dissolved wastewater as a continuous phase and sludge flocs, particulate wastewater, and biological products, organic content and micro-organism are the dispersed phases [8,46]. Due to its hydrophilicity nature, it traps a large amount of water molecules within the sludge floc and makes it difficult to be dewatered. Depending on the composition of the feed and the time at which the wastewater enters the aeration tank, the composition of the produced sludge may vary [64]. However, in general, the produced sludge from such a process has a poor dewaterability due to the presence of organic matters, including microbial cells, extracellular polymer substances (EPS), and residue organic pollutants [5]. Therefore, the treatment of the WAS is a significant concern in the wastewater treatment processes due to its complex nature and dynamic change in its composition [46,65].

Membrane Bioreactor (MBR) Activated Sludge

Implementing the MBR to the wastewater treatment can overcome the current problems in AS processes that are mainly associated with the separation of biomass from the treated water. MBR utilizes the micro- or ultra-filtration for the separation of biomass from the treated water instead of the settling process [12]. The technology combines AS process with a membrane separation process and operates similarly to conventional AS process. According to Table 2-2, one of the main disadvantages of the MBR is that the treatability of the sludge produced from this reactor is challenging due to its high stability [66]. Sludge produced from MBR is highly stable and less readily dewaterable [3]. Therefore, it is important to effectively separate the liquid and solid in sludge to reduce the cost of WAS treatment, reduce the load on treatment processes, transportation and final disposal [13].

Table 2-2. *Advantages and Disadvantages of MBR Process [66]*

Advantages	Disadvantages
• Smaller footprint and smaller reactor volume because of higher MLSS concentration and loading rate • Decreased sludge production • Higher and more consistent effluent quality as a result of membrane filtration • Lower sensitivity to contaminant peaks	• Relatively expensive to install and operate • Frequent membrane monitoring and maintenance • Limitations imposed by pressure, temperature, and pH requirements to meet membrane tolerances • Membranes may be sensitive to some chemicals • Less efficient oxygen transfer caused by high MLSS concentrations • Treatability of surplus sludge is questionable

Colloidal Particles Stability and Destabilization

Contaminated water or sludge contains different compounds which can be divided into; suspended solids (diameter of greater than 10^{-6} m), colloidal solids (diameter between 10^{-6} and 10^{-9} m) and dissolved solids (diameter of smaller than 10^{-9} m) [67]. Large particles with a large diameter and specific density of greater than 2000 kg/ m^3 have high settling velocity and will settle in water by the gravity [67]; however, for the colloidal system, the gravitational force is negligible, and the surface phenomena are predominate [68]. These particles are very small and have a large surface area with a very small ratio of mass to surface area. They carry similar charges (usually negative charges) in water which maintain them in suspension due to the repulsive forces between them [69]. The high stability of the colloidal particle of sludge for a long period can be explained through the mechanisms of repulsion effect of electrostatic surface charges, hydrogen bonding, hydrophobic and ionic interactions and physical enmeshment [10]. DLVO (Derjaguin-Landua-Verwey-Overbeek) theory describes the stability of the colloidal system by introducing two independent forces; attractive van der Waals force and electrostatic repulsive forces. The sum of these two forces gives the net energy (V_t) between the particles [70]. As shown in Figure 2-2, minimizing the net interaction energy, reduces the stability of the colloidal particles [71,72].

The destabilization of the colloidal solids can be achieved through electric double layer compression which is the results of charge neutralization using a counter charged particle [68]. An electrical double layer consists of two chief layers in its structure, the inner Stern layer where ions with opposite charges are tightly bounded to the surface of the particles, limiting movement of ions, and the outer diffuse layer where ions are free to move. The outer limit of the Stern layer is defined by the shear surface, which is the interface of the inner and outer layers. The maximum potential which is known as Nernst potential occurs at the surface of the particle and it reduces across the Stern layer due to the existence of the particles with oppositely charged. This phenomenon is defined as the Zeta Potential, which is measured at the surface of the shear plane and is the main reason for the colloid's stability (Figure 2-3). Zeta potential represents the differences between the electrical charges of the first and second layer and measures the extent of the repulsion forces between the colloidal particles [68,73]. The magnitude of zeta potential indicates the potential stability of the colloidal system. Therefore, a colloidal system is more stable when the zeta potential value is more positive greater than +30 mV or more negative of lower than -30 mV [74].

The electric repulsive force between the particles can be reduced by the role of coagulants/ flocculants in the coagulation/flocculation process. The four mechanisms through which the colloidal system gets destabilized are as follow:

1. Double layer compression
2. Adsorption and charge neutralization
3. Adsorption and inter-particle bridging
4. Agglomeration of particles and precipitation

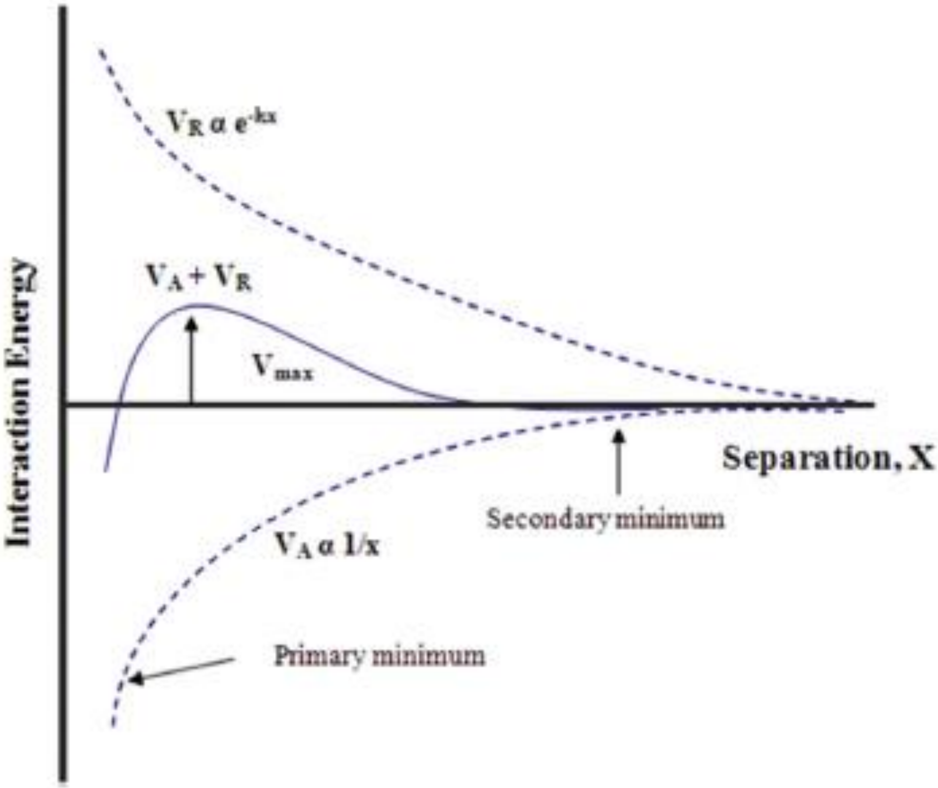


Figure 2-2. DLVO theory [68]

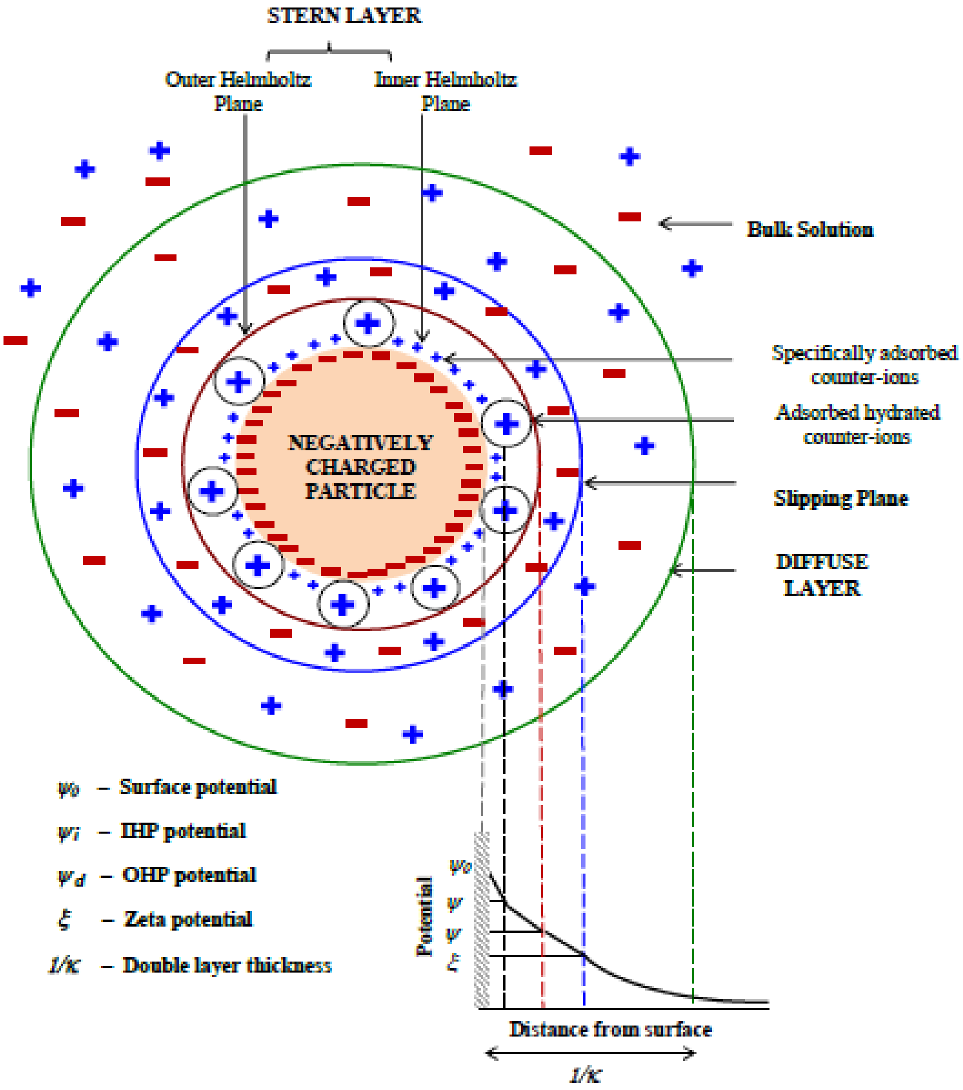


*Figure 2-3***.** Electrical double layer [68]

Electrical Double Layer Compression.

Electric double layer compression refers to reducing the thickness of the electrical double layer through which the system gets destabilized. To do so, counter charged ions are introduced into the solution through metal salts/electrolytes in case of coagulation/flocculation. By compressing the electrical double layer, the zeta potential approaching 0 mV. This condition is referred to as an optimum condition or optimum destabilization condition [68].

Adsorption/ Charge Neutralization.

In the destabilization mechanism, the counter charged ions will be adsorbed on the surface of the colloidal particles and neutralize particle's surface charge. In other words, Van der Waals force overcomes the repulsive force; particles approach each other and coalesce as illustrated in Figure 2-4 [68].

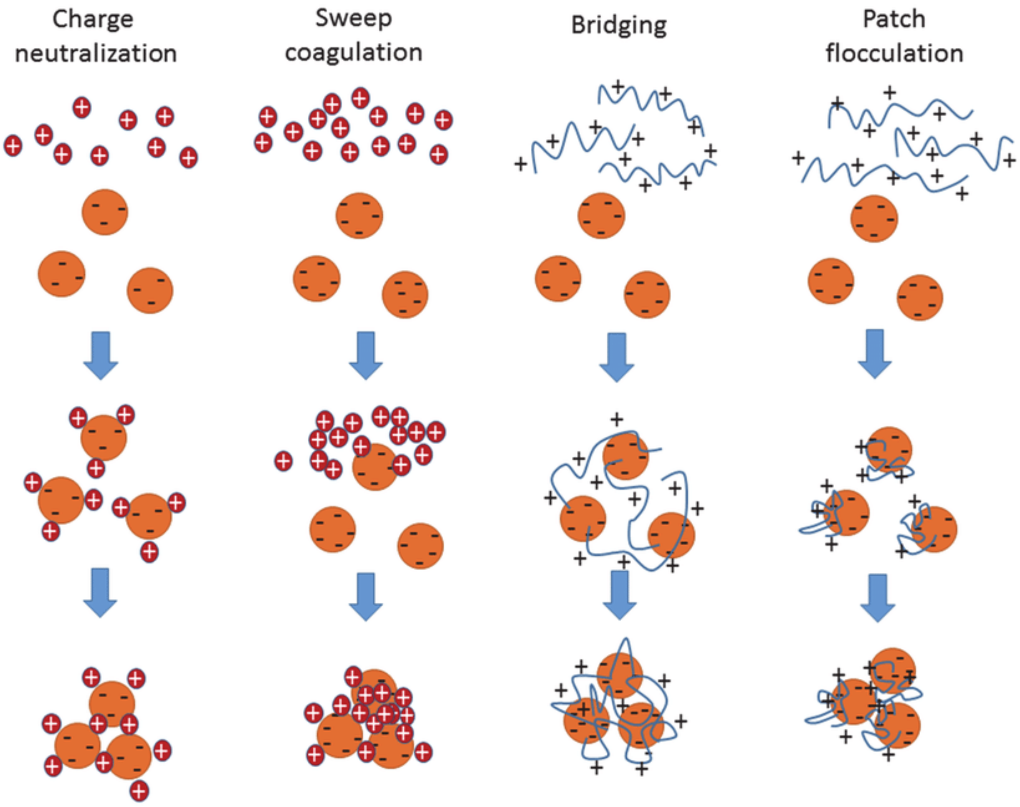


*Figure 2-4***.** Coagulation/flocculation mechanisms [75]

Adsorption/ Inter-particle Bridging.

Coagulants/flocculants can form link/bridges when they are polymerized. The polymerized coagulants or polymers have reactive groups on their chains, which make them possible to be adsorbed to the colloidal surface by charge-charge interactions and hydrogen bonding. Big particles will be produced because of bridging of the colloidal particle, and hence destabilization occurs. In this mechanism, there is a possibility of re-stabilization of the colloidal particles if the system has overdosed. In such a case, the polymer’s chains will be attached to all available colloidal particles with some free extended chains, which are not attached to any particles. Therefore, the free chain will reattach to the same particle and cause destabilization. Additionally, rapid mixing could result in re-stabilization of the colloidal particles by breaking the bridging mechanism between them [68,76] (Figure 2-4).

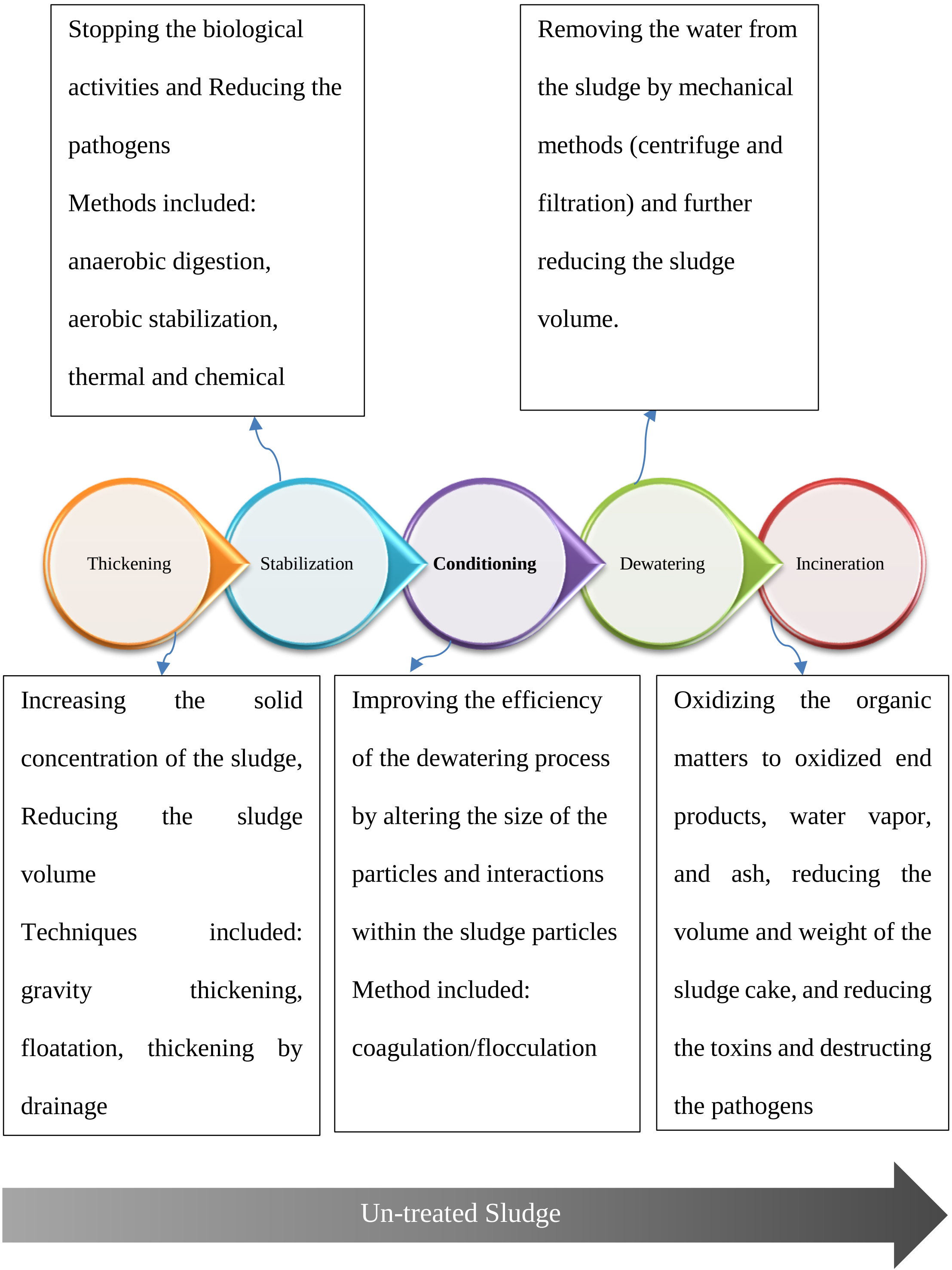
Agglomeration of Particles and Precipitation.

Sweep coagulation or entrapment of particles happens when a high concentration of coagulants/flocculants are added to the sludge. In this case, metal salts react with hydroxide ion and form of insoluble metal hydrates, which is in the form of sludge blanket and precipitate. The formed precipitates entrap colloidal particles during and after precipitation.

Sludge Treatment Plant

The main processes in the sludge treatment are thickening, stabilizing and finally dewatering the sludge [62,77]. The untreated sludge is firstly thickened, stabilized, and then followed by conditioning. Subsequently, the sludge will be dewatered and incinerated before disposal (Figure 2-5).

Conditioning process is one of the crucial steps before dewatering, to improve the efficiency of the dewatering. This step alters the size of the particles, their distribution, reduces the surface charge of the sludge particles and load on the dewatering step by enhancing the separation of the water from the sludge [62].



Stopping the biological activities and Reducing the pathogens

Methods included: anaerobic digestion, aerobic stabilization, thermal and chemical

Removing the water from the sludge by mechanical methods (centrifuge and filtration) and further reducing the sludge volume.

Increasing the solid concentration of the sludge, Reducing the sludge volume

Techniques included: gravity thickening, floatation, thickening by drainage

Improving the efficiency of the dewatering process by altering the size of the particles and interactions within the sludge particles

Method included: coagulation/flocculation

Oxidizing the organic matters to oxidized end products, water vapor, and ash, reducing the volume and weight of the sludge cake, and reducing the toxins and destructing the pathogens

Figure 2-5. Typical sludge treatment steps

Coagulation/Flocculation in Sludge Conditioning.

As mentioned above, WAS dewatering is challenging due to the highly compressible and colloidal nature of the sludge solids and its high organic content [56]. EPS, bound water content, zeta potential which represent the stability of the sludge colloidal particles and yield stress that indicated the rheological behavior of sludge [35] are the most critical sludge properties which affect the dewater-ability of sludge.

To improve the dewaterability of the WAS, many attentions have been given to the various pre-treatment methods including mechanical [78], electro-chemical [79,80], thermal [81,82], chemical [83,84], enzyme [85], microbiology [86], ultrasound [87], microwave [88], advanced oxidation processes (AOPs) [89] treatments, and etc.

In water treatment processes, one of the most well-known pre-treatment technologies for solid-liquid separation is coagulation/flocculation process [15,17,90,91]. The coagulation process aims to neutralize the negative charges of the stabilized colloidal particles where these destabilized particles aggregate and form micro flocs [17,31,32,92]. Whereas, in the flocculation process, the destabilized particles propagate to gather and agglomerate into larger flocs. This technology is cost-effective and user-friendly wastewater treatment technology and is widely used for treating several types of wastewaters such as tannery and textile industry wastewater [93,94], pulp and paper mill wastewater [95], industrial wastewater [96], removal of natural organic matter [97,98] and boron from water [99]. Aside from the wastewater treatment, the technology employed in many industrial fields such as mining [100] and oil extraction [101].

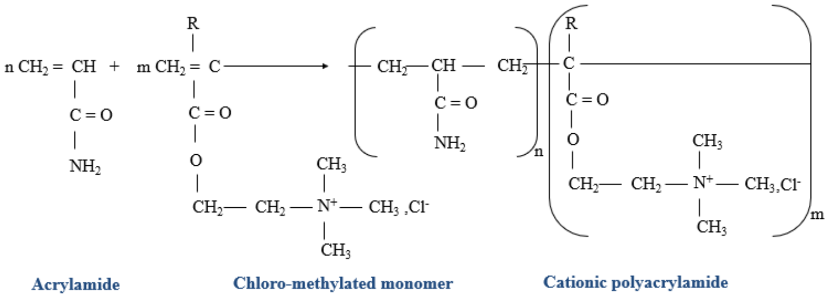
Coagulation/flocculation technology comprises of two primary mechanisms, namely, charge neutralization and bridging effect which is suitable for both water and wastewater treatment as well as sludge dewatering [102,103]. In sludge dewatering process, charge neutralization in addition to breaking down the stability of the charged particles enhances the free water and reduces the thickness of the hydrated shell of sludge particles through compression of the electric double layer [104]. Moreover, charge neutralization can weaken the water-trapping capability of the sludge by destroying its network structure [13,105]. The coagulation/flocculation mechanisms for both sludge dewatering and contaminant removal including suspended colloids and natural organic matter in water and wastewater treatment are similar; however, the treatment conditions and the objectives of these two processes are different. Coagulation/flocculation technology applied in water and wastewater treatment aims in removing various contaminants and purifying the water, while in sludge dewatering, the separation of the water from solids and construction of the suitable structure of sludge cake with good filtration performance are the main objectives [106,107].

In general, the efficiency of the coagulation/ flocculation process depends on the selection of an appropriate coagulants/flocculants, as each coagulant/flocculant exhibits different structural characteristics (i.e., charge characteristics, ionic properties, functional group, and MW) [108,109] and have different affinity for the contaminant. Therefore, depending on the target contaminant, a suitable coagulant/flocculant must be selected to achieve high charge neutralization on the basis of DLVO theory [110]. Coagulants can be categorized into organic and inorganic coagulants. Inorganic coagulants including trivalent-metal salts such as aluminum sulfate, ferric chloride, poly-aluminum chloride (PAC), etc. are the most commonly used coagulants for the insoluble suspended solids in water that carry negative charges and organic coagulants are polymers with high CD and low MW such as polyDADMAC and polyamine [15–17]. On the other hand, the most widely used flocculants are organic polymeric materials including synthetic and natural polymers [13,15]

In recent years, cationic polyelectrolytes such as CPAM which is the basis of many commercial flocculants [31] are used as a flocculent, and they showed a significant enhancement in the solid-liquid separation processes [6,10,12,13,20]. Figure 2-6 shows the synthesis of CPAM which is a univalent polyelectrolyte having a positively charged functional group. The cationic charge is brought by a quaternary ammonium function fixed on a long polymer chain. These type of flocculants are mainly used in the treatment of potable water, wastewater from different sources, and sludge conditioning [15].

Parameters of Organic Polyelectrolytes Affecting the Conditioning

Different parameters will influence the efficiency of the organic polyelectrolyte in the conditioning of the sludge which subsequently affects the dewatering efficiency. These parameters are; CD, MW, and molecular structure of the organic polyelectrolyte. Depending on the type of the sludge to treat, the organic matter content, and the type of equipment used for the dewatering, an appropriate polyelectrolyte should be selected. For example, for municipal and industrial sludge that contain high organic matter, a polyelectrolyte with high CD is more suitable, or if the centrifuge is used for the dewatering process, a high to very high MW is best adapted due to the high shearing applied to the flocs [16]. Table 2-3 shows the efficiency of PAM-based flocculant on dewatering of AS.



Note: if R=H -> ADAM (dimethylaminoethyle acrylate)
if R=CH3 -> MADAM ((dimethylaminoethyle methacrylate)

Figure 2-6. Synthesis of cationic polyacrylamide (redrawn from [73])

Table 2-3. *Review on the Efficiency of Synthetic Polyelectrolytes on the Flocculation Behavior of Sludge*

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref
Cationic PAM	Activated sludge	• CST	• Reducing CST to 9 and 13 where lower MW polymer is performing better where they have the same CD of 60%	[4]
Cationic (FO 4490 SSH, FO 4690 SSH, FO 4498 SSH, FO 4698 SSH, FO 4498 XXR, FO 4698 XXR) acrylamides	MBR sludge	• Zeta potential • Turbidity • Floc size • CST • Settling rate	• PAM structure, CD, and MW substantially influenced the suspension turbidity and zeta potential. • A higher CD is more effective in reducing particle surface charge and supernatant turbidity for linear PAM • Lowest residual turbidity and negative zeta potential were obtained for highly branched structured of PAM (FO 4698 XXR) • Flocs size was independent of MW and CD of PAMs	[111]

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref
			and strongly dependent on the PAMs concentration • The structure and CD of PAMs were significant factors in the efficiency of flocculation and dewatering • Linear structured PAMs have resulted in the highest CST reduction • Settling rate was directly proportional to the flocs size	
Cationic polyelectrolyte; Polydiallyldimethyl Ammonium chloride (PDADMAC), clarifloc and stockhausen	Analogue/ real ^{1}CAS	• CST	• Addition of Ca (II) improves the sludge dewatering • Highest reduction in CST was obtained when PDADMAC was used after the addition of Ca (II) for both synthetic and real sludge • For all polyelectrolytes, the highest reduction of CST was at 2.5 mM of Ca (II)	[41]

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref
			• The exitance of Ca (II) ion reduces the polyelectrolytes dose	
[2]CPAM (TPADL, PADL, TPAD, PAD)	[3]WAS	• Zeta potential • Flocs size (D_{50})	• CPAM exhibited a significant dewatering performance • Significant reduction in zeta potential using all four CPAM • Lower optimum dose corresponding to zero zeta potential for TPADL • Shifting the flocs size distribution, representing the bigger floc formation • 79-85% increase in the floc size and 79% reduction in zeta potential	[6]
Cationic Acrylamide base flocculant (AM-$DEAC_3$, AM-$DEAC_6$, AM-$DEAC_{12}$)	CAS	• CST • Flocs size (D_{50})	• 72% reduction of CST • Increasing in the flocs with polyelectrolytes dosage • MW and CD of polyelectrolytes are key factors affecting eh	[40]

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref
			performance of sludge conditioning and dewatering • The polyelectrolyte with a high content of cationic monomer, high cationic degree, and moderate MW compare to other polyelectrolyte had the strongest hydrophobic association	
CPAM (Fennopol K5060)	Municipal AS	• Turbidity	• 91% reduction in turbidity	[5]
Cationic polyacrylamides (CPAM-10, CPAM-80)	Fresh AS	• Turbidity • Settling rate • Floc size	• Almost 50% reduction in the sediment thickness was obtained using cationic PAM • Large floc sizes and low turbidity was obtained using CPAM • The highest settling rate achieved by using CPAM-	[64]

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref
			80 at low dose and CPAM-10 at high dose	
low MW cationic polyacrylamide (CPAM-10), high MW cationic polyacrylamide (CPAM-80)	Municipal AS	• Turbidity • Zeta potential • Settling rate	• Both polyacrylamides, improve the turbidity and lower the zeta potential • By adding PAMs, zeta potential reduces but remains negative • High molecular weight PAM has higher flocculation efficiency (higher reduction in zeta potential and turbidity) • Settling rate improved by 30% for CPAM-10 and 40% for CPAM-80	[112]
Cationic polyacrylamide (CPAM)	WAS	• CST	• Significant improvement of sludge dewatering by using magnetic field pre-treatment compare to using CPAM alone	[14]

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[1] Conventional Activated Sludge
[2] Cationic polyacrylamide
[3] Waste Activated Sludge

Organic flocculants studied and used for AS conditioning have predominantly been cationic in nature [4,6,14,40–43] and with PAM polymers featuring prominently [14,113]. This is a consequence of the inherent affinity of the positively-charged ionogenic for the negatively charged suspended particles, thereby affecting charge neutralization of the latter [45].

However, while their application to inorganic suspensions has encompassed optimization of the polyelectrolyte architecture [45], this aspect appears to have received much less attention for their application to biological sludge from wastewater treatment. As a result, there remains a scarcity of information and knowledge regarding polyelectrolyte efficacy and characteristics for the specific duty of AS conditioning and consolidation. This gap is especially evident for MBR sludge which is known to be more challenging to dewater than classically AS due to their generally smaller floc size and higher EPS content [43,46]. Despite this, the limited work conducted in polyelectrolyte dosing of MBR sludge appears to have been primarily directed at membrane fouling inhibition [47,48].

Hybrid Coagulation/Flocculation

To accelerate the flocculation efficiency and improve the settlement of the flocs, polymeric flocculants can be used in conjunction with the coagulants known as hybrid coagulation-flocculation process [4]. Sludge conditioned with coagulants and flocculants as the hybrid system is rarely reported; little is known about the application of the hybrid coagulation-flocculation process for sludge conditioning and dewatering [114]. (Figure 2-7)

Recently several studies on hybrid coagulation-flocculation process have looked at improving the flocculation of the suspended particle in wastewater. They tended to focus on:

i. Impact of using organic coagulants combined with organic polymers in the treatment of pulp and paper mills wastewater [115] and municipal AS [116].
ii. Influence of inorganic coagulants combined with organic polymers in the treatment of AS [4,117], municipal anaerobically digested bio-solid waste [118], alumina suspension [119] and pulp and paper mill wastewater [120].
iii. Synergistic effects of chemical flocculation/conditioning of AS through combining with inorganic [4,20,121–124] and oxidative chemicals or technologies [121,125,126].
iv. Impact of dosing order of the inorganic coagulant and flocculant on activated sewage sludge dewatering performance during the conditioning process [114,127].

For example, Al-Dawery [112] showed that combing a high MW cationic PAM with an anionic PAM can massively reduce the turbidity and zeta potential and improve the settling rate compare to when each flocculents are used alone. Similarly, the work of Chen et al. [117] on the influence of hybrid coagulation-flocculation system showed that using hybrid system reduces the optimum dose and improves the CST which is an indication of dewaterability of the activated sludge.

Molecular weight, polymer’s structure, and CD are the most important characteristics of polymers. To achieve high efficiency in dewatering of sludge with a minimum dose of the polymer; these characteristics need to be considered [15,31,128]. Although the studies mentioned above have investigated the dewatering ability, and performance efficiency of the hybrid systems, yet little is known in the open literature on the influence of PAM’s architecture, MW and CD on electro-kinetic properties and dewaterability of sludge when combined with strong or weak polyelectrolyte organic coagulants [31]. Combination of PAM with strong and weak polyelectrolytes such as polyDADMAC and polyamine respectively is expected to have an influence on the electro-kinetics of flocs size and consequently the dewaterability of a real highly stable MBR sludge. Therefore, it is crucial to investigate the synergistic influence of organic coagulants; polyDADMAC (FL 4440) and polyamine (FL 2949) combined with six different PAMs (with different architecture, MW and CD) on the flocculation and dewatering enhancement of highly stable MBR sludge which has been extracted from an industrial MBR treating petroleum effluents.

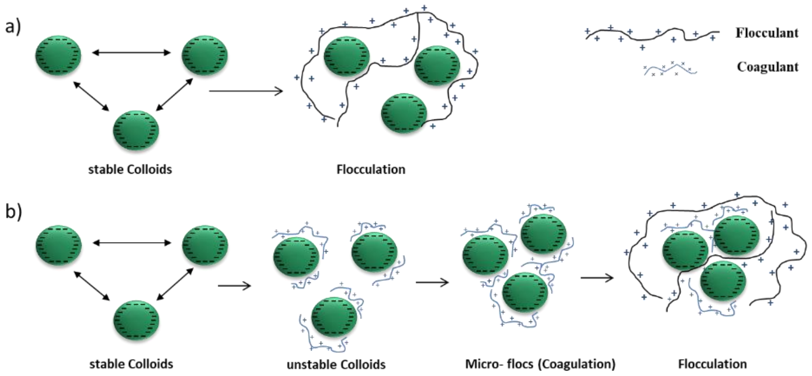


Figure 2-7. Destabilization of stable colloids through a) flocculation and b) hybrid coagulation-flocculation processes

Rheology of Sludge

Fluids are characterized as Newtonian or non-Newtonian, depending on their viscosity behavior as a function of mainly shear rate, shear stress, and deformation history. Newtonian fluids are described as the flow behavior of fluids where there is a linear relationship between shear stress [τ, mPa] and shear rate [$\dot{\gamma}$, s^{-1}]. For the homogeneous and non-dispersive fluids (Newtonian), viscosity can be simply attained from the ratio between shear stress (τ, mPa) and shear rate ($\dot{\gamma}$, s^{-1}) given in Eq.2.1:

$$\mu = \frac{\tau}{\dot{\gamma}} \qquad Eq. 2.1$$

However, in reality, most of the fluids such as wastewater sludge have non-Newtonian flow behavior, where their viscosities are dependent on the shear rate (Shear thinning or Shear thickening) or on the deformation history (Thixotropic fluids). Non-Newtonian fluids result in a non-linear relation between shear rate and shear stress, thereby exhibit yield stress or time-dependent viscosity (apparent viscosity) [129].

Sludge behaves as a non-Newtonian fluid where its rheological properties depend on shear rate and time. For non-Newtonian fluids, the viscosity may decrease with shearing that is called shear thinning fluids (pseudoplastic), or it may increase with shearing for shear thickening fluids (dilatant) [129]. Some Non-Newtonian fluids show a thixotropic behavior, i.e., they undergo through shear thinning upon the application of shear followed by shear thickening when the shear is removed or reduced.

Visco-plastic fluids require threshold stress to initiate the flow called yield stress. Fluid starts to flow at this threshold stress and exhibit either a constant viscosity (τ plastics) or a shear thinning behavior. There are several rheological models available in the literature for non-Newtonian fluids [8,130]. Most of these models are pure empirical models describing shear stress or apparent viscosity as a function of shear rate or yield stress. Some of them are given in Table 2-4 [8,130]. Sludge is mainly characterized by pseudoplastic or Bingham plastic models [37].

Table 2-4. *Non-Newtonian Shear Stress-Shear Rate Models*

Model	Equation	
Power-law (Ostwald de Vaele) Shear-thinning (pseudoplastic) (n < 1) Shear-thickening (dilatant) (n > 1)	$\tau = k\dot{\gamma}^{n}$	Eq.2.2
Bingham	$\tau = \tau_B + k\dot{\gamma}$	Eq.2.3
Herschel and Bulkley (0 < n < ∞)	$\tau = \tau_0 + k\dot{\gamma}^{n}$	Eq.2.4
Casson	$\tau^{0.5} = \tau_o^{0.5} + \mu_\infty^{0.5}\dot{\gamma}^{0.5}$	Eq.2.5
Sisko	$\mu = \mu_\infty + k\dot{\gamma}^{n-1}$	Eq.2.6
Cross	$\frac{\mu - \mu_\infty}{\mu_o - \mu_\infty} = \frac{1}{1 + (\lambda\dot{\gamma})^{m}}$	Eq.2.7
Carreau	$\frac{\mu - \mu_\infty}{\mu_o - \mu_\infty} = (1 + ((\lambda\dot{\gamma})^{2})^{\frac{n-1}{2}}$	Eq.2.8

The Bingham and Herschel-Bulkley models (see Eqns.2.3 and 2.4) are widely used to describe the non-Newtonian behavior of activated sludge. The magnitude of Bingham yield stress, $\tau_{B,}$ is an indicative parameter for assessing the strength of floc in a flocculated suspension such as those existing during the pumping and filtration processing. Bingham yield stress is also used as expressive of the amount of stress needed to break the flocculated suspension to a suspension containing smaller assembled flocs or primary particles [38].

The rheological properties can be investigated if periodic or dynamic experiments are performed through the viscoelastic properties' measurements. In this way, it is possible to obtain information on the equilibrium state of the flocculated networked dispersions without disturbing internal supermolecular structures. The viscoelastic properties of materials are usually determined from oscillatory tests by applying a sinusoidal input strain and recording the subsequent sinusoidal shear stress in a strain-controlled rheometer. At low-stress amplitudes, the viscoelastic properties of materials (i.e., elastic modulus; G', loss modulus; G'', complex dynamic modulus; G*, and complex viscosity; η*) are not strained or stress dependent. The linear region where the rheological properties were not strained, or stress-dependent is called the linear viscoelastic region (LVR).

Equation 2.9 relates the three moduli [131,132]:

$$G^* = G' + iG'' \qquad \text{Eq.2.9}$$

While Eq.2.10 define the absolute value of the complex dynamic modulus ($\left|G^*\right|$).

$$\left|G^*\right| = \sqrt{(G'(\omega))^2 + (G''(\omega))^2} \qquad \text{Eq.2.10}$$

Viscoelastic material also possesses complex dynamic viscosity (η*) where:

$$\eta^* = \frac{G^*}{\omega} \qquad \text{Eq.2.11}$$

In this equation, ω denotes the angular frequency in rad/s.

The elastic modulus (G'), viscous modulus (G'') and complex viscosity (η*) obtained from dynamic oscillatory measurements can be used as a strong tool for assessing flocculation kinetics of networked suspensions [11,29,39]. The information collected from such measurements may provide important information on floc strength and flocculation mechanism of colloidal dispersions. In oscillatory measurements, flocculated suspensions are subjected to deformation by applying sinusoidal input strain which varies harmonically with time. At low applied strain/stress, there exists a linear region where both G' and G'' are not strained, or stress-dependent called the linear viscoelastic region (LVR). Strain or stress sweep, conducted by varying the amplitude of the input signal at a constant frequency, is used to determine the limit of the LVR by identifying a critical value of the sweep parameter. The critical value of the sweep parameter is defined as the strain/stress value where G' falls to 90% of the plateau value [11].

It is worthy of mentioning that although many researchers used the rheological methods to assess the sludge quality and treatment (conditioning and dewatering) yet the focus in most publications are concerned with shear flow behavior only while paying less attention to the importance of the viscoelastic properties of such flocculated networked.

Most of the previous studies on the rheological behavior of AS have focused on the following:

- The influence of solid content on the rheological behavior of AS [50,133–135]
- The influence of solid retention time on the rheological behavior of MBR sludge [136–138]
- The impact of solid concentration and temperature on the rheological property of municipal sewage sludge [139] and AS in an airlift MBR [140]

Table 2-5 reviews the effect of solid concentration on the rheological behavior of AS.

Table 2-5. *Review on the Effect of Solid Concentration on the Rheological Behavior of Activated Sludge*

Type of AS	Solid concentration (g/l)	Geometry	Shear rate (s^{-1})	Model	Results	Ref
MBR	2.7-47	^{1}DCC	0-22000	^{3}PL	• AV function of MLSS	[137]
Dewatering	0.27-0.64		0-120	^{4}NM	• Apparent viscosity is related to the network strength	[138]
Lab-scale MBR	3.7-22.9	^{2}CC	3-1300	PL & ^{5}B	• B model performs better than the PL model	[136]
Dewatering	2.5-10		NM	NM	• Rheology can be used to control dewatering	[141]
Lab-scale MBR	2.74-16		25-1000	Different models	• Shear thinning behavior • Static and dynamics yield stress for MBR and CAS systems • B model is suitable under low MLSS concentration of less than 10 g/l for CAS	[140]

Type of AS	Solid concentration (g/l)	Geometry	Shear rate (s^{-1})	Model	Results	Ref
WWTP	3.5-4	NM	36.7-73.4	B	• Strong correlations between dispersed mass concentration, resistance to filtering (capillary suction time) and rheological parameters. • The development of inter-particle networks causes resistance to flow.	[51]
Municipal AS	2-4	CC	0-1000	B	• Increasing the TSS increases the shear stress and yield and result in higher viscosity	[50]
Municipal sludge	18-20%	CC	0-300	Ostwald de Vaele	• Sludge exhibited shear -thinning behavior • Higher solid concentration and lower temperature	[139]

Type of AS	Solid concentration (g/l)	Geometry	Shear rate (s^{-1})	Model	Results	Ref
					resulted in higher shear stress	
Municipal AS		CC	0-1200		• Non-Newtonian flow behavior • Only a small difference between shear yield stress values of pure and conditioned sludge, reflecting the weak strength of the flocs formed	[112]
Pilot MBR	0-18.7	CC	1-1000	Casson	• With increasing the shear rate, the apparent viscosities decrease • Sludge exhibit shear thinning behavior • Solid concentration and shear rate affect the flow behavior of sludge	[140]

Type of AS	Solid concentration (g/l)	Geometry	Shear rate (s^{-1})	Model	Results	Ref
	2.8%-9.2%	CC	1-1000	HB	• Apparent viscosity and yield stress increase with increasing the total solid concentrations • It exhibits time dependent behavior	[142]

[1]DCC double concentric cylinder
[2]CC concentric cylinder
[3]Power low model
[4]Not-Mentioned
[5]Bingham model
[6]Herschel-Bulkely model

Table 2-6 shows a review of the efficiency of polyelectrolytes on the dewatering and rheological behavior of sludge.

Few researchers have shown the influence of conditioning on the rheological behavior of sludge which is significant for cost and selection of the proper equipment and sizing, handling of the sludge and transportation [37,49,50]. Besides, limited researches have been conducted on correlating the sludge dewatering (i.e., CST) [37,51], electro-kinetics (i.e., zeta potential, ζ, and turbidity) and flocs size parameters to the rheological characterizations [52,53]. It is challenging to optimize the type and dose of flocculants due to the heterogeneous and complex nature of AS [18,19]. Additionally, in the past, the characterization of solid-liquid separation of flocculated suspensions was common to either focus on the free settling region of the suspension through ζ, turbidity and floc size measurements, or on the behavior of networked suspension either in the form of sediment or a filter cake through rheological measurements. A combination of results from these regimes for the same system is rarely investigated and, if complete knowledge of the characterization from individual suspended particles of sludge to a fully networked sludge is required, it is necessary to correlate the degree of flocculation of the sludge with its rheological behavior.

Studies on the influence of organic flocculants and coagulants structure and type on the combined degree of flocculation and rheological behavior of industrial MBR sludge are either rare or not available in the open literature. Therefore, it is important to focus on the rheological characteristics of the polyelectrolytes flocculated MBR sludge and correlate them to their degree of flocculation and dewatering.

Table 2-6. *Review on the Efficiency of Polyelectrolytes on the Dewatering and Rheological Behavior of Sludge*

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref.
Cationic polyelectrolyte; Polydiallyldimethyl Ammonium chloride (PDADMAC), clarifloc and stockhausen	Analogue/real [1]CAS	Viscosity	● The polyelectrolytes have increased the liquor viscosity	[41]

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref.
^{2}CPAM (TPADL, PADL, TPAD, PAD)	^{3}WAS	Apparent viscosity	• The apparent viscosity of polymers increases linearly with concentration	[6]
Cationic Acrylamide base flocculant (AM-DEAC$_{3}$, AM-DEAC$_{6}$, AM-DEAC$_{12}$)	CAS	Apparent viscosity	• Floc strength was determined through measuring the sludge viscosity • Floc strength has increased by increasing the polyelectrolytes dosage which is as a result of an increase in the viscosity of the sludge system • The most compact flocs were formed by using a polyelectrolyte with a high content of cationic monomer and high cationic degree and enhanced the settling rate and floc strength	[40]

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref.
Cationic polyacrylamides (CPAM-10, CPAM-80)	Fresh AS	Floc density	• Floc densities, compactness and sizes increase with increasing the PAM dosages • Formed flocs have low shear yield stress, thus a weak strength of flocs	[112]
Cationic polyacrylamides	AS		• Sludge dewaterability and the floc compactness have improved	[85]
Cationic polyacrylamide high MW (CPAM-80)	Municipal AS	Viscosity	• Using conditioners enhance the settling rate, however, increasing the dose of conditioners reduce the yield stress and viscosity • Both fresh and conditioned sludge exhibit shear thinning behavior • Increasing the total solid concentration	[50]

Synthetic Polyelectrolytes type	Type of sludge	Investigated parameters	Main outcome	Ref.
			increases the total solid concentration	
Cationic polyacrylamide	Wastewater sludge		• Unconditioned sludge shows viscoelastic liquid-like behavior • Conditioned sludge with polymer results in solid-like behavior • Conditioned sludge with polymer forms rigid structure • Addition of the polymers at their optimum doses improve the viscosity of the sludge	[37]

[1] Conventional AS
[2] Cationic polyacrylamide
[3] Waste Activated Sludge

CHAPTER 3: METHODOLOGY

Materials

Sludge was collected fortnightly from the membrane tanks of a small (50 m3/day capacity) MBR installation at a nearby petroleum industry site in Qatar, the MBR feed comprising a blend of gas processing effluent and gas field produced water. The sampled sludge was immediately transferred to the laboratory and stored at -4°C for no more than four days prior to testing. The physical and chemical characteristics of the sludge samples were determined before conditioning. These characteristics including; TSS, VSS, COD, Conductivity, pH, ζ, turbidity, floc size, and CST were measured at the beginning and end of each week according to the standard methods [12,143]. Table 3-1 summarizes the characteristics of sludge at the average value of 15-20 measurements for each test.

The six PAM flocculants tested in this study, supplied by SNF Floerger (France), were characterized by the supplier according to their molecular architecture (linear, slightly branched and highly branched), MW (4-10 million Da) and CD (40 - 60%). The characteristics of these PAMs are listed in Table 3-2.

Two organic coagulants (FL 4440 and FL 2949), categorized by the supplier according to their MW and CD were supplied by SNF Floerger, France (Table 3-3).

Table 3-1. *The Characteristics of MBR Sludge*

Sludge property	Value	Min	Max	Relative Standard deviation (RSD)
TSS, $g.L^{-1}$	11.2	10.1	12.5	1
VSS, $g.L^{-1}$	10.1	9.13	11.3	1
VSS/TSS, %	90.1	89.8	90.8	0.3
SVI, $ml.g^{-1}$	89.9	84.3	94.9	4
COD, $mg.L^{-1}$	82	75	88	3
NaCl, $mg.L^{-1}$	853	850	857	4
Conductivity, $\mu S.cm^{-1}$	1380	1362	1398	15
Cond. temp., °C	15	13	17	2
pH	7.7	7	8.3	0.5
pH temp., °C	25	25	25	0
Zeta potential, mV	-15	-19	-11	3
Turbidity, NTU	2603	2048	2928	13
D_{50}, µm	17	13	22	3
CST, s	15	13	17	1

Table 3-2. *PAM Reagent Characteristics*

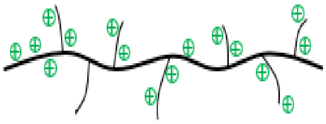
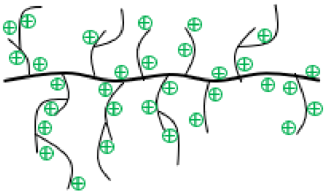
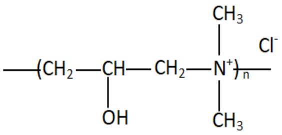
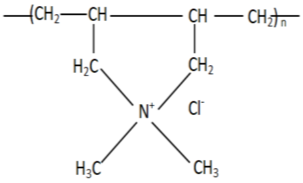
Name	CD (%)	MW ($g.mol^{-1}$)	Structure	
FLOPAM FO 4490 SSH	40%	7-10 million	Linear	
FLOPAM FO 4690 SSH	60%	7-10 million	Linear	
FLOPAM FO 4498 SSH	40%	7-10 million	Slightly branched	
FLOPAM FO 4698 SSH	60%	7-10 million	Slightly branched	
FLOPAM FO 4498 XXR	40%	4-7 million	Highly Branched	
FLOPAM FO 4698 XXR	60%	4-7 million	Highly Branched	

Table 3-3. *Organic Coagulant Reagent Characteristics*

Name	CD (%)	MW ($g.mol^{-1}$)	Structure
FLOQUAT FL 2949 (PolyAmine)	Very High	60000	 $-\!\!\left(CH_2-CH(OH)-CH_2-N^+(CH_3)_2\right)_n\!\!-\ Cl^-$
FLOQUAT FL 4440 (PolyDADMAC)	Very High	100000	

Methods

PAM, polyDADMAC and polyamine stock solutions of 2 g/L concentration were prepared by stirring the samples in deionized water for 5 hours using a magnet stirrer. Coagulation and flocculation tests were conducted on the prepared sludge using a jar test apparatus (Stuart Flocculator SW6, UK) comprising six sets of 1L beakers stirred with standard rectangular paddles (Figure 3-1).

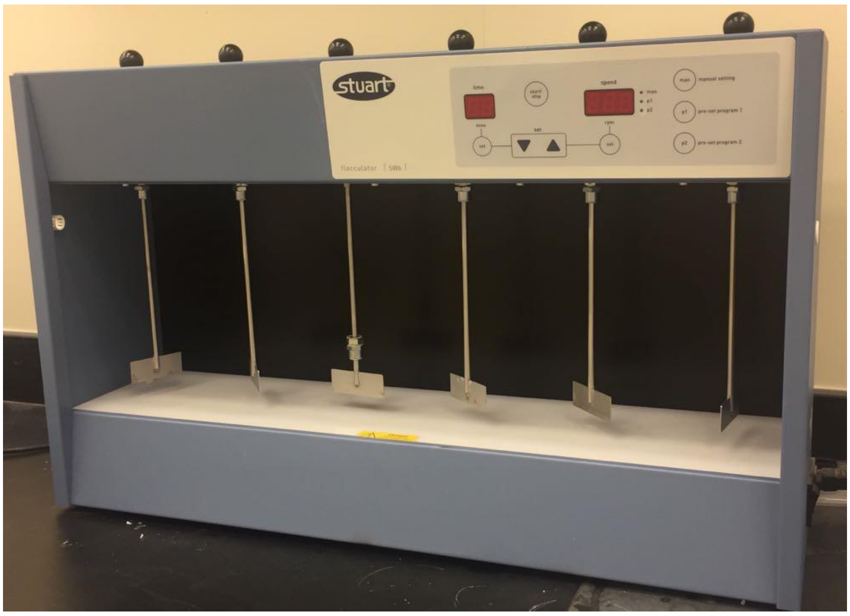


Figure 3-1. Jar test apparatus

For the flocculation test, specific volumes (providing the desired of PAM dose to the sludge) of PAM solution were added to 250 ml sludge samples while simultaneously mixing at 180 rpm which is equivalent to velocity gradient (G)=350 s^{-1} for 2 min followed by slow mixing at 50 rpm (G=52 s^{-1}) for 20 min. Dewaterability (CST measurement), suspended particles removal (turbidity measurement) and mixing time can be correlated to ensure that the optimum G values are selected [144,145]. In this study, the abovementioned G values were fixed for all PAMs and dosages based on the maximum turbidity removal. The flocculated samples were transferred to a measuring glass and allowed to settle for 15 min. The supernatant was extracted entirely using pipet at a fixed level below the suspension surface for turbidity (in NTU), and zeta potential (ζ, mV) analysis and the volume of the sludge was measured by reading the value on the beaker [5]. For ζ measurements, samples were pre-filtered using 0.45 μm filter paper. The supernatant was extracted from the flocculated sludge following a standardized protocol [11]. The residual solid volume was determined, and the flocculated sludge was used for flocs size and bulk capillary suction time analysis (Figure 3-2). For the coagulation test, the same procedure was applied; however, the samples were mixed at 200 rpm (G=400 s-1) for 3 minutes.

The optimum doses of coagulants and flocculants were obtained based on the ζ and turbidity measurements and to enhance the flocculation and dewaterability of MBR sludge, a hybrid system of organic coagulants and polyelectrolytes were used.

For the hybrid coagulation-flocculation tests, the optimum doses of organic coagulants were added prior to PAMs addition. The samples containing coagulants were mixed at 200 rpm for 2 mins, followed by further mixing with PAM of known dose for a period of 2 min at 180 rpm (G=350 s^{-1}), and subsequently, the mixture was mixed for 20 min at a low speed of 50 rpm (G=52 s^{-1}). The produced flocs were then allowed to settle for 15 min.

In this study, each measurement being replicated 3-5 times with an experimental error of less than 5%. For reproducibility analysis, relative standard deviation (RSD) for each parameter is reported along with the experimental results.

Turbidity, a measure of removal efficiency of suspended particles was measured using a Hach *2100N* (US) turbidity meter (Figure 3-3), particle size, expressed as D_{50} with Mastersizer 2000 (Malvern Instruments Ltd., UK) (Figure 3-4), ζ with *Zetasizer ZEN3600* (Malvern Instruments Ltd., UK) (Figure 3-5), and finally CST was determined using a Triton *319 Multi-purpose CST* (Triton Electronics Limited, UK) (Figure 3-6), all according to standard methods [143].

While CST is widely accepted as a sludge dewaterability indicator [146,147], it is generally the case that the measurement provides an indication more of sludge filterability than consolidation [145]. The parameter does not fully reflect the efficiency of those dewatering processes which proceed wholly or partially through consolidation, such as centrifugation. As such, CST data reported in this study are considered to represent filterability, whereas the measurement of the sludge volume reduction is representing consolidation.

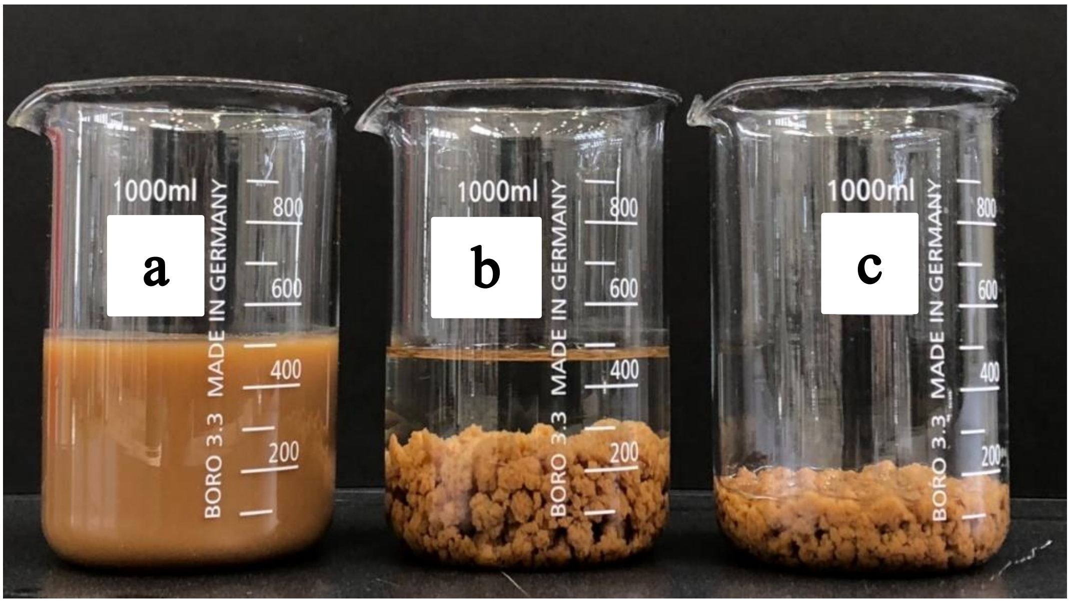


Figure 3-2. MBR sludge: a) as received, b) after flocculated with PAM and c) sludge dewatered

Figure 3-3. Hach 2100N (US) turbidity meter

Figure 3-4. Mastersizer 2000 (Malvern Instruments Ltd., UK)

Figure 3-5. Zetasizer ZEN3600 (Malvern Instruments Ltd., UK)

Figure 3-6. Triton 319 Multi-purpose CST (Triton Electronics Limited, UK)

Rheological Measurements

PAM, coagulants and sludge samples were prepared similarly to the previous section (3.2) with the same amount and concentration. After mixing the samples for 2 min at high speed of 180 rpm and 20 min at a low speed of 50 rpm, the resultant flocs were allowed to settle for 15 mins. Flocs were taken for rheological analysis after extracting all supernatant from the samples.

The rheological parameters were measured at a temperature of 25.0 ± 0.1°C using a strain-controlled instrument (Anton Paar Rheometer Model MCR 302) (Figure 3-7). All the tests were done through cup and bob measuring geometry.

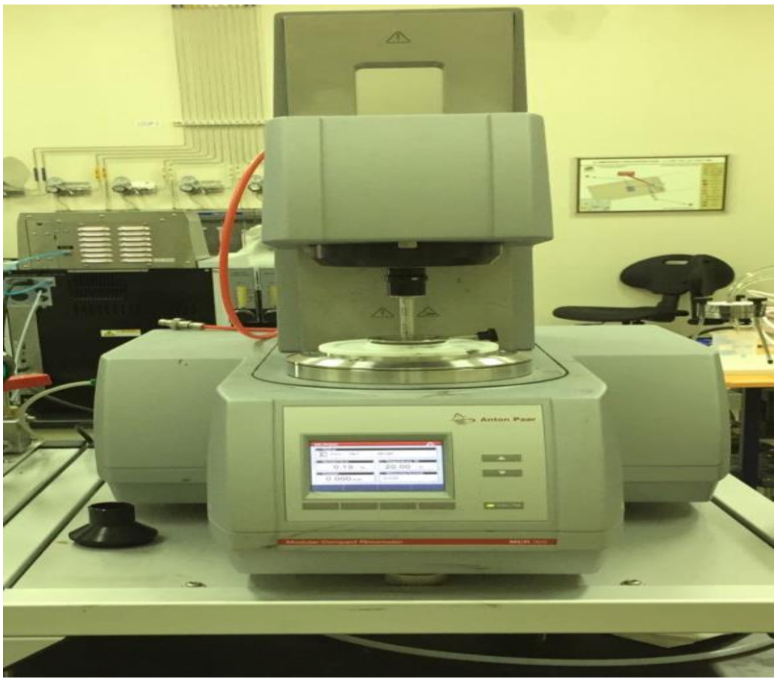


Figure 3-7. Anton Paar Rheometer Model MCR 302

The prepared sludge samples were premixed to get uniform samples and were loaded into the concentric cylinder. Before conducting any measurement, the samples are required to reach stable rheology (morphology); hence, 5 minutes equilibration time was given for the samples before starting the measurements.

The first measurement was conducted to examine the flow behavior of sludge. The shear rate was varied from 0.01 to 1000 s^{-1}, and shear stress and viscosity were recorded as a function of shear rate. G' and G'' were obtained as functions of the applied frequency (0.1 – 500 rad/s) at a constant strain of 0.3% that has been selected by conducting a strain sweep test at a fixed frequency of 6.28 rad/s where all the tested samples were within the LVR (see Figure 3-8 as an example). The *G*' and *G*" were obtained by extrapolating the low applied frequency to the zero coordinate. Finally, to examine the thixotropic behavior of sludge samples, time-dependent measurements were conducted (viscosity vs. time at a constant shear rate). In this study, the results were reproducible an experimental error of less than 5%.

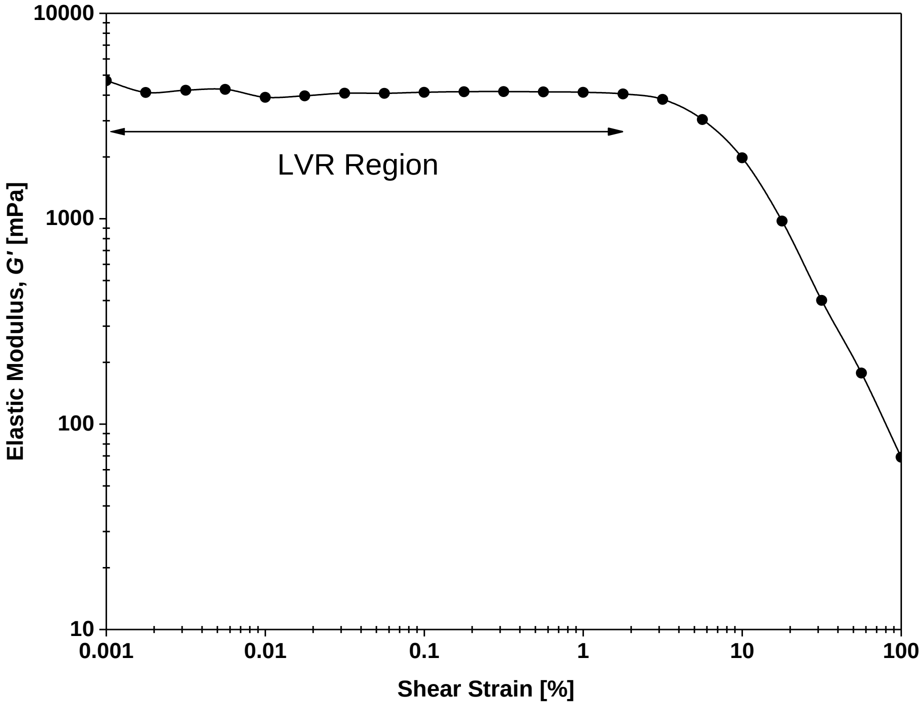


Figure 3-8. Evaluation of elastic modulus during strain sweep test for unconditioned sludge

CHAPTER 4: RESULTS AND DISCUSSION

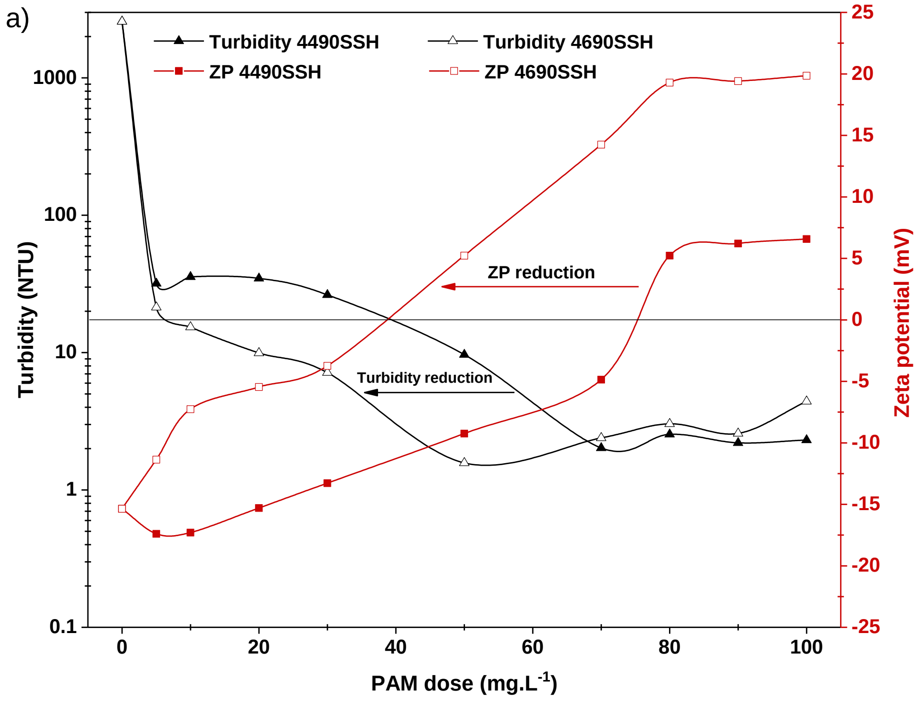
Influence of Polyelectrolyte Architecture on the Electro-kinetics and Dewaterability of Industrial Membrane Bioreactor (MBR) Activated Sludge

Objective

This section investigates the influence of six different PAM flocculants with different molecular architecture (linear, slightly and highly branched), CD and MW on the electro-kinetics and dewatering of highly stable industrial MBR sludge. The impact of PAM on flocculation is manifested in the supernatant turbidity, particle zeta potential, sludge CST, floc size and settleability. Turbidity removal and reduction in zeta potential are used to identify the optimum polymer dose.

Turbidity, Zeta potential and Capillary Suction Time

Trends in supernatant turbidity and zeta potential with PAM dose has indicated minimum turbidity at a low absolute ζ value (Figure 4-1).



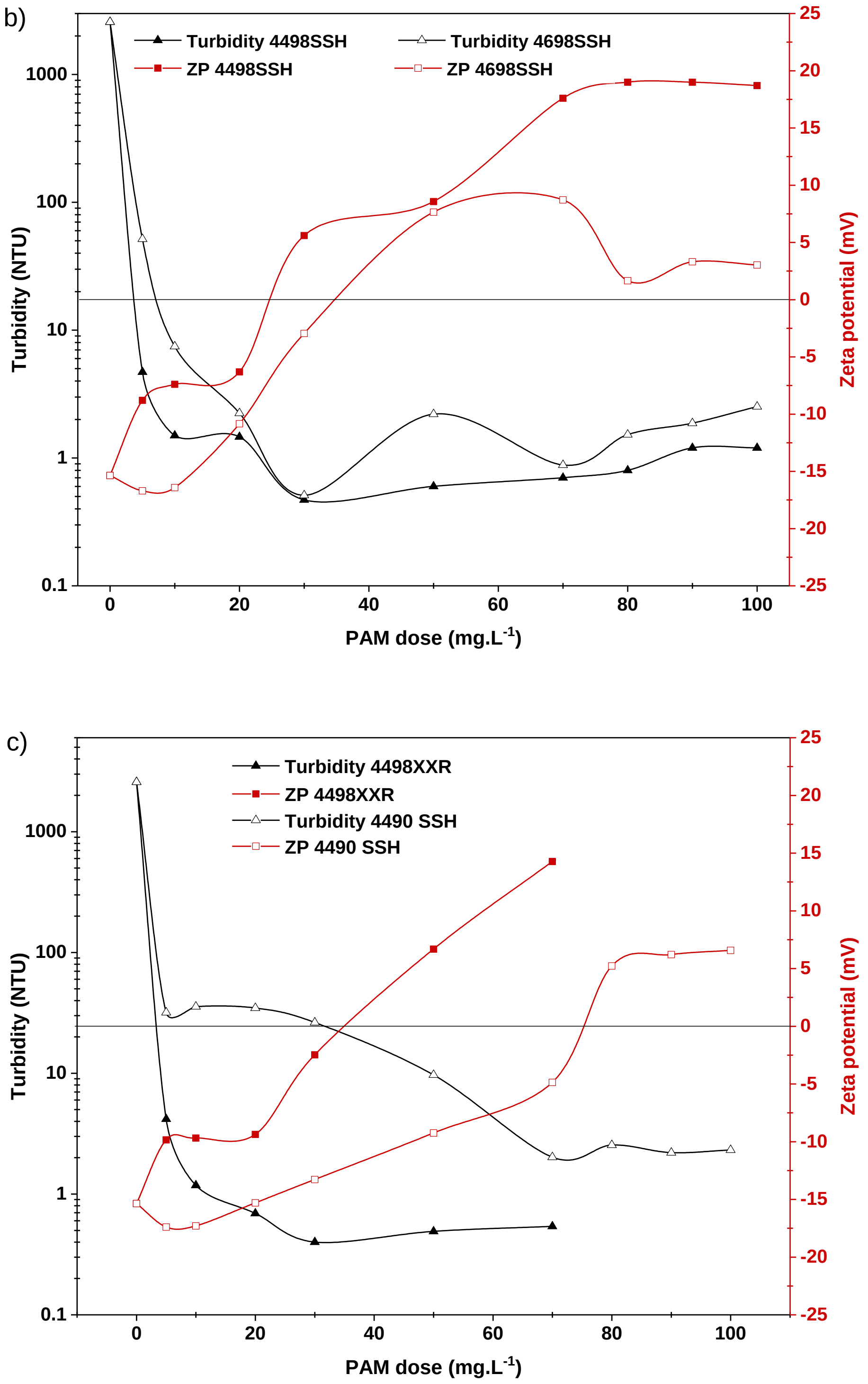


*Figure 4-1***.** Turbidity (RSD=0.02-3%) and zeta potential (RSD=0.02-4%) of a) linear b) slightly branched c) highly branched

There are a variety of ζ ranges for minimum turbidity removal depending on the treatment processes [12,148,149]. In this treatment process, for the water clarity requirement and good quality flocs in terms of type and strength of the surface electrical charges of the sludge particles, the optimum PAM dose was equated to the dose providing the minimum supernatant turbidity of below 2 NTU and ζ value between ±5 for each of the PAM reagents tested (Figure 4-1 and Table 4-1). On this basis, the highest optimum dose of 70 $mg.L^{-1}$ was associated with 4490 SSH, a linear PAM with 40% CD and a MW of 7–10 million $g.mol^{-1}$, compared with the lowest value of 10 $mg.L^{-1}$ for 4698 XXR, a highly-branched PAM of 60% CD with a MW almost half that of the linear PAM (MW of 4–7 millions). The optimum dose values for the remaining PAMs were 50 $mg.L^{-1}$ for the FO 4690 SSH (linear, 60% CD) and 30 $mg.L^{-1}$ for the FO 4498 SSH (slightly branched, 40% CD), FO 4698 SSH (slightly branched, 60% CD) and FO 4498 XXR (highly branched, 40% CD) products.

The results indicate all tested polyelectrolytes are being able to achieve charge neutralization at a sufficiently high dose of 20–70 $mg.L^{-1}$ depending on the polyelectrolyte characteristics. The trends evident from the data are:

a) An improved performance (manifested as a decrease in the dose required to achieve a target change in ζ and reduction in supernatant turbidity) on increasing the CD from 40% to 60% for the linear architecture (Figure 4-1a).

b) Comparability of the attained zeta potential and supernatant turbidity at a given dose between the 40% and 60% CD polymers for the slightly and highly branched architectures (Figure 4-1b and c).

c) Significant reduction in both the required dose and supernatant turbidity from the high-MW linear to lower-MW branched polymers.

The supernatant turbidity attained for the highly branched 4698 XXR polymer; 0.4–0.91 NTU at a dose of 10 mg.L^{-1}, was thus significantly less than the corresponding range of 2–2.5 NTU recorded for the linear 4490 SSH polymer at doses above 70 mg.L^{-1}. Residual supernatant turbidity of the high MW and slightly branched 4498 SSH PAM is compared with the lower MW and highly branched 4498 XXR polymers. The mean residual supernatant turbidity for 4498 SSH and 4498 XXR (Figure 4-1b and c) are determined at an optimum dose as 0.47 ± 0.03 NTU and 0.40 ± 0.69 NTU, respectively. These trends reflect the efficacy of both CD and polymer branching on charge neutralization, where branching increases the number of polymer tails with positive ionogenic sites for electrical neutralization of the inherently negatively-charged particles [29]. Overall, a 99% reduction in turbidity was obtained using all types of PAMs.

The results show the significant impact of CD, MW and polymer branching on charge neutralization of the sludge particles. All PAM reagents were able to reverse the negative ζ values at a specific dose. The required optimum dose depends on PAM type and reflects the preponderance of charge neutralization and polymer bridging. The subsequent reduction in ζ reduces the repulsive forces between the colloidal particles. Additionally, a bridging mechanism takes place where the long chain of PAM is adsorbed onto the surface of the sludge particles via PAM amide group. The long loops and tails of PAM extend into the solution well beyond the electrical double layer region and attach to the adjacent particles leading to bridging.

CST is used to measure the dewaterability or filterability of the pure and conditioned sludge. High CST value reflects a poor dewaterability, whereas low CST represents a good dewaterability.

CST and turbidity were found to follow similar trends versus PAM dose (Figure 4-2). The original CST value of 14.8 ± 1 s for the unconditioned sludge was reduced to 5.2, 6.6, 7.3, 7.1, 6.7, and 6.1 seconds for the FO 4490 SSH, FO 4690 SSH, FO 4498 SSH, FO 4698 SSH, FO 4498 XXR and FO 4698 XXR PAMs, respectively at the optimum PAM doses (Table 4-1). An overall reduction of 52–65% in CST is obtained.

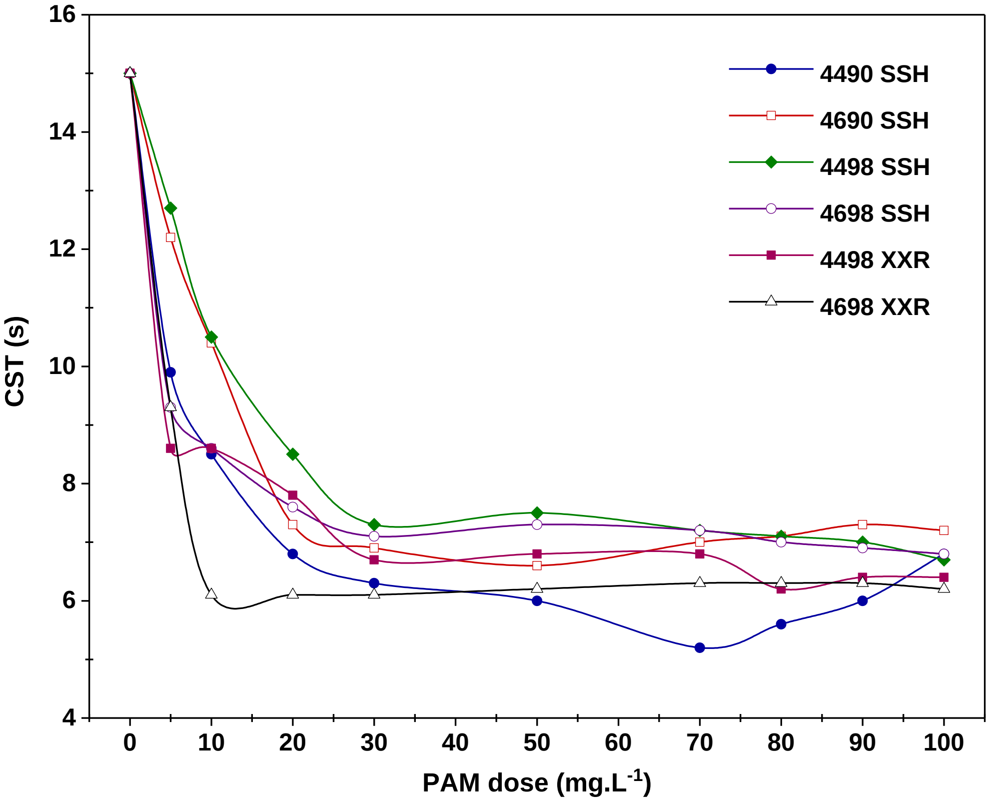


Figure 4-2. Capillary suction time of 4490 SSH and 4690 SSH (RSD = 0.5–1%)

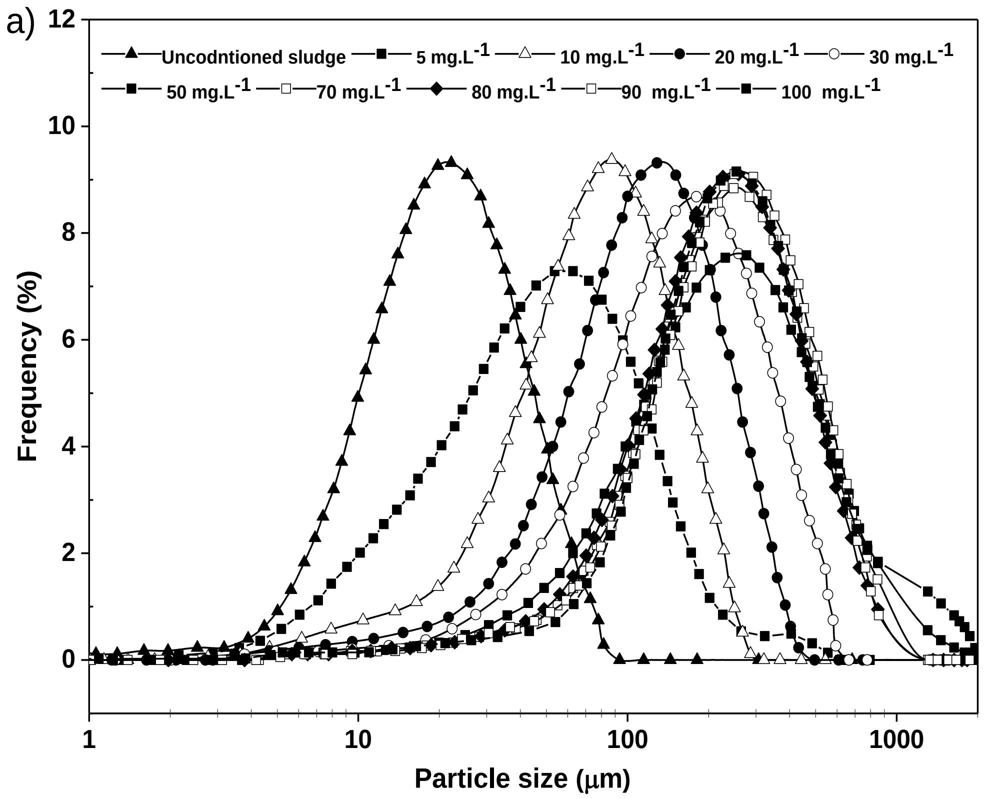
Table 4-1. *CST, s, as Function of PAM Dose (RSD:0.5–1%)*

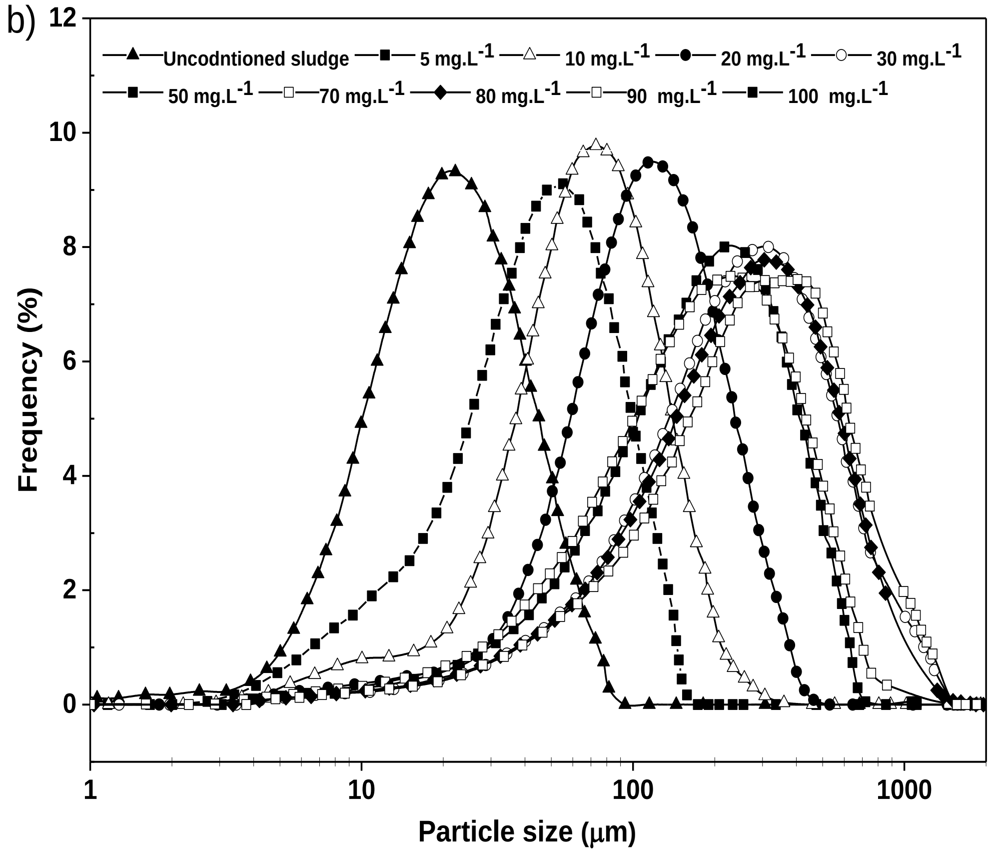
PAM's dose, mg.L^{-1}	4490 SSH	4690 SSH	4498 SSH	4698 SSH	4498 XXR	4698 XXR
0	15	15	15	15	15	15
5	9.9	12.2	12.7	9.3	8.6	9.3
10	8.5	10.4	10.5	8.6	8.6	6.1
20	6.8	7.3	8.5	7.6	7.8	6.1
30	6.3	6.9	7.3	7.1	6.7	6.1
50	6.0	6.6	7.5	7.3	6.8	6.2
70	5.2	7.0	7.2	7.2	6.8	6.3
80	5.6	7.1	7.1	7.0	6.2	6.3
90	6.0	7.3	7.0	6.9	6.4	6.3
100	6.8	7.2	6.7	6.8	6.4	6.2

The outcomes of this study are generally comparable with those reported in the literature for charge neutralization [6,40], reduction in turbidity [10,20,42,64,125,150] and CST [4,20,40–42]. Differences between the results from the current study and those previously reported relate to the sludge and PAM characteristics. Previously reported studies have mainly related to conventional activated sludge, with little focus on MBR sludge conditioning. Zhou et al. [6] reported a shift in ζ from −29 mV to + 5 mV using synthetic Acrylamide (AM) based flocculant in flocculation and dewatering of conventional WAS. In other work, Zemmouri et al. [42] stated a 54–95% reduction in turbidity and 81–91% reduction in CST when using synthetic polyelectrolytes in the flocculation and dewatering of WAS. This compares to turbidity reduction values ranging from 18 to 32% using an acrylamide-based flocculant [151] to 91–92% using a cationic PAM [5,150], also for WAS conditioning. The turbidity reduction of 99% achieved in the current study would appear to reflect the benefit of the combined favorable architecture and surface charge characteristics.

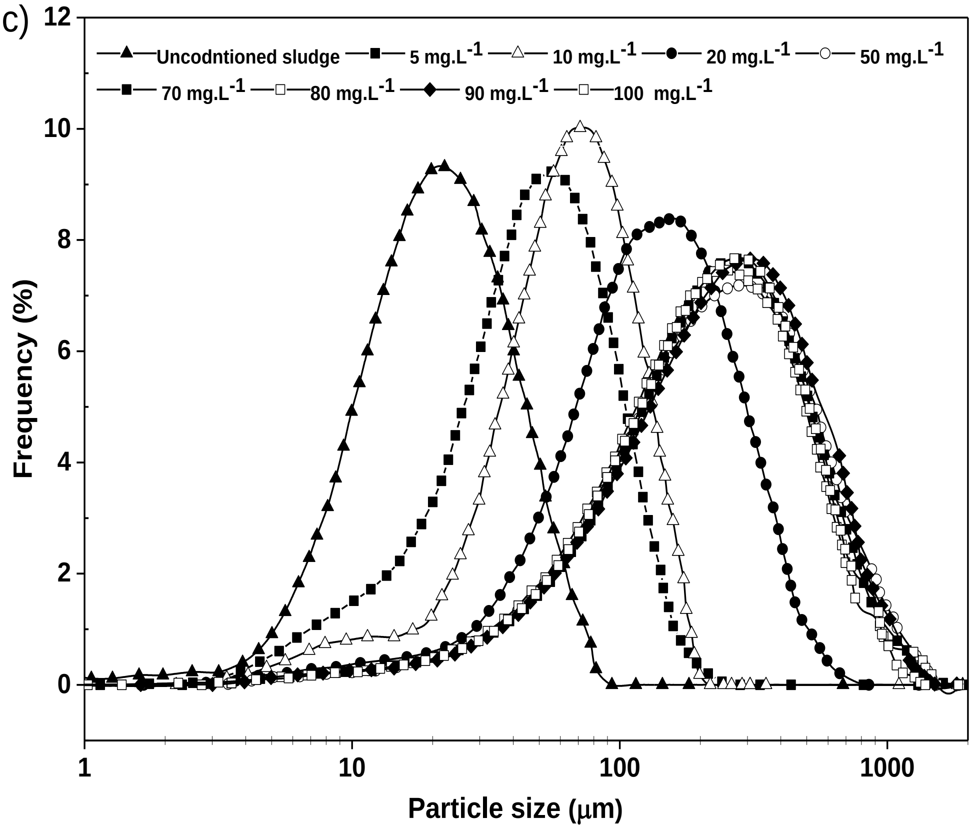
Floc Size

Floc size determination showed a similar distribution for all samples. Figure 4-3 shows the particle size distribution (PSD) of MBR sludge flocculated with different PAMs. Increasing the flocculant dose, increased the surface concentration of PAM on the sludge particle and consequently increased the floc size. For sludge conditioned with FO 4490 SSH PAM, the D_{50} increased from around 17 µm (unconditioned sludge) to 260 µm at a PAM dose of 70 mg.L^{-1}. Above this dose, surface saturation occurred, and the floc size remained largely unchanged. At the optimum doses of all PAMs, identified on the basis of residual turbidity and ζ, the largest flocs (241–246 µm) corresponded to the linear PAMs (50 and 70 mg.L^{-1} for the 4690 and 4490 SSH products, respectively) which is also shown in Figure 4-4a, that the PAMs with high optimum doses, i.e., FO 4490 SSH and FO 4690 SSH shifted the particle size distribution more toward the right. The lower optimum doses (10 and 30 mg.L^{-1}for the 4698 and 4498 XXR products respectively), yielded much smaller D_{50} values of 70 and 163 µm, respectively. This suggests that saturation had not been reached in these cases. However, at a selected unified PAM dose of 70 mg.L^{-1} (Figure 4-4b), XXR (highly branched) behaved similarly to SSH (linear and slightly branched) despite the MW of the SSH product being twice that of the XXR structure.

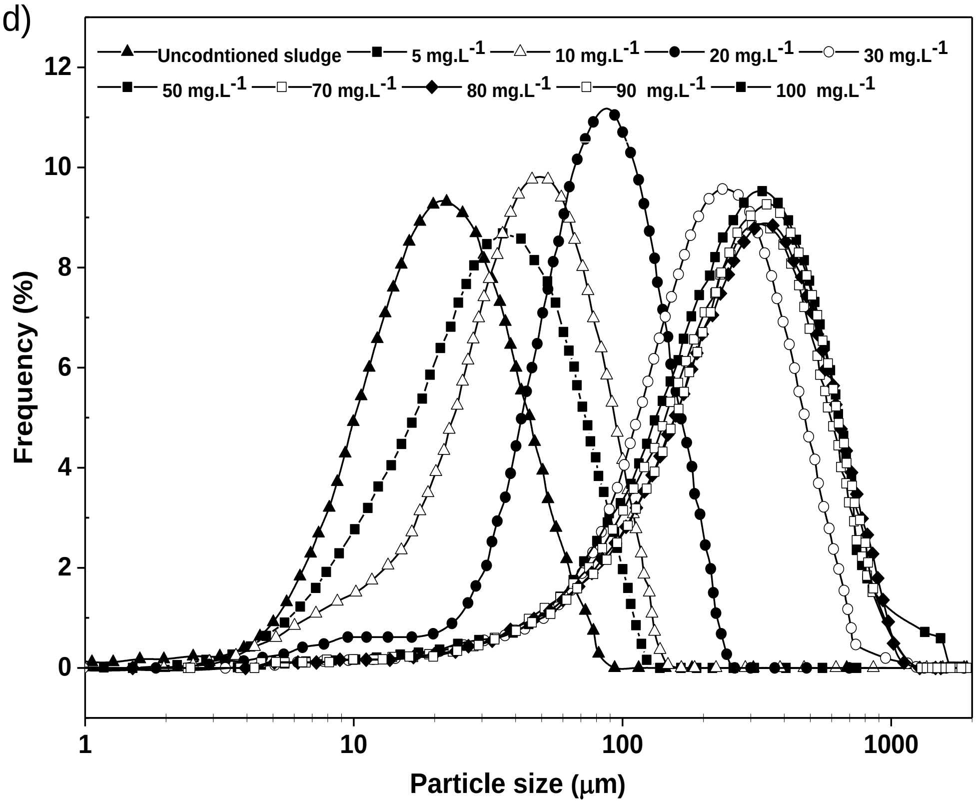

a)
Uncodntioned sludge
5 mg.L-1
10 mg.L-1
20 mg.L-1
30 mg.L-1
50 mg.L-1
70 mg.L-1
80 mg.L-1
90 mg.L-1
100 mg.L-1
Frequency (%)
Particle size (μm)
0
2
4
6
8
10
12
1
10
100
1000


b)
Uncodntioned sludge
5 mg.L-1
10 mg.L-1
20 mg.L-1
30 mg.L-1
50 mg.L-1
70 mg.L-1
80 mg.L-1
90 mg.L-1
100 mg.L-1
Frequency (%)
Particle size (μm)
0
2
4
6
8
10
12
1
10
100
1000

c)


Uncodntioned sludge
5 mg.L^{-1}
10 mg.L^{-1}
20 mg.L^{-1}
50 mg.L^{-1}
70 mg.L^{-1}
80 mg.L^{-1}
90 mg.L^{-1}
100 mg.L^{-1}
Frequency (%)
12
10
8
6
4
2
0
1
10
100
1000
Particle size (μm)

d)


Uncodntioned sludge
5 mg.L^{-1}
10 mg.L^{-1}
20 mg.L^{-1}
30 mg.L^{-1}
50 mg.L^{-1}
70 mg.L^{-1}
80 mg.L^{-1}
90 mg.L^{-1}
100 mg.L^{-1}
Frequency (%)
12
10
8
6
4
2
0
1
10
100
1000
Particle size (μm)

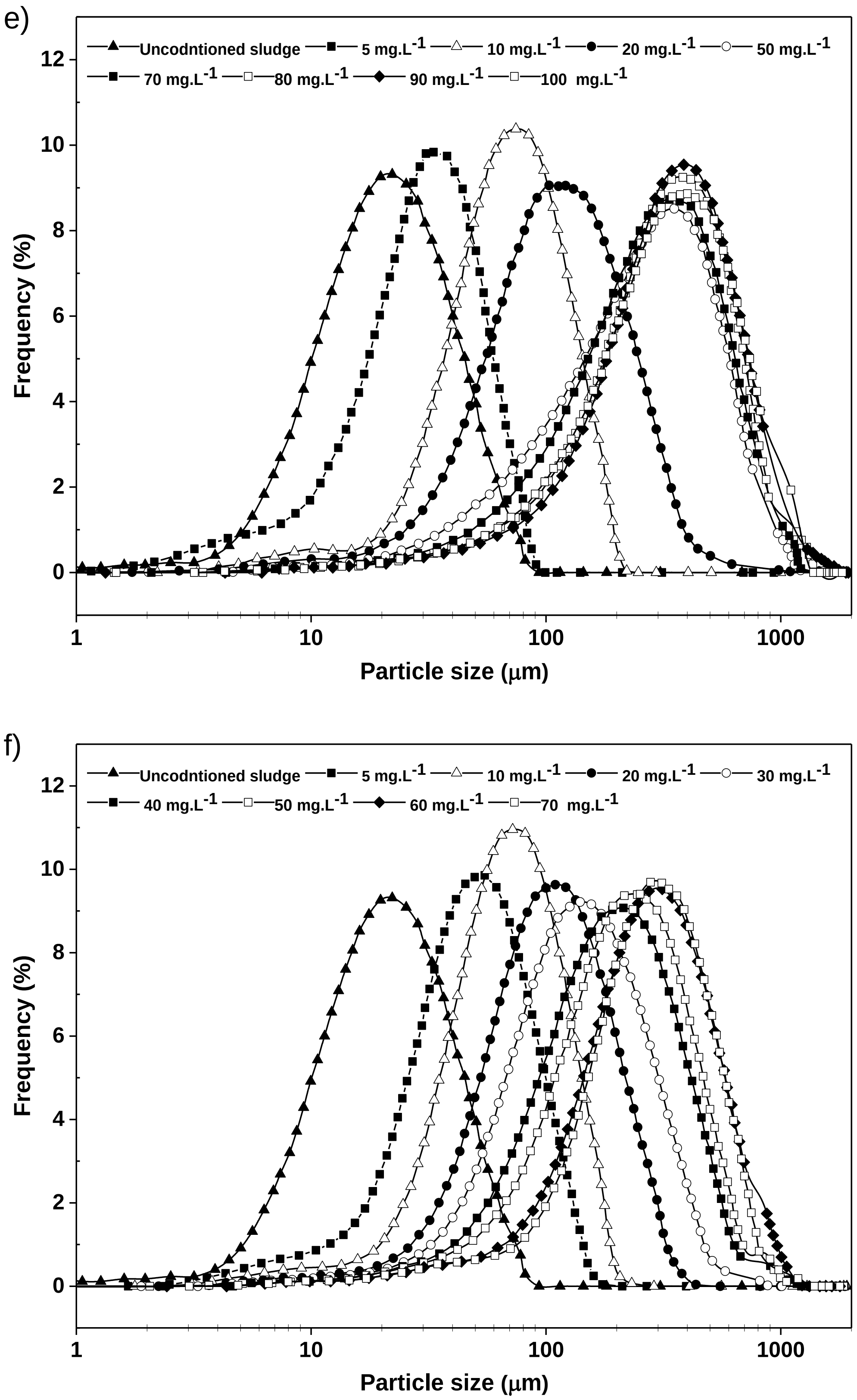
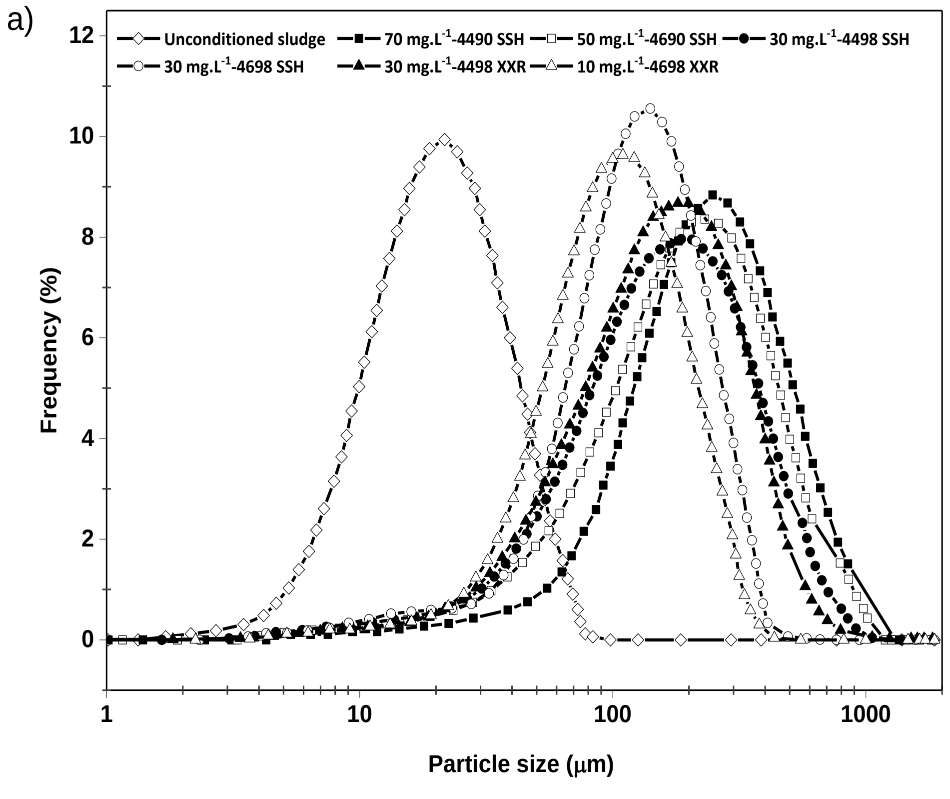


Figure 4-3. Particle size distribution for the sludge flocculated using a) FO 4490 SSH b) FO 4690 SSH c) FO 4498 SSH d) FO 4698 SSH e) FO 4498 XXR f) FO 4698 XXR

Results indicate that when the highly branched flocculants are used, more side tails of PAM are available for adsorption onto the sludge particle surface; reducing the MW does not significantly affect the floc formation. Figures 4-4 and 4-5 show that at a considerably high dose of 70 mg.L^{-1}, the floc size is independent of PAM characteristics. The exception being one of the branched polymers (4498 XXR) which generates anomalously larger flocculated particles at a high PAM doses. These findings are generally comparable with those reported in the literature for conventional AS flocs [6,20,40,121].



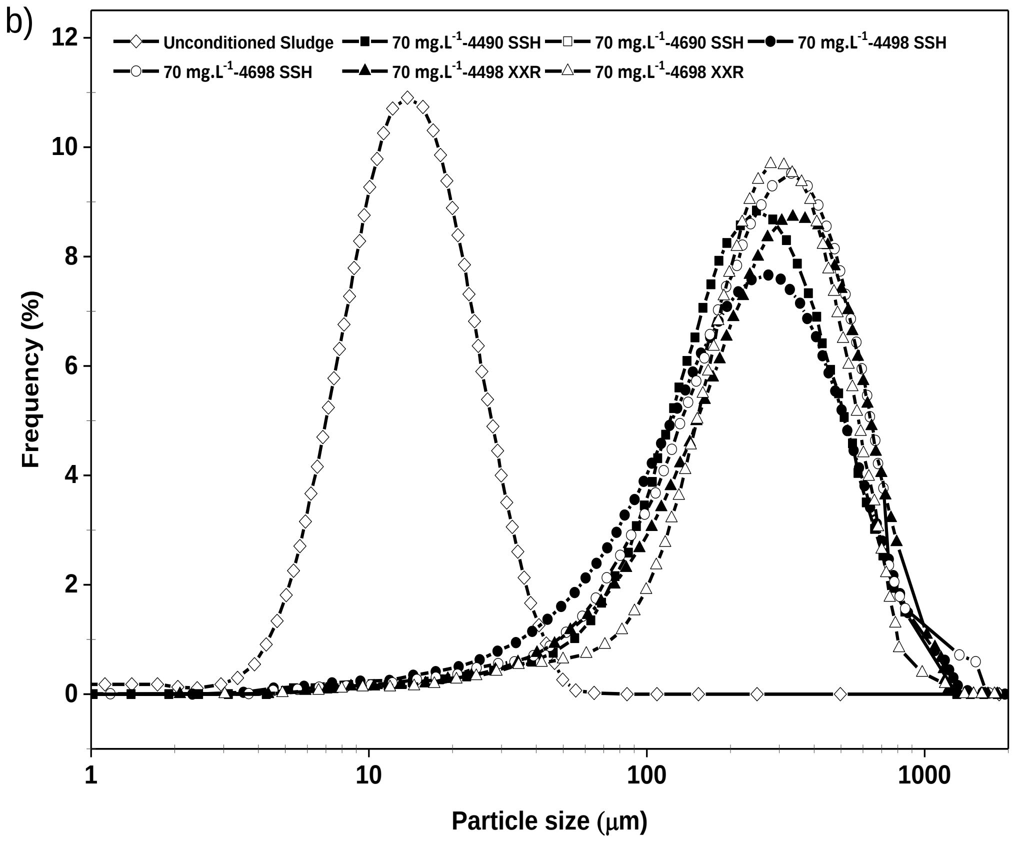
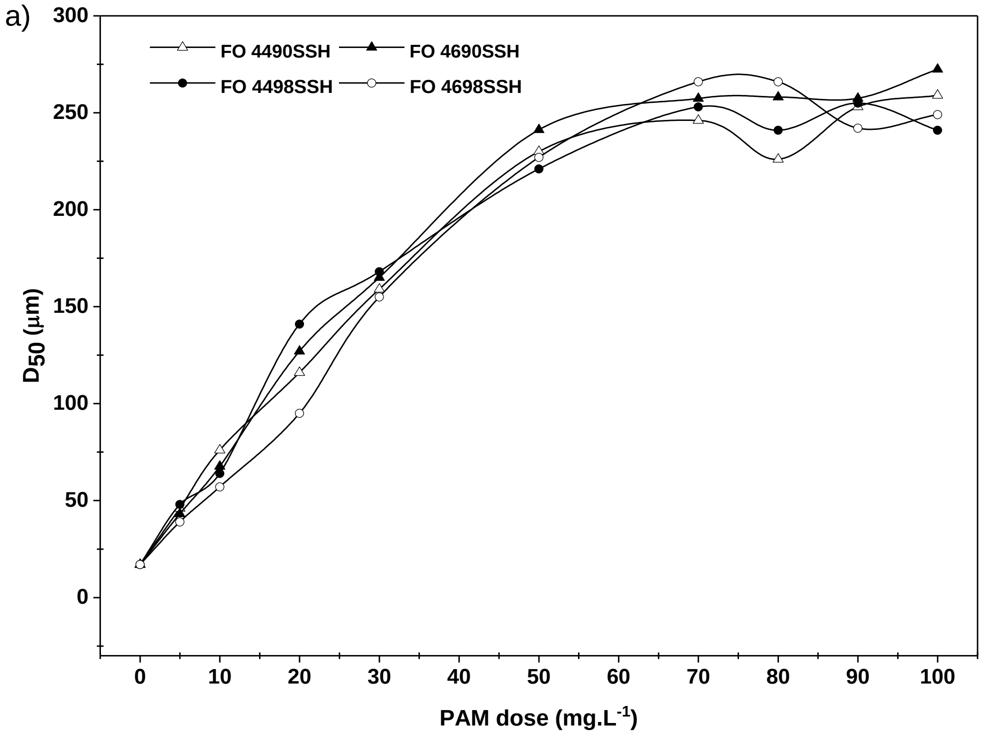


Figure 4-4. PSD of MBR sludge flocculated at a) optimum dose b) unified dose of all PAMs



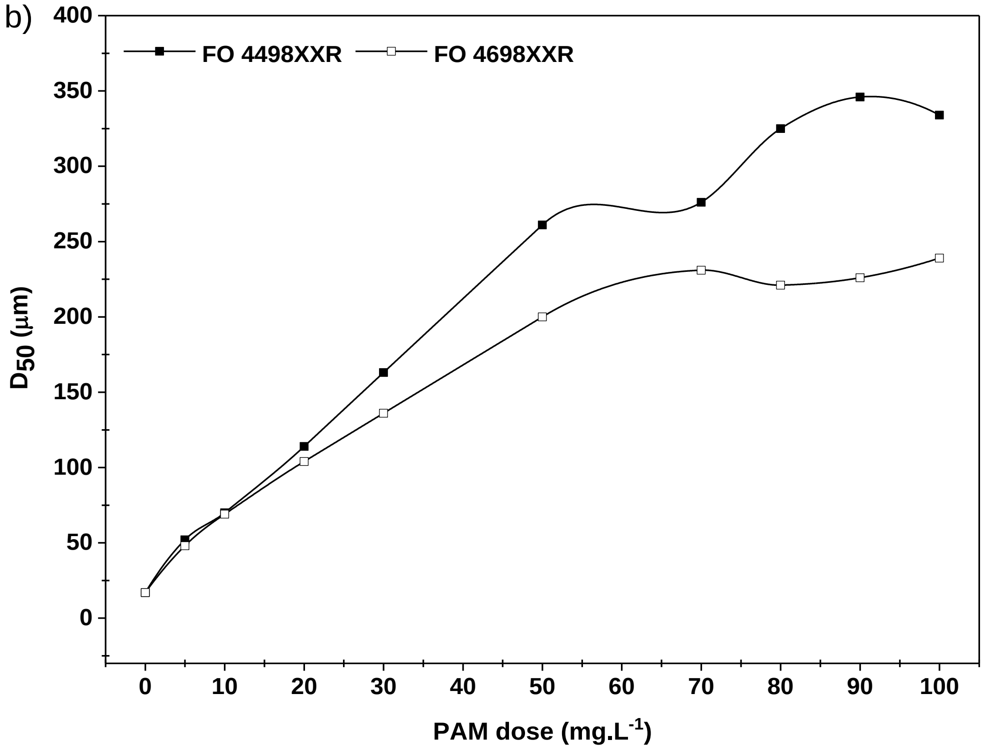


Figure 4-5. D_{50} (RSD=0.02-5%) as a function of PAM's dose for a) SSH (linear and slightly branched) b) XXR (highly branched) structured of PAMs

Although a larger floc is preferable in sedimentation processes to improve solid-liquid separation efficiency, this cannot be used alone as a measure of dewaterability or filterability since this does not take into the account floc strength and deformation. CST and volume reduction are more appropriate measurements in this regard. Results suggest that there is no direct correlation between flocculated particle size and CST specifically. The substantially smaller flocs are generated at a low optimum dose of 10 mg.L^{-1} for the highly branched and high-CD polymer (4698 XXR). At such a low dose, similar CST to 4490 SSH having a dose 70 mg.L^{-1} was obtained which reflects the differences in floc structure, strength and compressibility [152]. When a high-CD polyelectrolyte of low MW (i.e., highly branched FO 4698 XXR) is used, the bridging capability is improved as a consequence of the high CD and polymer branching which increases the charge neutralization and PAM adsorption on the particles surface [39]. Smaller and more compact flocs are thus produced in comparison with the lower CD polyelectrolyte (i.e., highly branched FO 4498 XXR) and a greater dewaterability and filterability subsequently achieved, as indicated by the lower CST values. Generally, across all tested PAM reagents, the CST increases with CD at the optimum dose.

Table 4-2 summarizes the optimum dosages of all PMAs used along with their corresponding values of turbidity, ζ, D_{50} and CST.

Table 4-2. *PAMs Optimum Doses Along with Measured Parameters at Their Optimum Doses*

Flocculent	Optimum dose (mg.L^{-1})	ZP (mV)	Turbidity (NTU)	D_{50} (μm)	CST (s)
4490 SSH	70	-4.86	2.0	245	5
RSD (%)		1.05	2.8	2.3	2.1
4690 SSH	50	5.22	1.57	241	7
RSD (%)		1.24	2.6	3.6	1.8
4498 SSH	30	5.6	0.47	155	8
RSD (%)		3.3	4.2	2.5	1.5
4698 SSH	30	-2.95	1.80	155	7
RSD (%)		1.2	1.8	3.5	1.2
4498 XXR	30	-2.48	0.40	163	7
RSD (%)		3.2	3.3	3.7	1.2
4698 XXR	10	-5.5	0.9	69	6
RSD (%)		2.4	2.5	2.34	1.3

Settleability/Volume Reduction

The percentage volume reduction in the sludge has been measured after extracting the supernatant from the conditioned sample. 30–61% reduction was achieved at optimum PAMs doses (Figure 4-6).

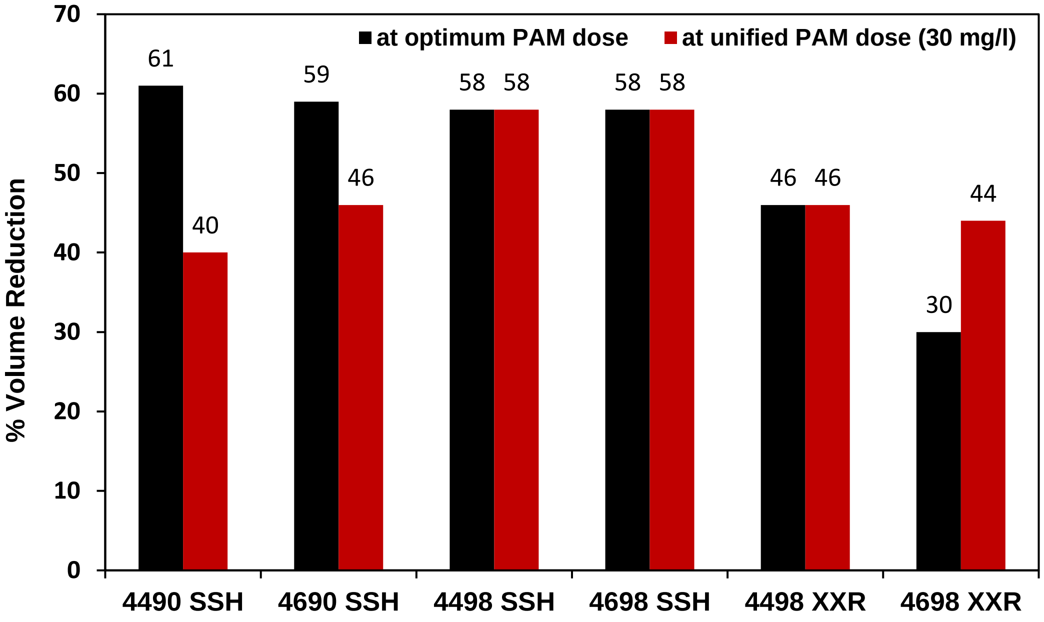


Figure 4-6. Comparison of % volume reduction (RSD = 1–2%) at optimum PAM's dose with unified PAM's dose of 30 mg.L^{-1}

Figure 4-6 shows that at the optimum dose the reduction in volume is directly proportional to PAM's MW and dose. The higher MW PAMs and/or higher PAM's dose resulted in a higher volume reduction. In order to assess the effect of MW and CD on the settleability/volume reduction, a unified dose of 30 mg.L^{-1} was selected for all PAMs. At this unified dose, the volume reduction increased from 40 to 46% for a linear PAMs of a similar MW due to the increase in CD from 40% to 60%. It has been reported that the floc density and strength increase as the PAM CD increases [39]. In the case of slightly and highly branched PAMs, the behavior is similar. Generally, when comparing two different PAMs of the same MW and at an equal dose, floc size is the most significant performance indicator. However, the use of PAM with different MW and doses lead to different volume reductions regardless of the floc size. A comparison of all data for the key flocculation and dewaterability parameters based on a single PAM (FO 4690SSH) is shown in Figure 4-7. The optimum value for this PAM is reached at the steady state point where all of the parameters (CST, volume reduction and D_{50}) are at their optimum values. Beyond this point, at higher doses, charge reversal and subsequent floc dispersal occurred [20].

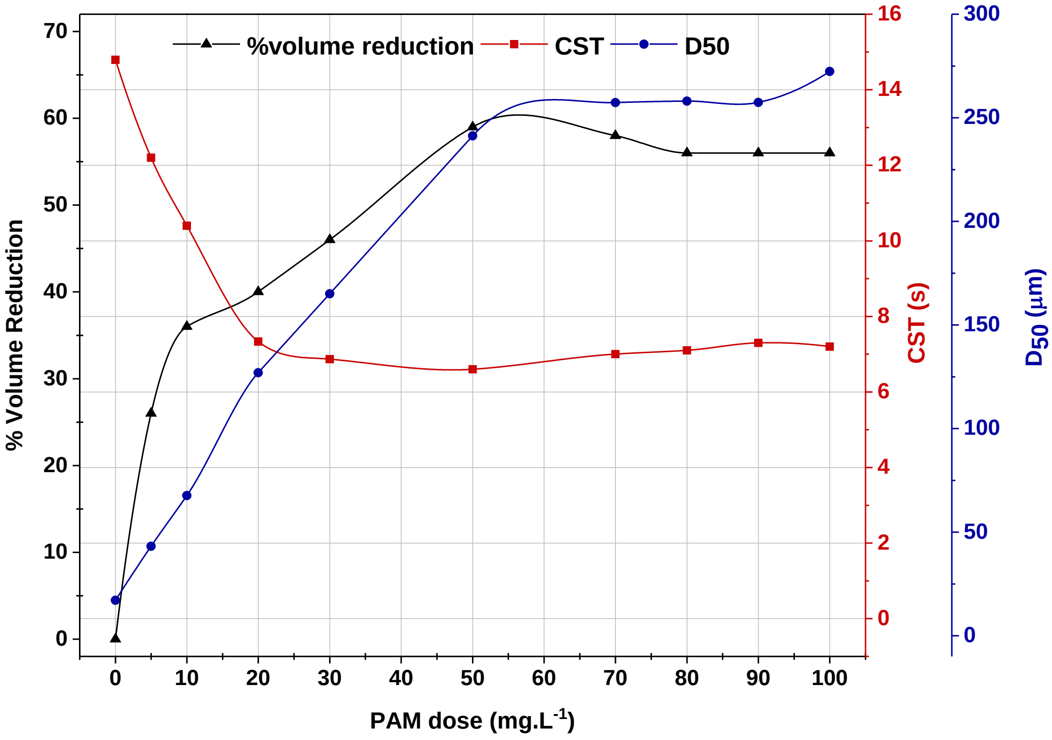


Figure 4-7. %Volume reduction, CST, and D_{50} as a function of PAM dose (FO 4690 SSH)

Enhancement of Flocculation and Dewaterability of MBR Activated Sludge Using a Hybrid System of Organic Coagulants and Polyelectrolytes

Objective

This section investigates the influence of hybrid coagulation-flocculation system on the flocculation and dewaterability efficiency of the MBR sludge Two organic coagulants, polyDADMAC and polyamine coupled with different PAMs are used and residual turbidity, zeta potential (ζ), flocs size and CST are used to assess the Impact of the hybrid system on the degree of flocculation and dewaterability of MBR sludge.

Conditioning of MBR Sludge with PolyDADMAC and/or Polyamine

FL 4440 and FL 2949 are highly charged low MW coagulants. They have a positive charge in every repeating unit and act as colloid destabilizers by reducing/neutralizing the overall negative surface charges of colloids. The use of these polyelectrolytes results in the formation of micro flocs that are much smaller in size in comparison with flocs produced by PAM flocculants. Figure 4-8 represents the trends in supernatant turbidity and zeta potential analysis of the MBR sludge samples flocculated with FL 4440 and/or FL 2949 coagulants. The optimum doses of these two coagulants were equated to the doses providing the maximum turbidity removal. Zeta potential has further supported the turbidity results demonstrating the reduction of the sludge's negative surface charge by 61 and 57% for FL 4440 and FL 2949, respectively.

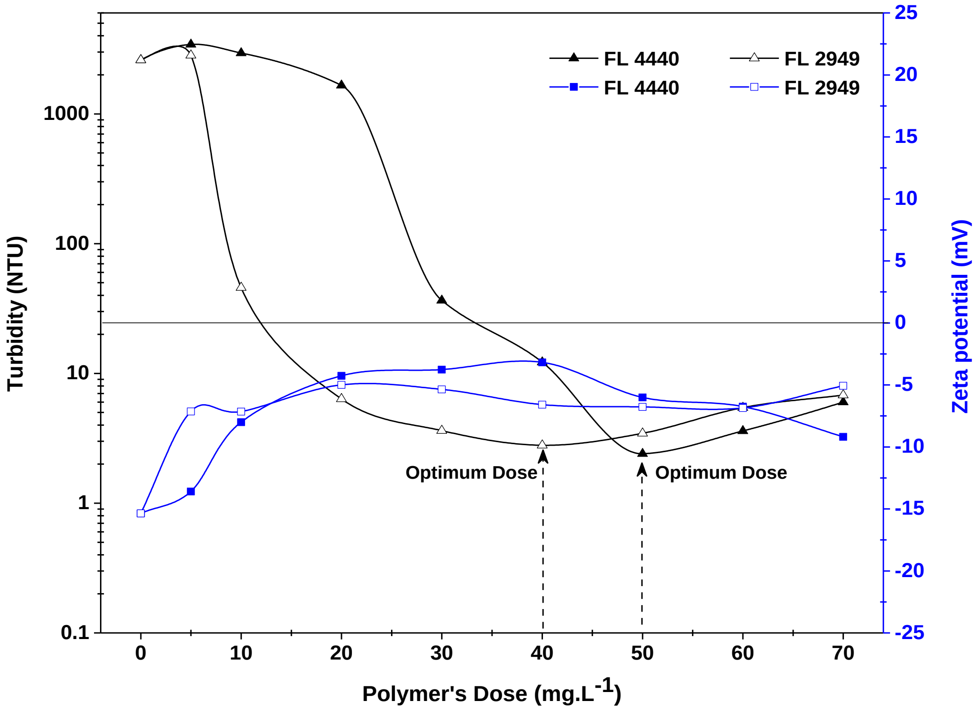


Figure 4-8. Variations in turbidity (RSD= 1-3%) and zeta potential (RSD= 1-3%) for MBR sludge conditioned with FL 4440 and FL 2949

For this treatment process, water clarity (i.e., turbidity below 3) was achieved when particle ζ values were in the range -7 to +5 mV. On this basis, the optimum doses of FL 4440 and FL 2949 were obtained as 50 $mg.L^{-1}$ and 40 $mg.L^{-1}$, respectively. The results of these two organic coagulants (Figure 4-8) indicate that although over the tested concentrations range, ζ doesn’t cross the PZC; they can achieve the maximum turbidity removal of 99.8% and 99.9% for FL 2949 and FL 4440 at ζ values of -6.6 and -6 mV, respectively. Ariffin et al. [115] showed a similar trend of ζ in the treatment of pulp and paper mill wastewater. It was observed that by increasing the dose of FL 4440, the ζ approaches almost PZC (ζ=0 mV) without crossing the PZC. Beyond the optimum doses of FL 4440 and FL 2949, turbidity tends to increase due to saturation condition [115,153].

Similar efficiency in turbidity removal was achieved by using polyDADMAC coagulant in the treatment of different types of wastewater [115,154]. For example, Razali et al. [153] have reported a 91% reduction in turbidity using polyDADMAC based coagulant having a MW of 105 kg.mol^{-1} in the treatment of pulp and paper mill wastewater. Additionally, Ebeling et al. [154] reported a 98% reduction in turbidity by using cationic polyamine in the treatment of aquaculture wastewater. Table 4-3 summarizes the obtained parameters for FL 2949 and FL 4440 at their optimum doses.

Table 4-3. *Measured Parameters of FL 4440 and FL 2949*

Name	Optimum dose (mg.L^{-1})	ζ (mV)	Turbidity (NTU)	CST (s)	D_{50} (µm)
FL 2949	40	-6.6	2.8	7	65
RSD (%)	--	1.2	1.5	2.2	2.2
FL 4440	50	-6	2.4	8	52
RSD (%)	--	1.05	1.05	1.2	2.3

A comparison of these two coagulants suggests the following:

(i) Significant improvement in turbidity removal when FL 2949 is used and removal of up to 98% is achieved at 10 mg.L^{-1} while for FL 4440 23% of turbidity is obtained at the same coagulants' dose of 10 mg.L^{-1}. This is due to the fact that FL 2949 has a high concentration of the active contents (50%) in comparison to FL 4440 (40%), which results in a higher impact on the overall surface charge reduction and electrostatic attraction [31].

(ii) Comparable behavior of zeta potential (ζ) between FL 4440 and FL 2949 has been achieved (see Figure 4-8).

The main mechanism of coagulation processes is the surface charge reduction/neutralization through electrostatic patch mechanism. In this mechanism, particles get close to each other due to the overall negative charge reduction and the electrostatic attraction between them; they produce micro flocs [15,153]. Both FL 4440 and FL 2949 coagulants were able to act as destabilizers and hence produced micro flocs.

Influence of PolyDADMAC/Polyamine Combined with PAM

Hybrid coagulation-flocculation of FL 2949 and FL 4440 was used to enhance the flocculation effectiveness and achieve the required water clarity at the lowest possible doses of PAMs. The same set of PAMs was used in this work (Table 3-2). The conditioning of MBR sludge was conducted in two stages: initially, polyDADMAC and polyamine were added at their optimum doses followed by use of six different PAMs. Figure 4-9 shows an example of residual turbidity and ζ analyses of MBR sludge flocculated with FO 4490 SSH coupled with FL 2949 (Figure 4-9a) and FL 4440 (Figure 4-9b) while the rest of the results are tabulated in Tables 4-4 and 4-5.

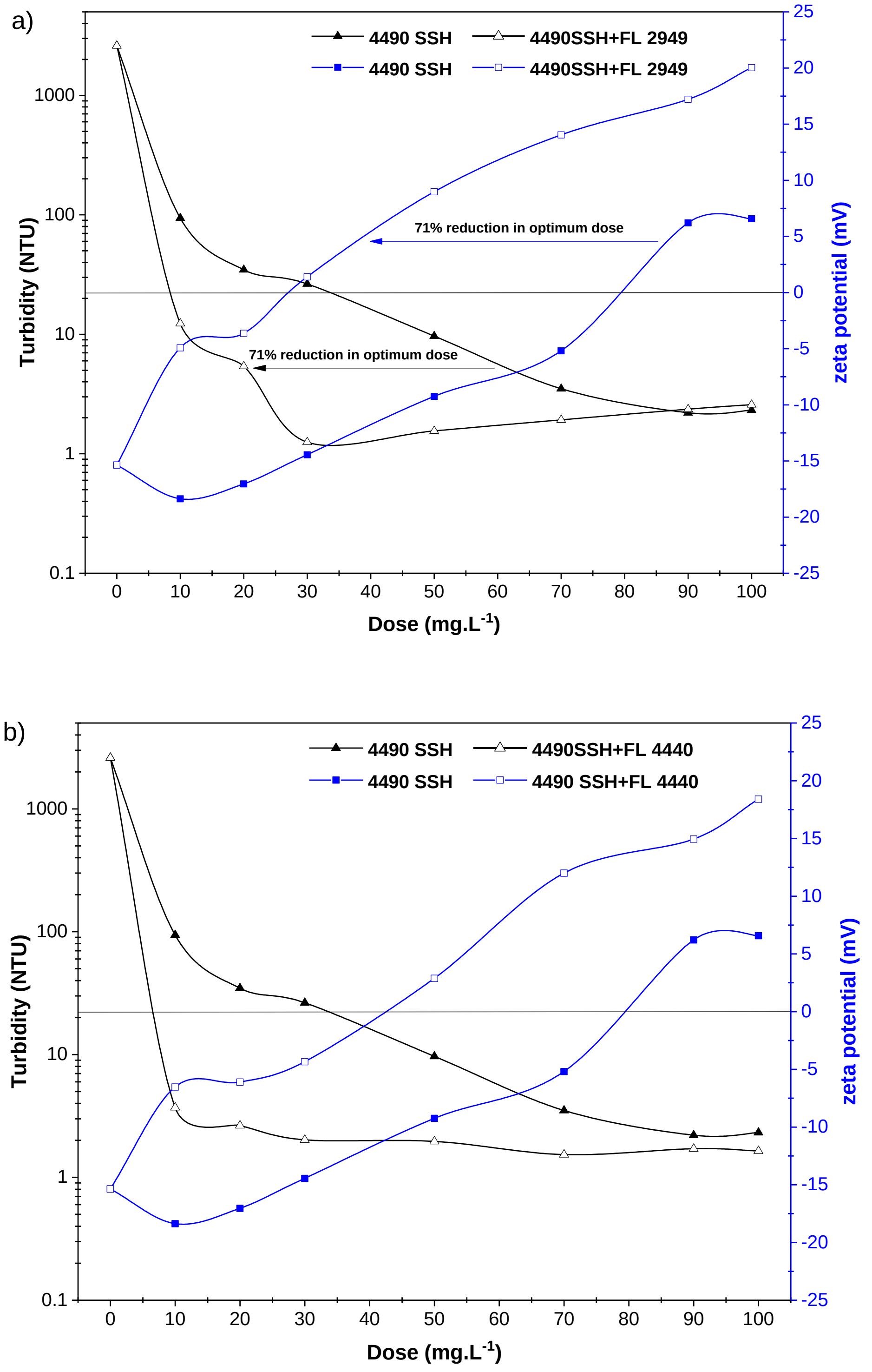


Figure 4-9. Turbidity (RSD= 1-4%) and zeta potential (RSD= 1-5%) trends for MBR sludge conditioned using FO 4490 SSH (linear PAM) combined with a) FL 2949 b) FL 4440

Table 4-4. *Turbidity (RSD= 1-4%) and Zeta Potential (RSD= 1-5%) Trends for MBR Sludge Conditioned Using Six Different PAMs Combined with FL 4440 Coagulant*

PAM's Dose	FL 4440+FO 4690 SSH		FL 4440+FO 4498 SSH		FL 4440+FO 4698 SSH		FL 4440+FO 4498 XXR		FL 4440+FO 4698 XXR	
$mg.L^{-1}$	Turbidity (NTU)	ZP (mV)	Turbidity (NTU)	ZP (mV)	Turbidity (NTU)	ZP (mV)	Turbidity (NTU)	ZP (mV)	Turbidity (NTU)	ZP (mV)
0	2603	-15	2603	-15	2603	-15	2603	-15	2603	-15
10	2.86	-3.89	1.26	-3.95	3.4	-4.1	1.52	-3.35	1.1	-3.98
20	1.42	-3.14	2.9	-6.75	2.83	-6.81	0.55	-2.43	1.2	-3.5
30	1.07	-2.57	0.6	-1.6	0.58	-1.56	0.74	-3.52	0.7	-1.56
50	1.5	-0.62	1	-3.2	1.01	-3.21	2.11	2.52	1.01	-3.21
70	0.44	4.32	1	4.2	0.93	4.14	1.7	4.63	0.93	4.32
90	0.69	12.55	0.83	4.8	0.83	4.83	1.27	10.06	0.83	4.83
100	0.9	15.53	1.2	6.92	1.19	6.78	2.53	10.2	0.95	6.8

Table 4-5. *Turbidity (RSD= 1-4%) and Zeta Potential (RSD= 1-5%) Trends for MBR Sludge Conditioned Using Six Different PAMs Combined with FL 2949 Coagulant*

PAM’s Dose	FL 2949+FO 4690 SSH		FL 2949+FO 4498 SSH		FL 2949+FO 4698 SSH		FL 2949+FO 4498 XXR		FL 2949+FO 4698 XXR	
mg.L^{-1}	Turbidity (NTU)	ZP (mV)	Turbidity (NTU)	ZP (mV)	Turbidity (NTU)	ZP (mV)	Turbidity (NTU)	ZP (mV)	Turbidity (NTU)	ZP (mV)
0	2603	-15	2603	-15	2603	-15	2603	-15	2603	-15
10	0.96	-4.9	1.36	-2.9	1.2	-2.6	2.31	-5.43	1.4	-2.8
20	0.83	-4.42	0.83	-3.6	0.83	-3.7	1.13	-2.19	0.75	-3.65
30	0.58	-1.48	1.34	-2.5	1.21	-2.7	1.54	-2	1.32	-2.77
50	1.2	2.54	0.42	-3.13	0.44	-3.2	1.89	1.71	0.38	-3.13
70	0.8	5.07	0.56	4.8	0.58	4.6	2.52	7.22	0.61	4.77
90	0.67	7.06	0.85	10.9	0.9	11.15	1.72	15.1	0.91	11.1
100	1.62	19.5	1.57	11.95	1.7	12.2	1.44	13.8	1.57	11.8

When linear PAM (FO 4490 SSH) is used alone (Figure 4-1a), the highest turbidity removal is obtained at high PAM concentration of 70 $mg.L^{-1}$ after which the system reaches nearly steady state condition. However, adding FL 4440 or FL 2949 at their optimum doses can significantly improve ζ and residual turbidity by reducing the initial dose of FO 4490 SSH (linear PAM) to 20 $mg.L^{-1}$. Therefore, for this case, a 71% reduction in the initial optimum doses were achieved when combining it with 40 $mg.L^{-1}$ of FL 2949 and 50 $mg.L^{-1}$ of FL 4440. Conditioning of the sludge with the coagulant FL 2949 has reduced the required dose of FO 4490 SSH from ~ 80 $mg.L^{-1}$ to ~25 $mg.L^{-1}$ and reached the PZC (ζ=0 mV).

Figure 4-10 illustrates the reduced optimum doses of PAMs obtained using the hybrid system, and the results are compared with the required doses for each PAM when used individually. In general, the results showed significant reductions in the optimal doses when hybrid coagulation-flocculation is used in the conditioning of the MBR sludge. These reductions range from 50 to 80% depending on the dose and type of the polymer. Chitikela and Dentel [118] have also reported a 60% reduction of in the optimal doses by using the hybrid coagulation-flocculation system in conditioning and dewatering of anaerobically digested sludge. These reductions in the polymer's dose were more significant in the case of linear and slightly branched PAMs and less significant for highly branched PAMs.

The optimum doses were selected based on the maximum turbidity removal and ζ ranges -7 to +5. The overall charges of colloidal particles and their stabilities are measured by ζ, whereas turbidity is regulated by water clarity and particle presence. Combining these two parameters are crucial for determining the degree of clarification, the effectiveness of agents and optimizing the efficiency and economy of the water treatment facility [149,155]. On these bases, the highest reduction in PAM's initial optimum dose has been determined to be in the following order: FO 4490 SSH followed by FO 4690 SSH, FO 4498 SSH, FO 4698 SSH, FO 4498 XXR, and FO 4698 XXR. In terms of polymer CD, MW, and molecular structure, the influence of CD and MW are superior to the effect of molecular structure.

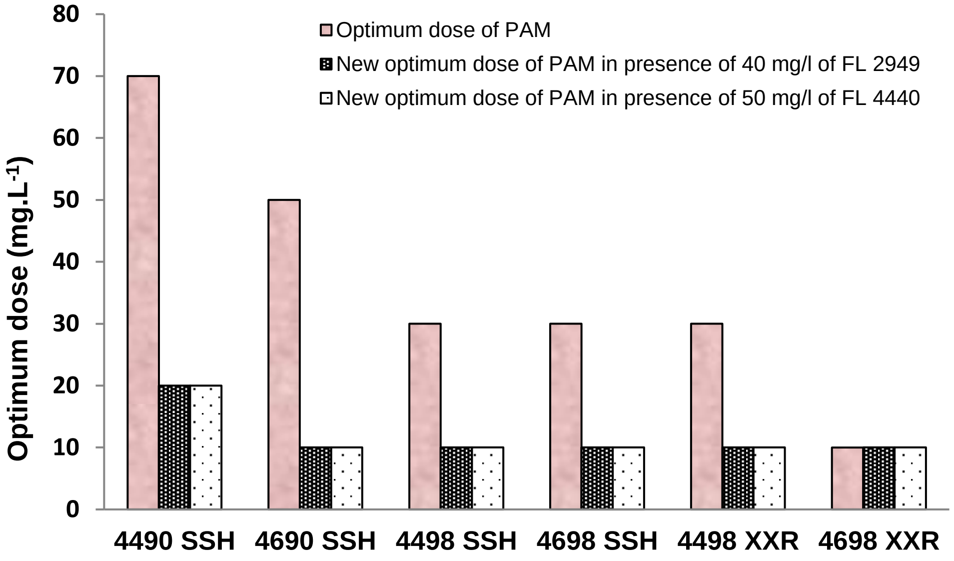


Figure 4-10. Optimum doses of MBR sludge conditioned with PAMs only and hybrid systems

Effect of Hybrid System on Floc Size Analysis and CST of MBR Sludge

To assess the dewatering ability of polyamine and polyDADMAC coagulants, CST was measured, and the trends of CST for MBR sludge flocculated with FL 2949 and FL 4440 are shown in Figure 4-11. At low concentrations, FL 4440 performs almost the same as FL 2949. However, at a high dose (i.e., above approximately 35 mg.L^{-1}), FL 2949 has shown better performance than FL 4440, and this is likely due to the differences in their structures and the higher percentage of the active content of FL 2949 [16]. Overall, 48 and 53% reduction in CST was achieved by using only FL 4440 and FL 2949 at their optimum doses, respectively.

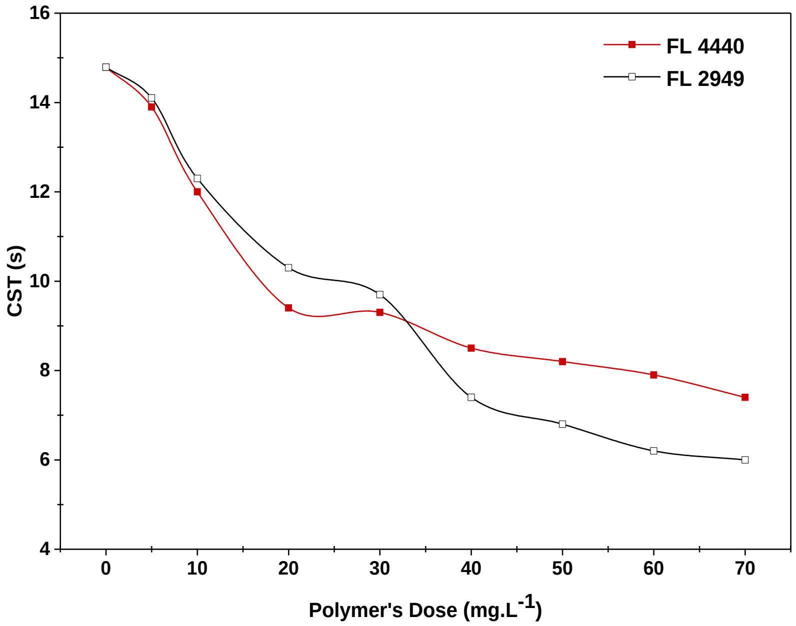


Figure 4-11. CST trends for MBR sludge conditioned with FL 4440 and FL 2949 (RSD= 1.2-3%)

Floc size analysis was also conducted on the sludge conditioned with coagulants only and coagulants-flocculants hybrid system. As mentioned earlier, polyDADMAC and polyamine coagulants act as destabilizers and produce small flocs. Figure 4-12 shows the particle size distribution of sludge conditioned with FL 2949 and FL 4440. By increasing the coagulant's dose, overall repulsive surface charges of the sludge colloidal particles have reduced through the compression of the electrical double layer. Consequently, the produced micro flocs size increase and the floc size distribution peak shifts to the right, representing a larger flocs formation. On the other hand, to compare the flocs produced using FL 2949 and FL 4440 coagulants, D_{50} was measured.

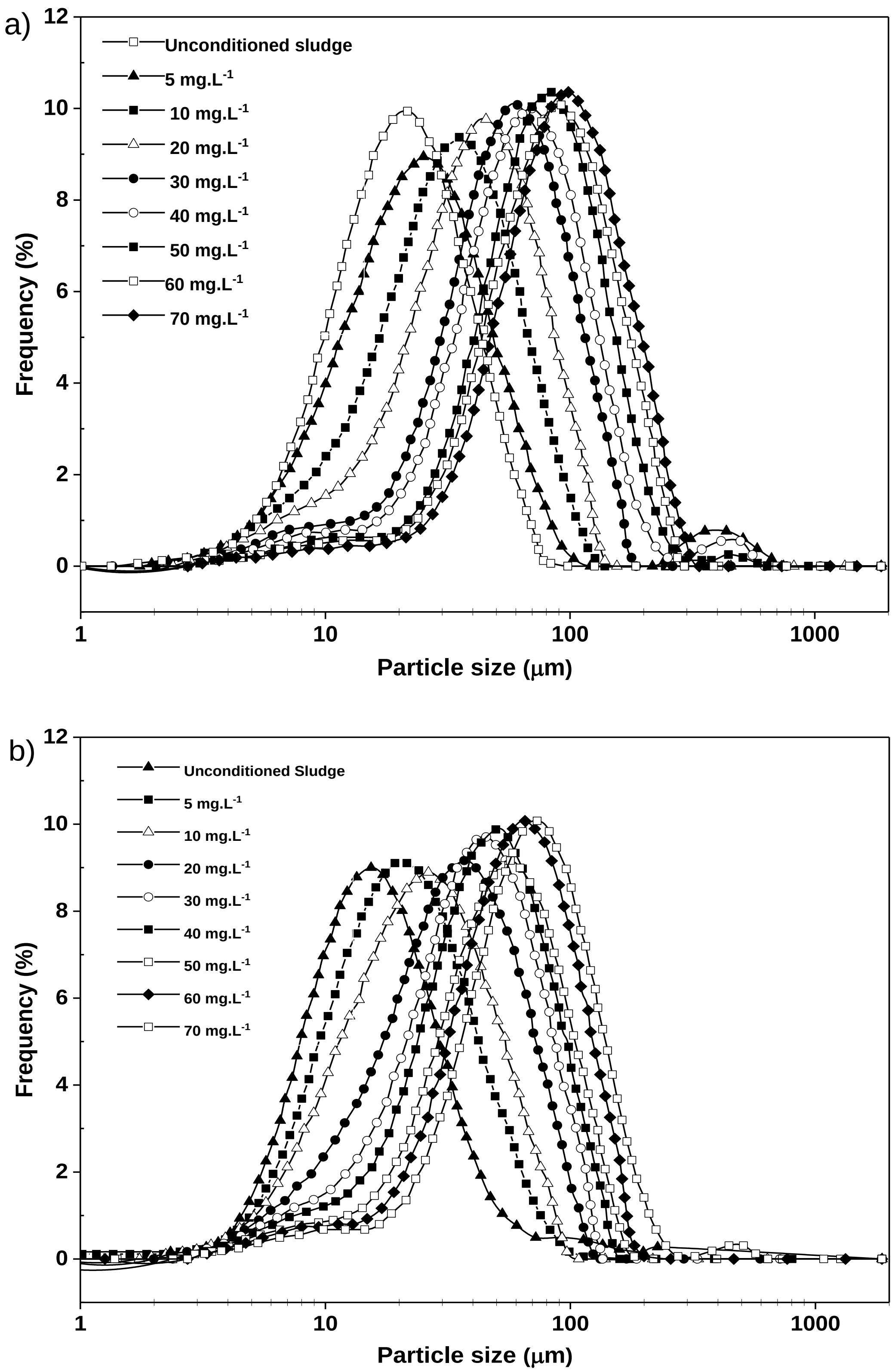


Figure 4-12. Floc size distribution of MBR sludge conditioned with different doses of FL 2949

Figure 4-13 shows the results of D_{50} for MBR sludge conditioned with FL 2949 and FL 4440. D_{50} has increased from 17 µm (unconditioned sludge) to 93 µm for FL 2949 and 62 µm for FL 4440 over the tested concentration range. This increase in floc size has reached 74 and 61% at their optimum doses of FL 2949 and FL 4440, respectively. Beyond the optimum concentration, surface saturation occurs, and only a little enhancement of approximately 4-6% in flocs size has been observed. Larger flocs are produced by using FL 2949 coagulant, which is likely due to its structure, low viscosity and higher active content as reported by the supplier SNF Floerger, France [16].

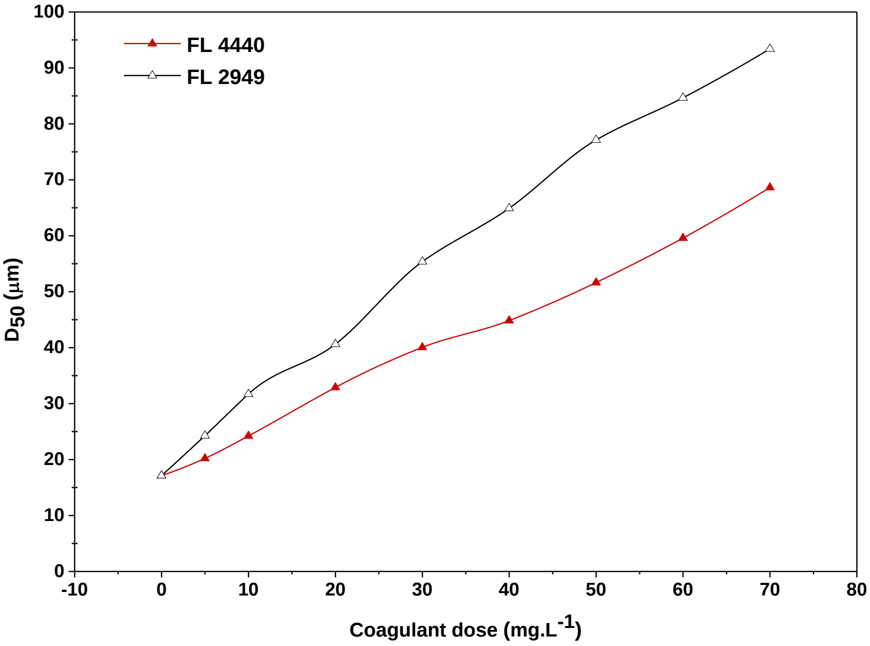
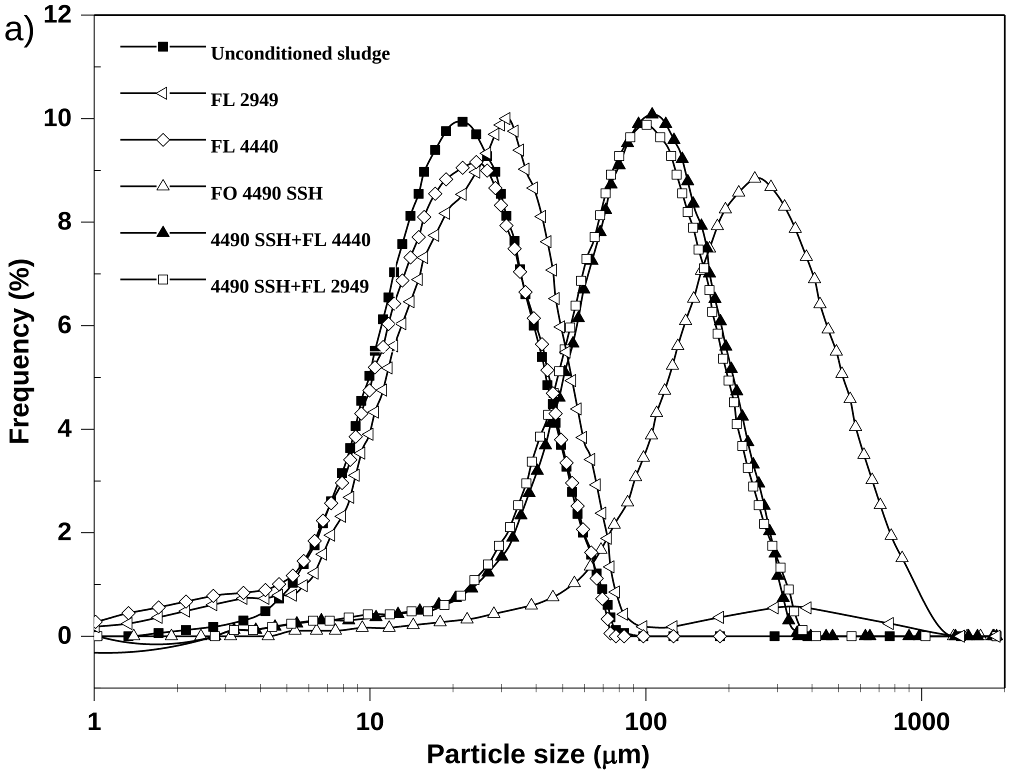


Figure 4-13. D_{50} trends for MBR sludge conditioned with FL 2949 and FL 4440 (RSD= 2-5%)

The same analysis was performed for the combined coagulation-flocculation system. Figure 4-14 shows the flocs size distribution of MBR sludge conditioned with linear PAMs (i.e., FO 4490 SSH and FO 4690 SSH) coupled with FL 2949 and FL

4440. The results were compared with flocs produced using coagulants individually (FL 2949 and FL 4440) at their optimum doses. In general, the flocs size has increased when either organic coagulants or PAMs are added to the MBR sludge having D_{50} =17 µm. However, when PAMs are used alone, larger flocs are produced compared to organic coagulants or hybrid systems where adsorption, charge neutralization and bridging mechanisms are involved.



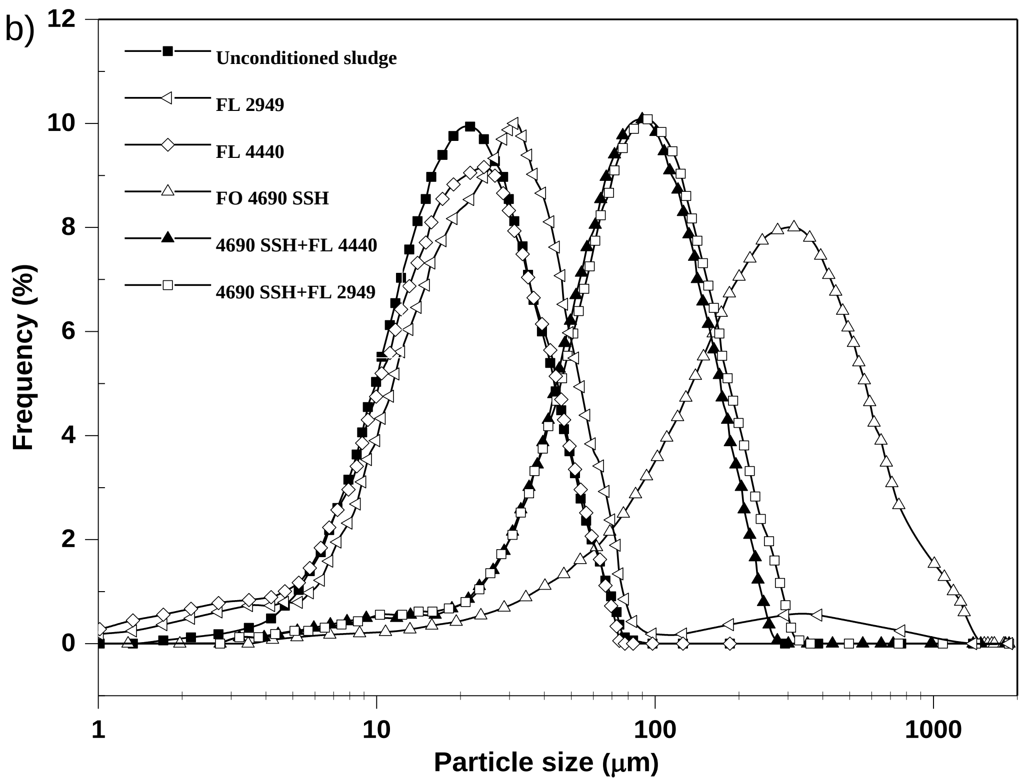


Figure 4-14. Flocs size distribution for MBR sludge conditioned with a) FO 4490 SSH b) FO 4690 SSH combined with FL 2949 and FL 4440 at their optimum doses

Addition of coagulants, at their optimum doses coupled with PAMs, significantly enhances the adsorption of the amide group of PAM into the surface as particles get close to each other. Consequently, the bridging efficiency of PAM is improved and as a result, smaller and more compact flocs are formed in hybrid coagulation-flocculation system rather than when PAMs are used alone. This mechanism is schematically illustrated in Figure 2-7. According to the D_{50} results shown in Figure 4-15a, comparing the D_{50} values of MBR sludge conditioned with PAMs and hybrid systems at their optimum doses, the influence of FL 2949 and FL 4440 on the linear structured PAMs is more significant followed by slightly and highly branched structured PAMs. CST results have further supported the flocs size measurements. CST values were used to assess the effects of conditioning on sludge filterability or dewater-ability. Usually, larger flocs result in lower CST values compared to smaller flocs with narrow capillaries which do not release the water easily [156,157].

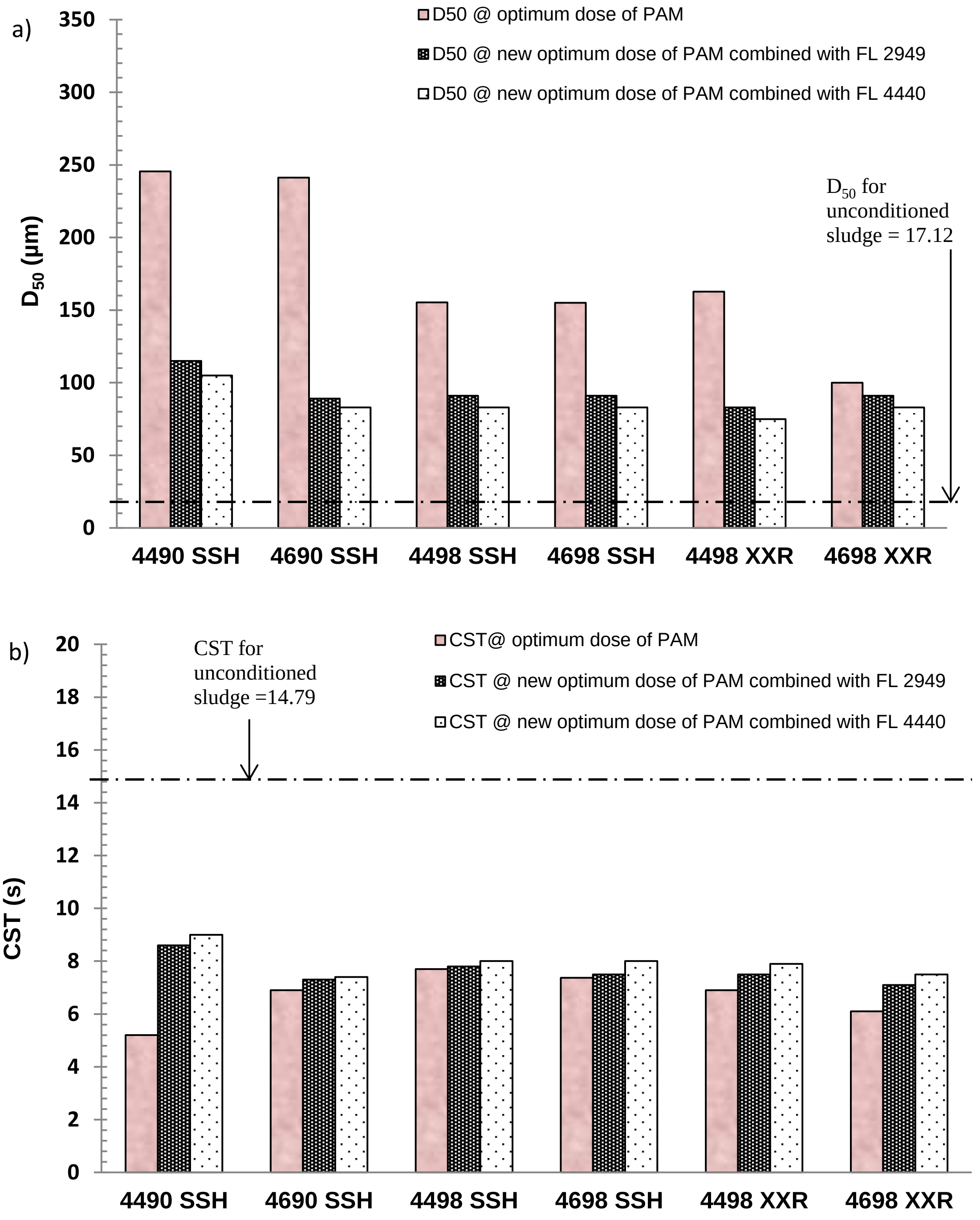


Figure 4-15. Variation in a) D_{50} and b) CST for MBR sludge conditioned with PAMs and hybrid systems at their optimum doses

As mentioned earlier, smaller and more compact flocs were produced when the hybrid coagulation-flocculation system was used. As results, CST increases compare to when PAMs are used alone (Figure 4-15b). However, the massive reduction in the flocs sizes does not increase the CST values significantly except when FO 4490 SSH (linear PAM) was used. In case of FO 4490 SSH (linear PAM), the reduction in the optimum dose from 70 $mg.L^{-1}$ (when PAM is used individually) to 20 $mg.L^{-1}$ (newly obtained dose for the hybrid system) has produced smaller flocs by 57%. This could be the reason for the observed high CST differences in this case. However, this effect could be eliminated by slightly increasing the concentration of FO 4490 SSH from 20 $mg.L^{-1}$ to 30 $mg.L^{-1}$. Additionally; Figure 4-15b shows that when PAMs are combined with FL 2949, larger flocs and consequently lower CST were obtained compared to when PAMs are combined with FL 4440.

The results obtained for flocs size and CST clearly indicate that high reduction in the flocs size does not impact the dewater-ability of the produced flocs (i.e., CST) significantly. For example, when FO 4690 SSH was combined with FL 2949 and FL 4440, the flocs size has reduced by 63 and 65%, respectively. However, CST is increased (i.e., dis-improved) by 5-7% only (Figure 4-15b). Consequently, reducing the flocs size doesn’t necessary significantly affect the dewaterability of the conditioned sludge, and these minor effects can be eliminated by slightly increasing in the PAMs concentrations.

Influence of Polyelectrolyte Structure and Type on the Degree of Flocculation and Rheological Behavior of Industrial MBR Sludge

Objective

This section investigates the impact of polyelectrolyte's type and structure on the rheological characteristics of industrial highly stable MBR sludge and relates them to its degree of flocculation and dewatering.

Effect of PAM Structure and Type on the Rheological Behavior of the MBR Sludge

Shear Flow Behavior

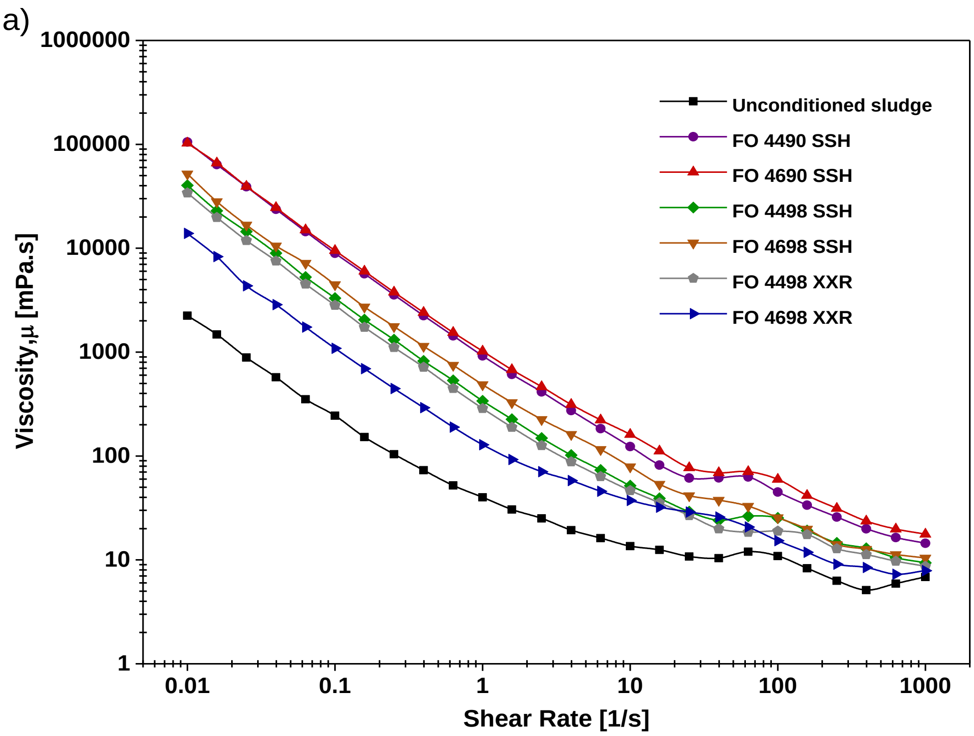
Figures 4-16a and b show the non-Newtonian behavior of the industrial MBR sludge before and after conditioning with various PAMs. According to this figure, for all tested PAMs, the shear rate is increasing with shear stress and decreasing with viscosity. Such trends confirm the pseudoplastic behavior of sludge samples which are commonly exhibited by a flocculated suspension.

Shear stress was correlated to shear rate using Bingham (Eq.2.3) and Herschel-Bulkley (Eq.2.4) models. The Regression Coefficient (R^2) was used for examining the capability of the selected model. Initially, yield stress was obtained by extrapolating the low shear data in a plot of shear stress vs. shear rate, and τ_o is obtained as the intercept. The obtained τ_o is used in the Herschel-Bulkley model (Eq.4.1) which is the linearized form of Eq.2.4, to get the flow behavior index, n.

$$\ln(\tau - \tau_o) = \ln k + n \ln \dot{\gamma} \qquad Eq.4.1$$

The flow behavior index, n was almost ~ 1 in all measurements; hence, the Bigham model (Eq.2.3) was the best model describing the rheological behavior of sludge samples with/without PAMs. Tables 4-6 and 4-7 summarizes the apparent viscosity, and yield stress for all PAMs treated MBR sludge understudy obtained from the Bingham model. When the shear stress reaches the threshold value, sludge samples start to flow, and viscosity starts falling. For all tested PAMs, the viscosity is decreasing with shear rate, and such extreme loss of viscosity represents the deterioration in floc structural strength. Unconditioned sludge has resulted in lower apparent viscosity compared to conditioned sludge with different PAMs. In general, the total suspended solids (TSS), or the concentration of colloidal particles and shear rate are the two important properties affecting viscosity and rheological properties of AS [50,136].

Figure 4-16a illustrates the dependency of the apparent viscosity of sludge samples on the concentration of suspended solids. Unconditioned sludge with lower TSS exhibits lower viscosity and yield stress. The higher viscosity and yield stress were obtained for the sludge samples conditioned with PAMs. This is likely due to the high TSS, which can be attributed to the high particle-particle and particle-PAM interactions of sludge samples when PAMs are used. Unconditioned sludge is more diluted and contains non-flocculated aggregates with less solid concentrations and behaves like a Newtonian fluid with low yield stress value. Therefore, it results in lower viscosity and yield stress. Adding PAM increases the viscosity and the yield stress of the sludge sample; however, depending on the type and the structure of the PAM, sludge samples with different viscosity and yield stress are obtained. For example, FO 4690 SSH (linear, 60% CD) PAM produces higher apparent viscosity and yield stress compared to FO 4490 SSH (linear, 40% CD). And the same applies to the slightly branched PAMs, where 60% CD results in higher apparent viscosity and yield stress. However, for the highly branched structured PAMs, a 40% CD is performing better than 60% CD. This occurs as a result of variations in the extent of interactions between MBR sludge and PAM. High charge density PAMs provide more active sites and get adsorbed onto the surface of the sludge particles more effectively [158]. This leads to a greater reduction in the surface charge of the sludge particles and a greater bridging interaction, hence producing highly viscous and stiff sludge flocs. Apart from CD, MW and concentration of PAM play a significant role in determining the strength of samples, related to apparent viscosities and yield stresses. The apparent viscosity of sludge conditioned with linear FO 4690 SSH (60% CD, 7-10 million g.mol^{-1}) is about three times higher than the apparent viscosity of sludge sample conditioned with highly branched FO 4698 XXR (60% CD, 4-7 million g.mol^{-1}). Having a long chain produces an extensive bridging in comparison to short-chain and result in stiffer and higher viscosity suspension.



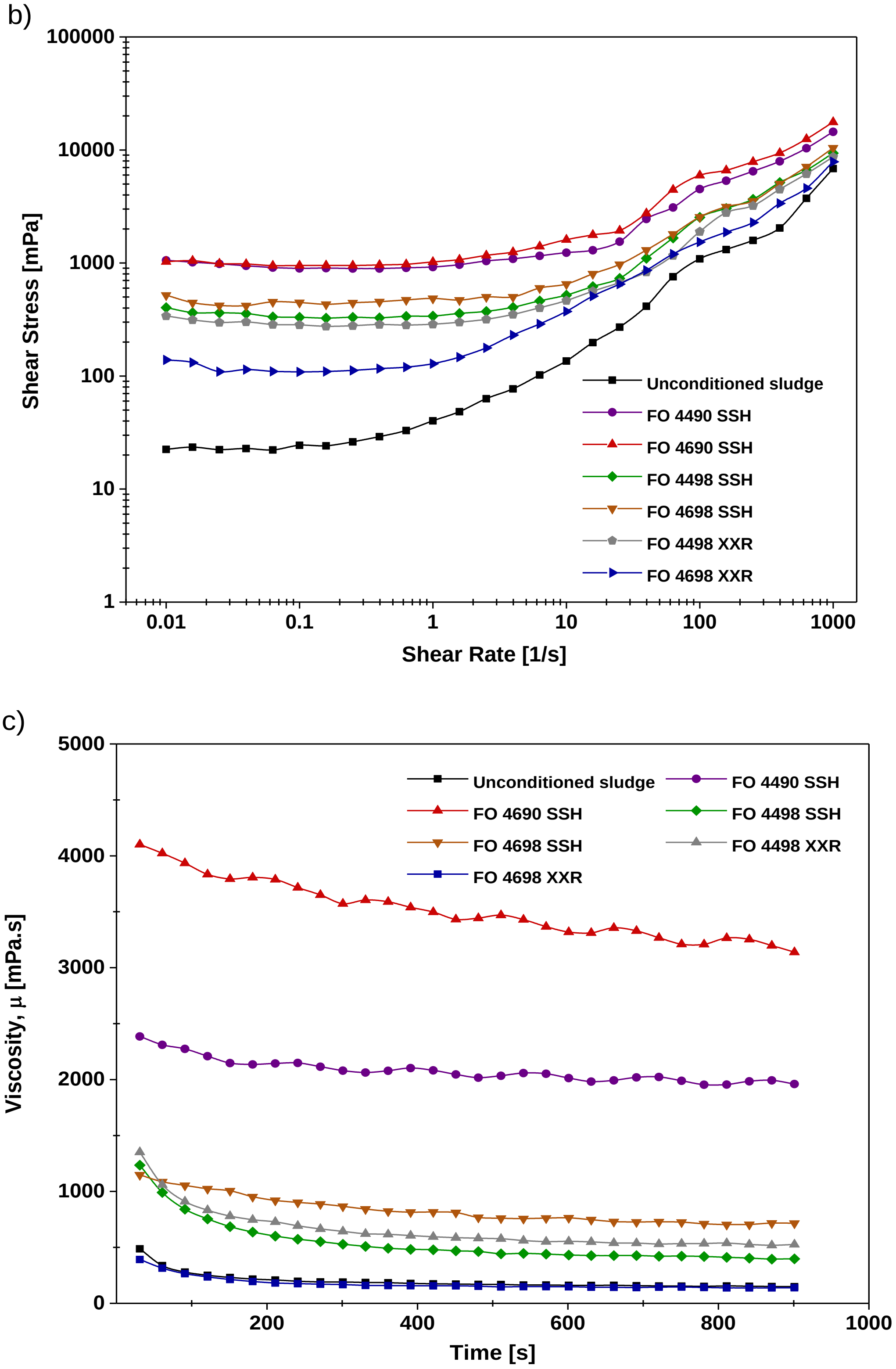


Figure 4-16. Variations in a) viscosity with shear rate b) shear stress with shear rate and c) viscosity with time for MBR sludge before and after conditioning with PAMs

Table 4-6. *Yield Stress of Sludge Before and after Conditioning with PAMs Obtained from Bingham Model at Optimum Dose*

Flocculent	τ_B [mPa]	Apparent viscosity, μ [mPa.s]	R^2
unconditioned sludge	28	2247	0.99
4490 SSH	877	105410	0.99
4690 SSH	991	102560	0.99
4498 SSH	293	40315	0.99
4698 SSH	449	51849	0.99
4498 XXR	281	34037	0.99
4698 XXR	199	13869	0.97

Table 4-7. *Yield Stress of Sludge Before and after Conditioning with PAMs Obtained from Bingham Model at Unified Dose of 30 mg.L*$^{-1}$

Flocculent	τ_B [mPa]	Apparent viscosity, μ [mPa.s]	R^2
4490 SSH	123	16034	0.99
4690 SSH	437	54419	0.98
4498 SSH	293	40315	0.99
4698 SSH	449	51849	0.99
4498 XXR	281	34037	0.99
4698 XXR	310	27790	0.99

To eliminate the effect of PAM dose on the apparent viscosity and yield stress, all the rheological parameters were measured at a unified PAMs doses of 30 mg.L^{-1}. The same trends were observed at the unified PAM dose of 30 mg.L^{-1}. Higher CD with higher molecular weight PAMs exhibited higher apparent viscosities and yield stresses.

Except in a case of highly branched structured PAMs, 60% CD produces higher apparent viscosity and yield stress compared to 40% CD at unified PAM dose. Here, the concentration of PAM plays a significant role. While unifying the PAMs doses to 30 mg.L^{-1}, the concentration of FO 4698 XXR (highly branched, 60% CD) has increased relative to its optimum concentration, therefore, resulting in higher apparent viscosity and yield stress compare to FO 4498 XXR (highly branched, 40% CD). In overall, a higher concentration of PAM, higher CD and long-chain polymer, i.e., higher MW, resulting in higher yield stress and apparent viscosity (see Figure 4-17 and Tables 4-6 and 4-7). Both FO 4690 SSH and FO 4698 XXR show similar behavior of yield stress at a low dose, but there is a significant difference in their yield stress at a high dose especially above 30 mg.L^{-1}. Campbell et al. [159] reported that increasing the polymer dosage, increases the yield stress and subsequently increases the apparent viscosity. Besides, both the conditioned and un-conditioned MBR sludge demonstrates time-dependent behavior where the viscosity is decreasing with time at a constant shear rate of 0.5 s^{-1}, and it confirms the thixotropic behavior of sludge samples (Figure 4-16c). The results suggested that the flocs are never reduced to their primary constituent particles or aggregates since the apparent viscosity, measured under equilibrium conditions, is different for each unconditioned and conditioned sludge. This proves the significant enhancement of the structural strength of MBR sludge by adding different types of PAMs; where after a long period of about 900 sec, the system does not return to its initial state. The different electrostatic attractions between the sludge and the different types of PAMs are an indication of the formation of different microstructures as evident from the different initial and equilibrium viscosities and structural breakdown. Tables 4-8 and 4-9 summarizes the initial and equilibrium viscosity of all tested PAMs. As illustrated in Figure 4-16c and Table 4-8, almost 20-70% reduction in initial viscosities were reported with the lowest reduction corresponding to FO 4490 SSH (linear, 40% CD) and the highest reduction for unconditioned sludge.

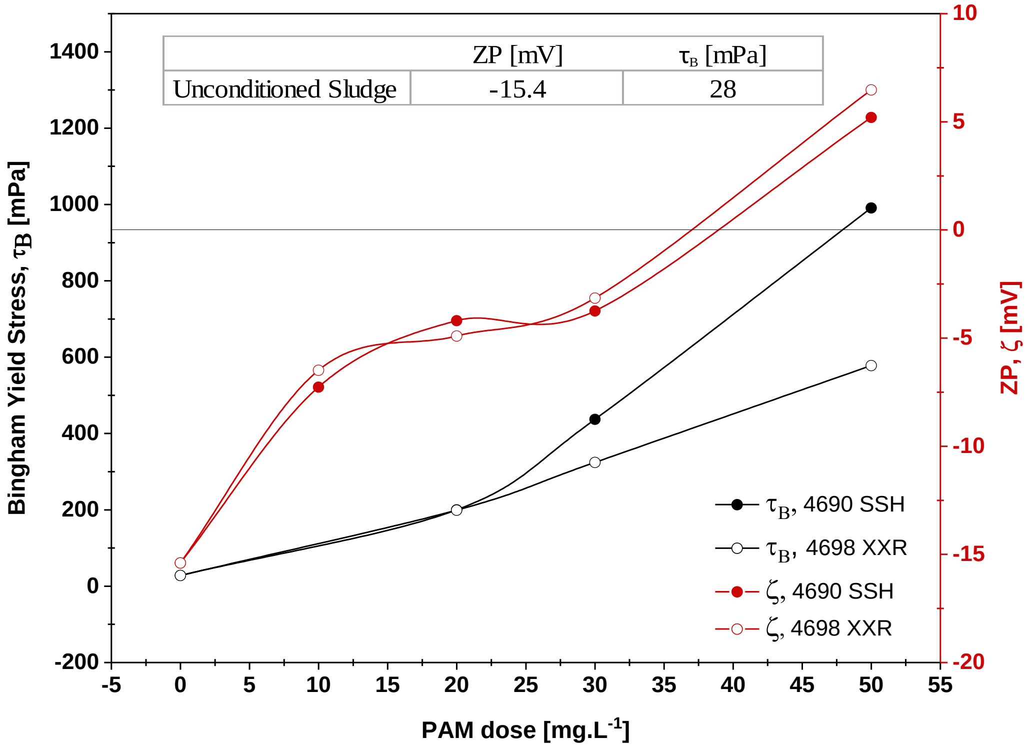


Figure 4-17. Bingham yield stress as a function of PAM dose

Table 4-8. *Initial and Eequilibrium Viscosities of Sludge Before and after Conditioning with PAMs at Optimum Dose*

Flocculant [unit]	Initial Viscosity [mPa.s]	Equilibrium Viscosity [mPa.s]
Unconditioned sludge	487	148
4490 SSH	2386	1960
4690 SSH	4101	3138
4498 SSH	1235	397
4698 SSH	1149	716
4498 XXR	1351	526
4698 XXR	392	140

Table 4-9. *Initial and Eequilibrium Viscosities of Sludge Before and after Conditioning with PAMs at Unified Dose of 30 mg.L*$^{-1}$

Flocculant [unit]	Initial Viscosity [mPa.s]	Equilibrium Viscosity [mPa.s]
4490 SSH	679	218
4690 SSH	1395	682
4498 SSH	1235	397
4698 SSH	1149	716
4498 XXR	1351	525
4698 XXR	977	435

Viscoelastic Behavior

Tables 4-10 and 4-11 summarize G' and G'' that are obtained by extrapolating the low applied frequency to the zero coordinate. The greater value of G' compare to G'' proves the viscoelastic solid-like behavior of sludge with and without PAMs and indicates a high structural gel-like strength of the conditioned MBR (refer to figures in Appendix A for more details). These findings are in good agreement with Chen et al. [37] findings on the impact of cationic polymer on the rheological behavior of flocculated sewage wastewater sludge.

Table 4-10. *Elastic and Viscous Modulus of Sludge Before and after Conditioning with PAMs at Optimum Dose*

	Optimum Dose [mg.L^{-1}]	
Flocculent	G' [mPa]	G'' [mPa]
unconditioned sludge	554	69
4490 SSH	12172	1219
4690 SSH	16030	1600
4498 SSH	5168	538
4698 SSH	5186	507
4498 XXR	5054	518
4698 XXR	2552	251

Table 4-11. *Elastic and Viscous Modulus of Sludge Before and after Conditioning with PAMs at Unified Dose of 30 mg.L*$^{-1}$

Flocculent	G' [mPa]	G'' [mPa]
4490 SSH	2313	226
4690 SSH	7021	690
4498 SSH	5168	538
4698 SSH	5186	507
4498 XXR	5054	518
4698 XXR	3703	368

As mentioned before, by increasing the PAM dose, floc size distribution peak will shift to the right, representing a larger flocs formation due to the number and the strength of the inter-particles and polyelectrolytes interactions through adsorption (via amine group), charge neutralization and bridging mechanisms. With increasing the dose of PAMs and formation of larger and strong/stiff flocs, elastic modulus (G') will increase due to the increased bridging between PAMs and negatively charged sludge particles [37]. These strong flocs are resistant to the structural breakdown as the angular frequency in oscillatory shear is increased.

Figure 4-18 shows the G' obtained from the LVR for the flocculated MBR sludge samples (at a strain of 0.3%) as a function of oscillatory frequency.

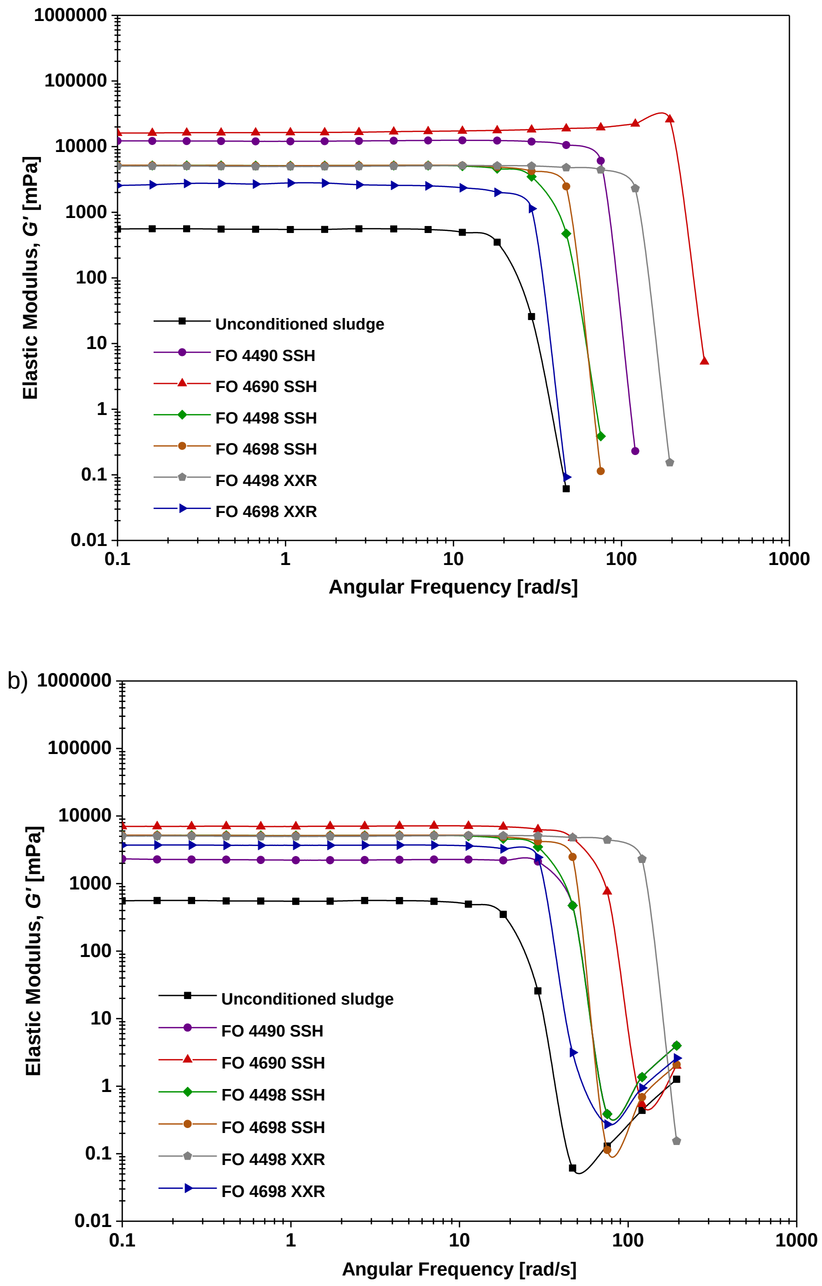


Figure 4-18. Elastic and viscous moduli of MBR sludge conditioned with PAMs at a) optimum PAM's dose b) 30 mg.L^{-1} PAM's dose

G$'$ also can measure the capacity of a material to store the mechanical energy during the application of oscillatory shear. According to Tables 4-10 and 4-11 and Figure 4-18, MBR sludge conditioned with FO 4690 SSH (linear, 60% CD) has the largest *G*$'$ and *G*″ both at the optimum and unified dose. Therefore, FO 4690 SSH has a higher capacity to store the mechanical energy and is capable to return to its initial configuration in the absence of mechanical force. Additionally, a more compact flocs with less bound water was formed using FO 4690 SSH. This was followed by sludge conditioned with FO 4490 SSH, FO 4698 SSH, FO 4498 SSH, FO 4498 XXR and FO 4698 XXR at their optimum doses (Table 4-10). The elastic (G') and viscous (G'') moduli measurements showed similar trends as shear yield stress measurements indicating that the strong sludge flocs of high τ_B are stiffer and more elastic flocs having high G' values. At high angular frequency, a sharp drop in G' and a sharp increase in G'' represented the transition from solid-like to liquid-like behavior.

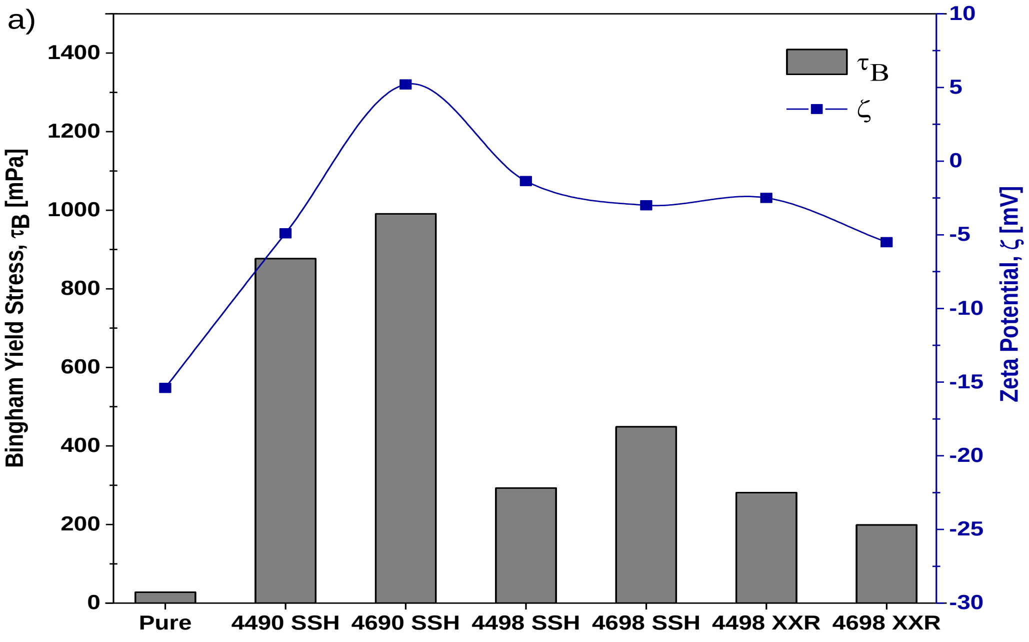
To assess the influence of MW and architecture on the flocculation efficiency and consequently the rheological behavior of MBR sludge, PAMs with the same CD were compared (FO 4690 SSH (linear), FO 4698 SSH (slightly branched), and FO 4698 XXR (highly branched)). The result showed that linear structured PAM with high MW (FO 4690 SSH) exhibited G' value of 16030 mPa which is almost 3 times higher than the G' value of FO 4698 SSH (slightly branched) of the same MW and 6 time higher than G' of FO 4698 XXR (highly branched) with 4-7 million g.mol^{-1} MW. In addition to the MW and architecture of the PAMs used, the CD was found to be a crucial parameter affecting the viscoelastic properties. For example, considering linear structured PAMs with same MW (7-10 million g.mol^{-1}), 60% CD (FO 4690 SSH) produces stronger flocs with high viscoelasticity behavior compared to 40% CD (FO 4490 SSH). Greater interactions between PAM chain and sludge particles would exist when a high CD PAM is used, since as the adsorption rate increases by increasing the CD. However, in some cases, when the branching of the polymer increases, the lower CD performs better than a high CD PAM.

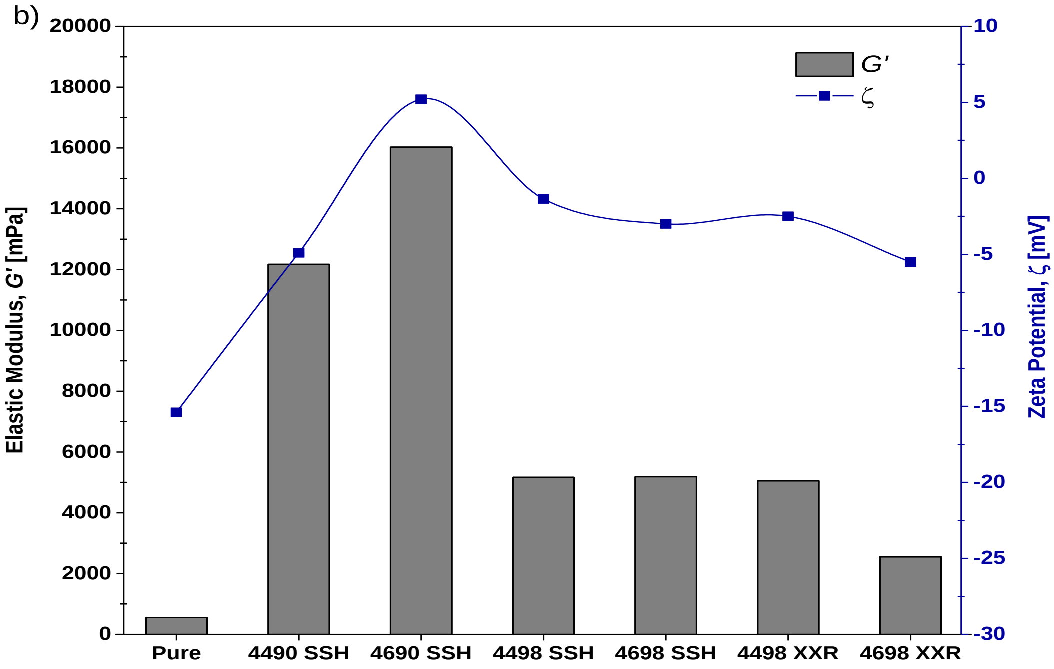
To eliminate the effect of PAM's doses as the optimum doses are different for each PAM, a unified dose of 30 mg.L^{-1} was selected to validate the impact of MW and CD on the PAM-sludge bridging mechanisms. The results showed, at this unified PAM's dose; still, FO 4690 SSH exhibited the highest G'; representing the strength of the flocs are formed using this flocculant. While FO 4490 SSH has the lowest G' and G'' values.

Flocculation vs. Rheological Behavior of the MBR Sludge Conditioned Using Different PAMs

Zeta Potential

ζ is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles and is one of the fundamental parameters known to affect stability [73]. A high value of ζ indicates the system is highly stable either with a negative surface charge or positive. When the system is highly stable, there are strong electrostatic repulsion forces between the particles. Therefore, less stress is required to initiate the flow and the system is less viscous. However, when PAMs are introduced into the sludge samples, positive charges of PAMs get attracted to the negative surface charge of sludge particles. Charge neutralization and bridging are the two main mechanisms in flocculation processes; thereby, the viscosity increases, and higher stress is needed to initiate the flow through the flocs breakdown. Figure 4-19 shows the relation of yield stress, elastic modulus, and viscosity with ζ for MBR sludge conditioned with different PAMs.


a)
Bingham Yield Stress, τ_B [mPa]
0
200
400
600
800
1000
1200
1400
Zeta Potential, ζ [mV]
10
5
0
-5
-10
-15
-20
-25
-30
τ_B
ζ
Pure
4490 SSH
4690 SSH
4498 SSH
4698 SSH
4498 XXR
4698 XXR


b)
Elastic Modulus, G' [mPa]
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
Zeta Potential, ζ [mV]
10
5
0
-5
-10
-15
-20
-25
-30
G'
ζ
Pure
4490 SSH
4690 SSH
4498 SSH
4698 SSH
4498 XXR
4698 XXR

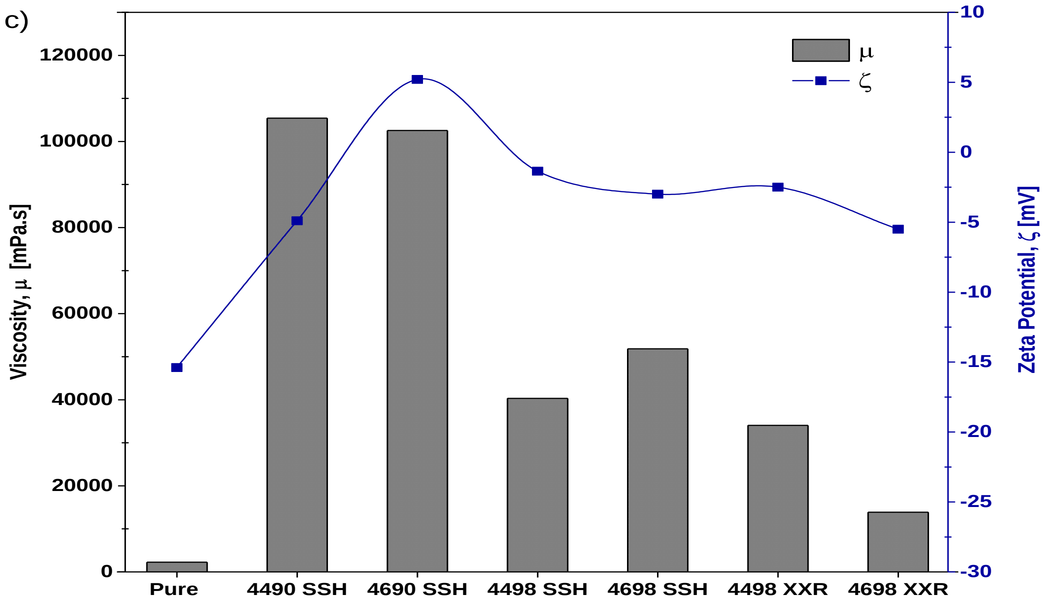


Figure 4-19. a) Bigham yield tress b) elastic modulus c) viscosity of MBR sludge as a function of zeta potential conditioned with PAMs at their optimum doses

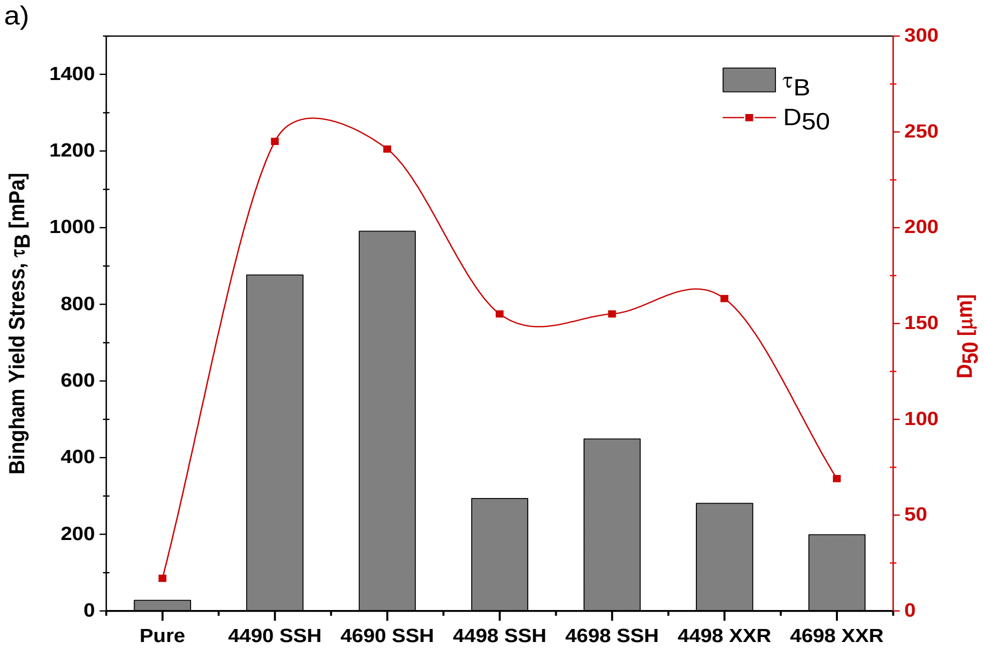
Unconditioned sludge resulted in the lowest rheological parameters having the highest negative ζ. On the other hand, FO 4690 SSH exhibited the highest yield stress, elastic modulus at its optimum dose. By reducing the negative ζ of the sludge particle surface and moving to the positive value, all the rheological parameters (i.e., yield stress, elastic modulus, and viscosity) have increased. Reducing the ζ reduces the stability of the colloidal particles, colloids flocculate and form bigger and denser flocs where they can settle faster; hence viscosity and yield stress increase. However, in addition to the ζ value, type and concentration of PAMs used, play a significant role in defining the strength and stiffness of the flocs produced. For example, FO 4690 SSH and FO 4698 XXR resulted in similar ζ value (ζ value between ±5 are considered almost similar) (see Figure 4-17). Both have the same dose of 30 mg.L^{-1} and 60% CD (Table 4-7). They are different in their structure (linear vs. highly branched) and MW (7-10 million vs. 4-7 million g.mol^{-1}). Almost 50% higher in apparent viscosity and elastic modulus and 25% higher in Bingham yield stress was obtained by using linear structured PAM FO 4690 SSH.

On the other hand, the effect of CD can be seen by comparing two PAMs of the same structure and MW, at either optimum or the same dose. For the linear and slightly branched structure PAMs, 60% CD is performing better than 40% CD at both optimum and unified dose. However, a highly branched structure has stronger and viscous flocs with a 40% CD. Therefore, in all cases, the lower ζ value resulted in higher rheological parameters due to stronger flocs that were formed by reducing the surface charges of the colloidal particles and destabilizing the sludge system. When they exhibit a similar ζ value, PAM's dose, type, and MW play an important role and need to be considered.

Flocs Size and CST

The same analysis was performed with flocs size D_{50} to further support the ζ results and their correlation with different rheological parameters. Figure 4-20 shows the plot of Bingham yield stress, elastic modulus and initial viscosity with flocs size (D_{50}) at the optimum doses of PAMs. This figure indicates smaller flocs results in lower yield stress, elastic modulus, and viscosity. However, other factors such as the type of PAMs will significantly affect the rheological parameters. For example, the effect of CD is clearly shown when comparing FO 4498 SSH and FO 4698 SSH. At the same optimum dose of 30 $mg.L^{-1}$ and approximately similar floc size, FO 4698 SSH resulted in higher yield stress and apparent viscosity; and a comparable result of elastic modulus. Even in the case of linear structured PAMs, FO 4690 SSH resulted 13% higher in τ_B and 40% higher in G' compared to FO 4490 SSH, despite their similar floc size of 245 and 241 µm for FO 4490 SSH and FO 4690 SSH, respectively. This shows the significance of the CD on the elasticity and strength of the flocs formed. For linear and slightly branched PAMs with a high MW, increasing the CD increases the τ_B and G', and for the highly branched structured with a low MW, the opposite is applied.

CST values were used to assess the effects of conditioning on sludge filterability or dewater-ability. Typically, larger flocs result in lower CST values compared to smaller flocs with narrow capillaries which do not release the water easily [156,157]. Figure 4-21 illustrates the variation in yield stress, elastic modulus and viscosity with CST for different types of PAMs used. According to this figure, there is a considerable reduction in CST from unconditioned sludge to sludge conditioned with different PAMs. And At the same time, there is a significant improvement in rheological parameters. CST can be related to the rheological behavior of activated sludge, but it is not always successful [37]. CST remains almost constant and independent of type and concentration of PAMs.



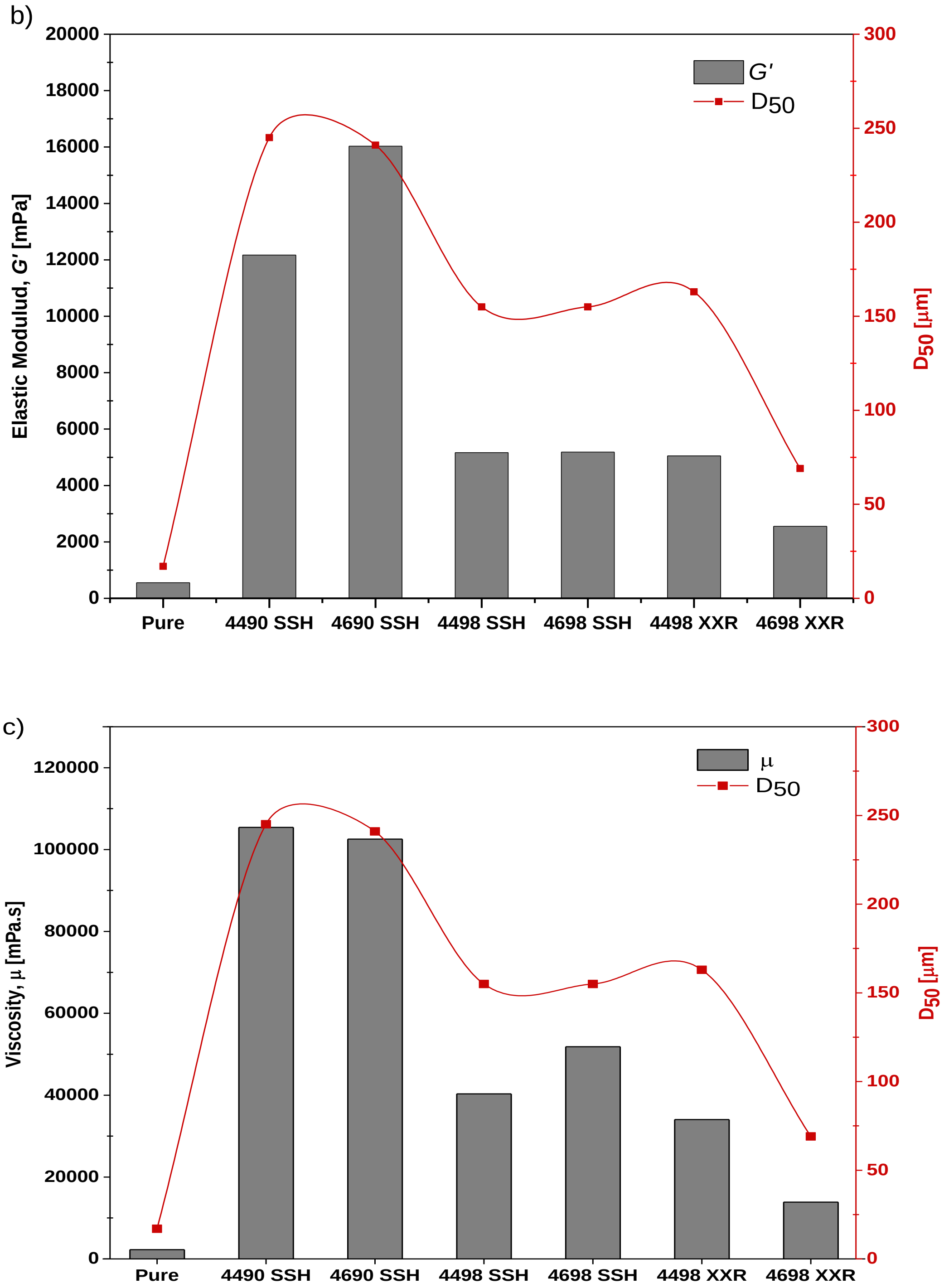
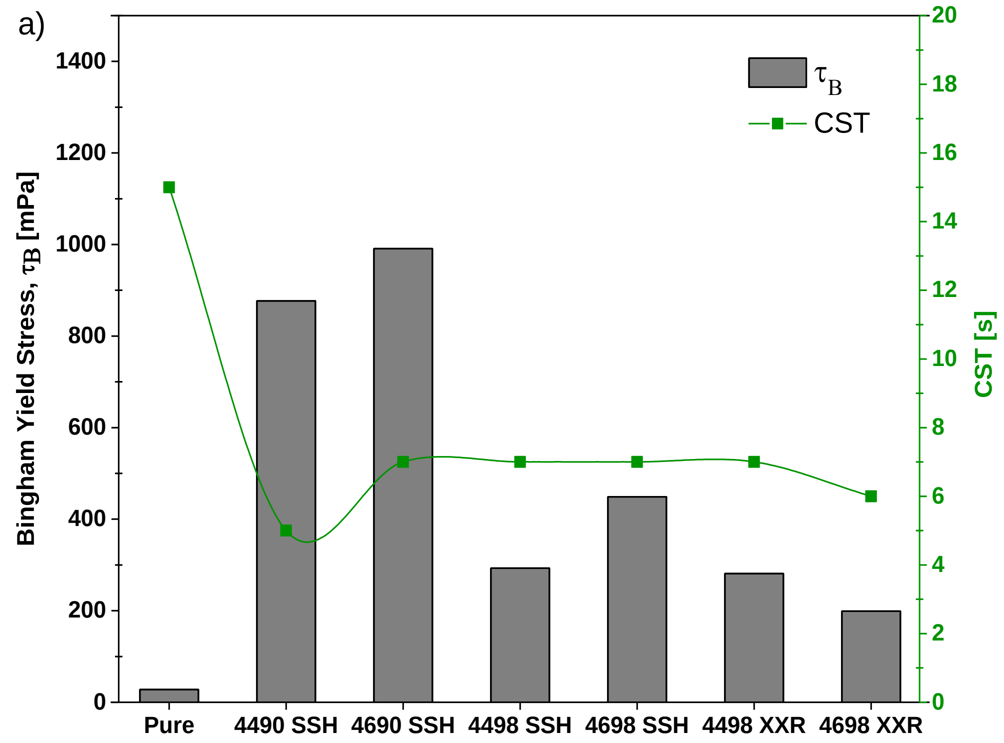
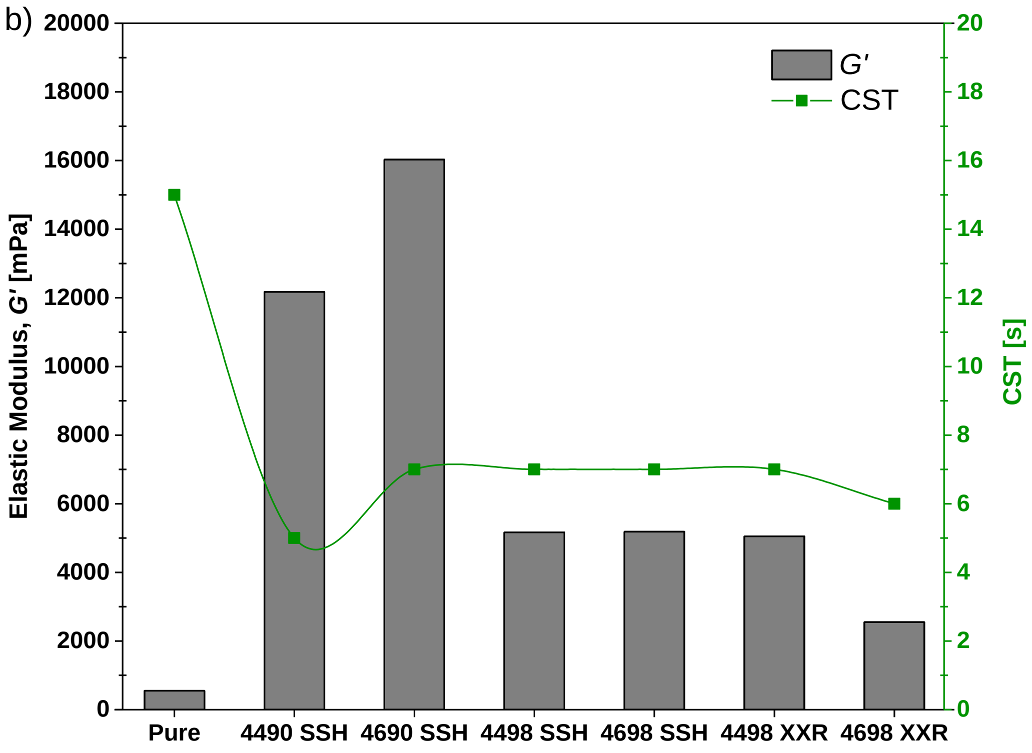


Figure 4-20. a) Bigham yield tress b) elastic modulus c) viscosity of MBR sludge as a function of D_{50} conditioned with PAMs at their optimum doses


a)
Bingham Yield Stress, τ_B [mPa]
0
200
400
600
800
1000
1200
1400
CST [s]
0
2
4
6
8
10
12
14
16
18
20
τ_B
CST
Pure
4490 SSH
4690 SSH
4498 SSH
4698 SSH
4498 XXR
4698 XXR


b)
Elastic Modulus, G′ [mPa]
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
CST [s]
0
2
4
6
8
10
12
14
16
18
20
G′
CST
Pure
4490 SSH
4690 SSH
4498 SSH
4698 SSH
4498 XXR
4698 XXR

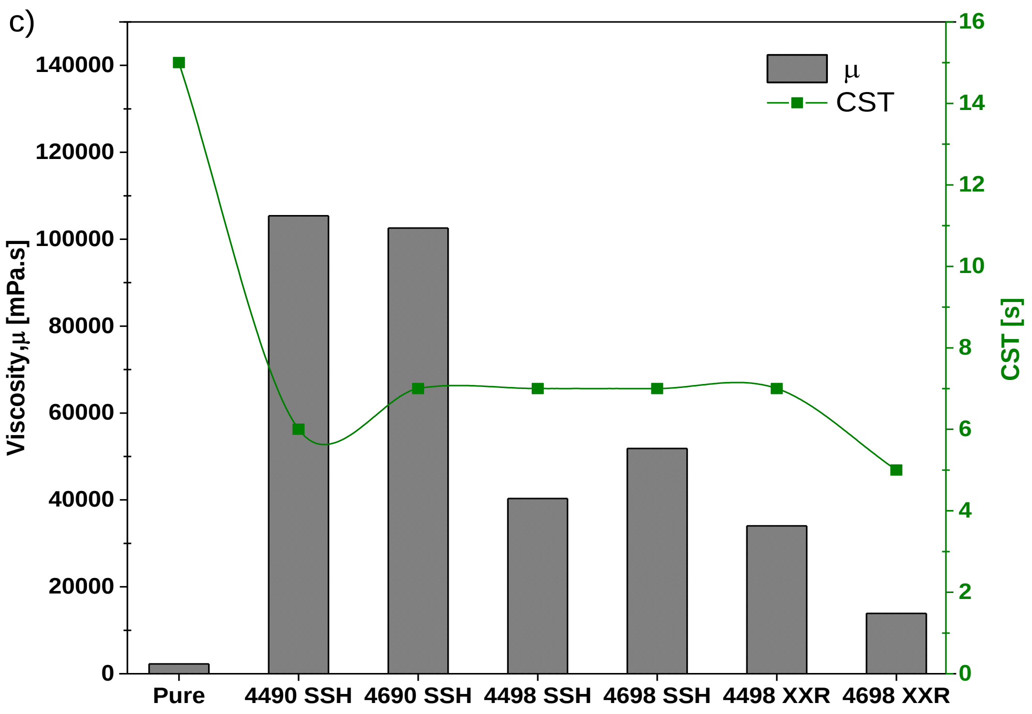
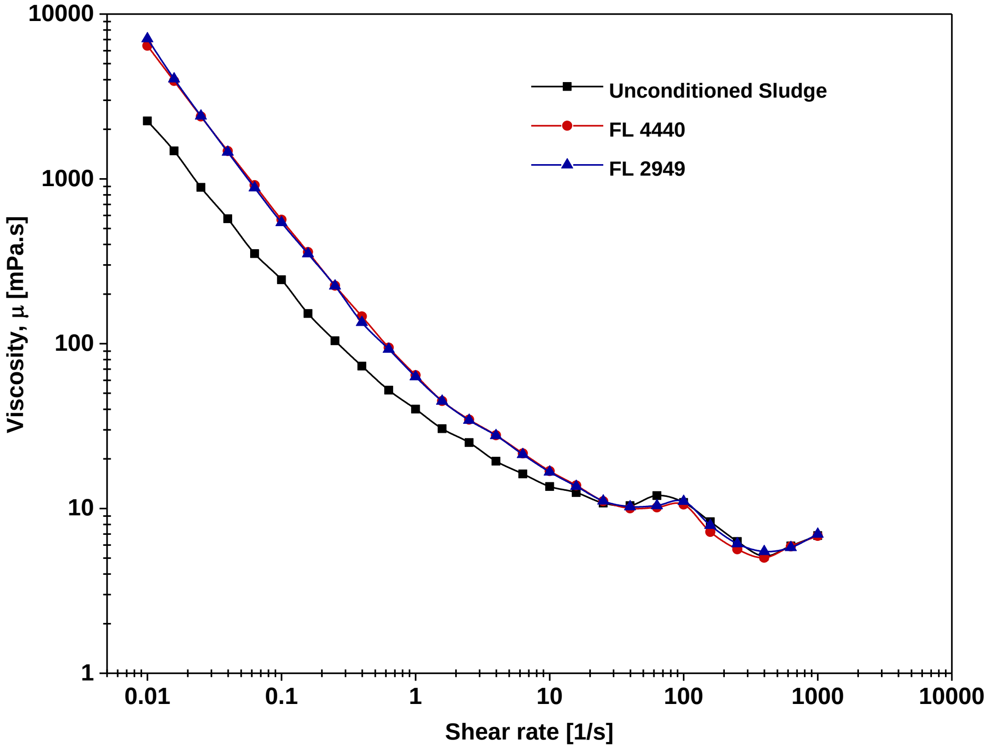


Figure 4-21. a) Bingham yield tress b) elastic modulus c) viscosity of MBR sludge as a function of CST conditioned with PAMs at their optimum doses

The Influence of Organic Coagulants and Flocculants on the Rheological Behavior of the MBR Sludge: Comparative Analysis

In this study, in addition to six PAMs, two organic coagulants; polyamine (FL 2949) and polyDADMAC (FL 4440) have been used. Figure 4-22 illustrates the shear thinning behavior of MBR sludge flocculated with polyamine and polyDADMAC. Similar to PAMs, the obtained results are the best fit into the Bingham model with R^2 of greater than 0.99. Additionally, Figure 4-23 represents its viscoelastic behavior where *G'* is greater than *G"*. Table 4-12 summarizes the rheological parameters of MBR sludge conditioned with polyamine and polyDADMAC. According to this table, there is a slight improvement in the rheological parameters of the MBR sludge by using polyamine and polyDADMAC and comparable behavior of all parameters between polyamine and polyDADMAC. However, when comparing them to the MBR sludge conditioned with PAMs, it can be noted that the flocs formed by PAMs through charge neutralization and bridging mechanisms are sufficiently large and strong and they are highly resistant to any breakage and deformation under applied shear stress. This can be seen from the yield stress and elastic modulus results. Higher viscous sludge with larger and stronger flocs is formed when PAMs are used in comparison to coagulants (i.e., polyamine and polyDADMAC). FO 4698 XXR which has produced the lowest viscosity, yield stress and elastic and viscous moduli among the different types of PAMs resulted in 71%, 54% and 42% higher yield stress, viscosity, and elastic modulus, respectively, compared to sludge conditioned with polyamine and polyDADMAC.



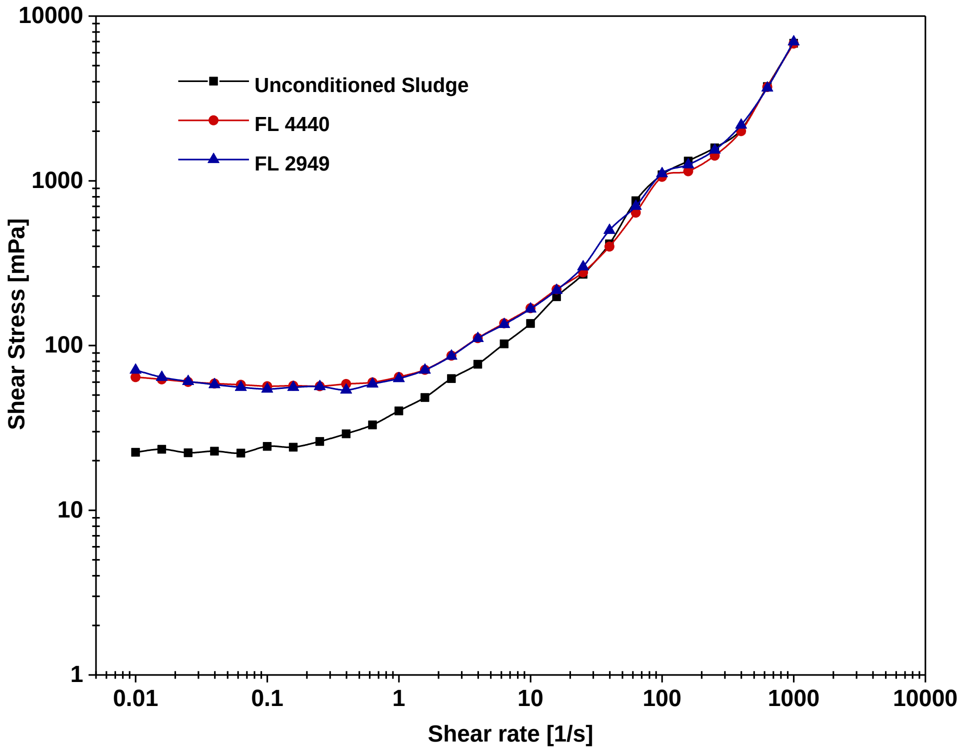
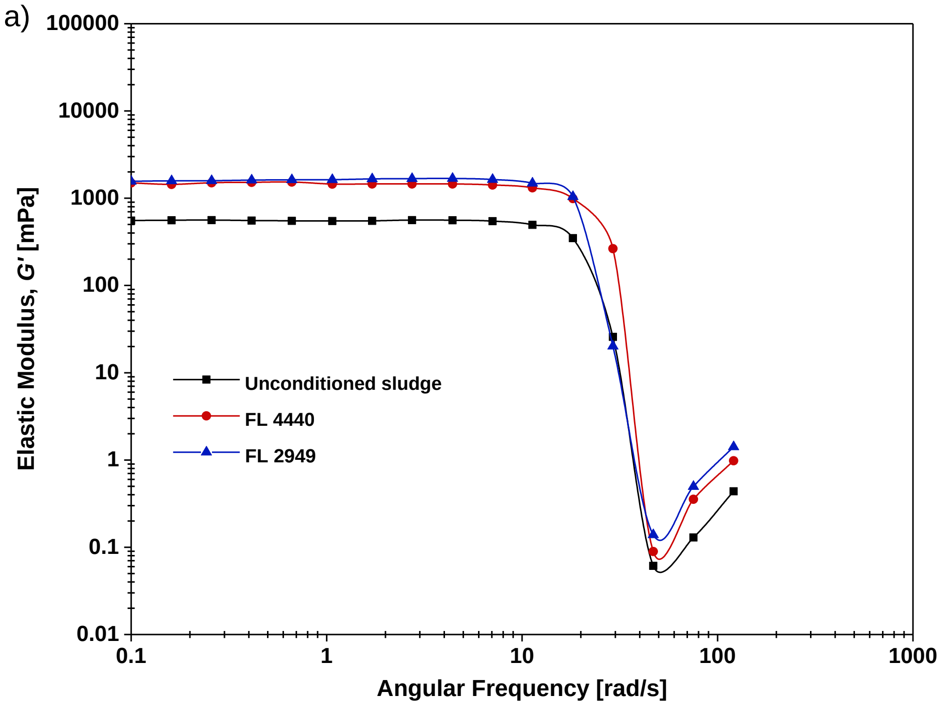


Figure 4-22. Variations in a) viscosity with shear rate b) shear stress with shear rate for MBR sludge conditioned with organic coagulants



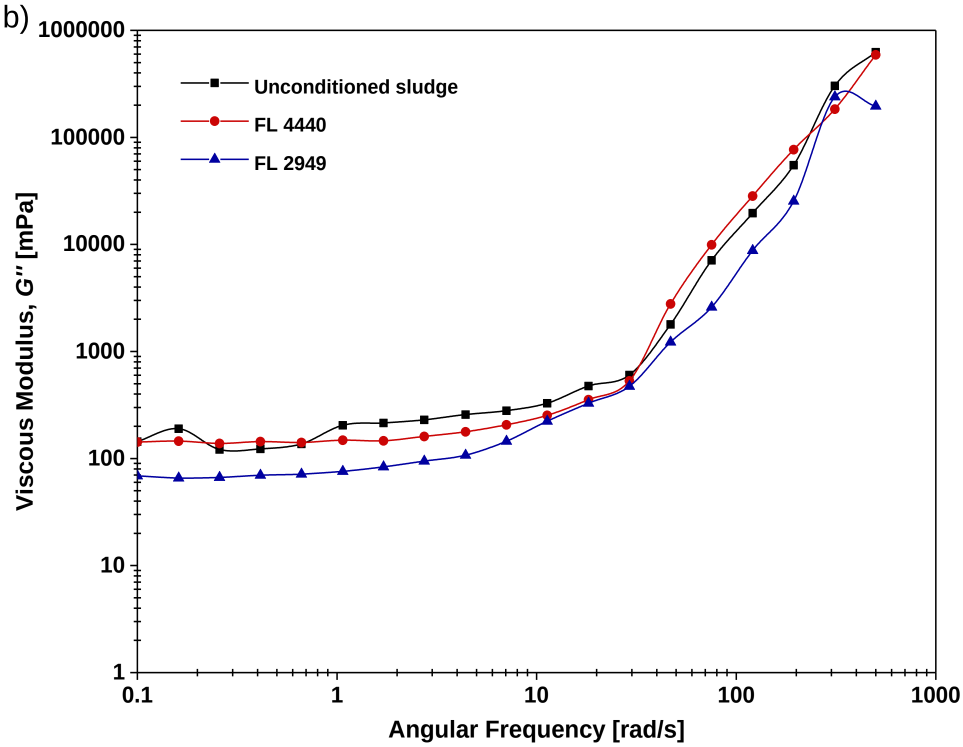


Figure 4-23. a) elastic and b) viscous moduli of MBR sludge conditioned with organic coagulants

Table 4-12. *Rheological Parameters of MBR Sludge Conditioned with Polyamine and PolyDADMAC (Bingham Model)*

Coagulant	Optimum dose [mg.L^{-1}]	τ_B [mPa]	Apparent viscosity,µ [mPa.s]	R^2	*G'* [mPa]	*G''* [mPa]
unconditioned sludge	--	28	2245	0.997	554	69
FL 2949	40	59	7088	0.998	1560	142
FL 4440	50	58	6422	0.995	1494	144

CHAPTER 5: CONCLUSION

The ultimate objective of this study was to understand the influence of polyelectrolytes characteristics in sludge conditioning, dewatering, and eventually defining the optimum conditions. This aim was achieved by combining a complete knowledge of the sludge-polyelectrolyte systems in the free settling region of the suspension through zeta potential, turbidity and floc size measurements, and the networked suspension region either in the form of sediment or a filter cake through rheological measurements, and finally correlating the degree of flocculation of the sludge to its rheological behavior.

Biological sludge contains suspended particles, which has a colloidal nature with a negative surface charge. Therefore, the polyelectrolytes used for the coagulation and flocculation of sludge were cationic polyelectrolytes, and their characteristics include, molecular architecture (i.e., linear, slightly branched, and highly branched), MW and surface CD that affect the flocculation mechanisms for high stable MBR sludge. The flocculation performance of polyelectrolytes characteristics was evaluated through ζ, supernatant turbidity, CST, floc size, settleability, and rheological measurements.

In the absence of any coagulating agent, the highly branched PAM with a MW of 4-7 million g.mol^{-1} and a 60% CD is considered as being the most efficient flocculant by having a maximum reduction in turbidity and surface charge reversal at the lowest possible dose of 10 mg.L^{-1}. Variations in PAM's charge density, MW, and the architecture were fundamental to distinguishing the flocculation efficiencies and dewatering performance demonstrated by all PAMs. A higher CD PAM is more effective in reducing particle surface charge and supernatant turbidity than a low charge density PAM. However, depending on the structure and MW, the effect of CD might vary. While high CD was a desirable property for the sludge conditioned using linear and highly branch structured PAMs, it did not greatly improve the flocculation performance for the sludge conditioned using slightly branch structured PAMs. Reducing the MW of PAM while increasing its degree of branching significantly reduces the particle absolute zeta potential and supernatant turbidity, permitting the use of lower doses.

Sludge floc size is mainly a function of PAM's dose; higher PAM's dose produces larger flocs. However, at a selected reference dose, MW plays a significant role in flocculation behavior. Producing large flocs cannot be used as an indicator of better dewatering characteristics of each flocculent tested. In some cases, floc compactness is observed to have a greater role in sludge dewatering than floc size. Therefore, CST was used to examine the impact of PAM structure on the dewater-ability performance of sludge. 52-65% reduction in CST were achieved using different characteristics of PAMs.

The presence of coagulants in tandem with PAM has improved the flocculation efficiency (i.e., electro-kinetics and dewatering) by lowering the optimum dose of PAMs. This was significant in linear structured PAMs followed by slightly and highly branched structure. The flocs sizes in all cases have reduced significantly due to the mechanisms through which coagulation-flocculation take place. However, the pronounced reduction in the flocs size did not greatly distress the dewater-ability behavior, which shows a great efficiency of hybrid coagulation-flocculation in the conditioning of the highly stable MBR sludge.

Influence of polyelectrolytes characteristics on the flocculation efficiency of MBR sludge can also be determined by measuring the rheological parameters. Rheological measurements showed that the MBR sludge with/without conditioning has a thixotropic (time-dependent) behavior with measurable yield stress. It exhibited a non-Newtonian shear thinning behavior and well represented by the Bingham model. The measurements of elastic ($G^{'}$) and viscous (G'') moduli proved the viscoelastic solid-like behavior of the MBR sludge with/without conditioning ($G^{'} > G''$). Bingham yield stress, τ_B, viscosity, µ, and G', were used for examining the rheological behavior of the conditioned MBR sludge. About 77-94% higher in τ_B, 86-96% in µ and 76-92% in G' were obtained by conditioning the sludge with different types of PAMs. These percentages vary depending on the type and structure of the PAMs. The highest $\tau_{B,}$ µ, and G' was obtained by using a linear structure PAM, FO 4690 SSH. This behavior was in good agreement with flocs size, D_{50}, zeta potential, ζ, and capillary suction time, CST. The results obtained by conditioning MBR sludge with different PAMs were compared with those obtained by conditioning with polyamine and polyDADMAC. Polyamine and polyDADMAC have raised the $\tau_{B,}$ µ and G' of the MBR sludge by 52%, 84%, and 63%, respectively. Overall, MBR sludge conditioned with PAMs having a high CD in the case of high MW (FO 4690 SSH, FO 4698 SSH) and low CD in the case of low MW (FO 4498 XXR), resulted in greater $\tau_{B,}$ µ and G' compare to those formed with polyamine and polyDADMAC. Therefore, PAMs are building a more compact network that highly reduces the trapped water within the sludge flocs.

CHAPTER 6: FUTURE PROSPECTS

Different measurements were performed for this study, and the results were tremendous compared to literature; however, the work can be further improved by conducting the following investigations, which was not applied due to the difficulty in accessing the MBR sludge and time limitation.

i. Response surface methodology, a combination of mathematical and statistical technique can be used to reduce the number of experiments, combine the effect of different independent parameters, which affect the flocculation efficiency such as pH, polymer's dose, and polymer type, and optimize the system outcome to achieve the best efficiency. Response surface methodology was performed only for one system of linear structured PAM.

ii. The efficiency of synthetic polyelectrolytes in flocculation and dewatering of MBR sludge should be compared with natural polyelectrolytes such as chitosan and polysaccharides.

iii. The rheological parameters of the hybrid coagulation-flocculation should be measured. Since the hybrid system is producing smaller flocs compare to when long-chain polymers are used individually, therefore, it is good to know the strength of the flocs produced using a hybrid system.

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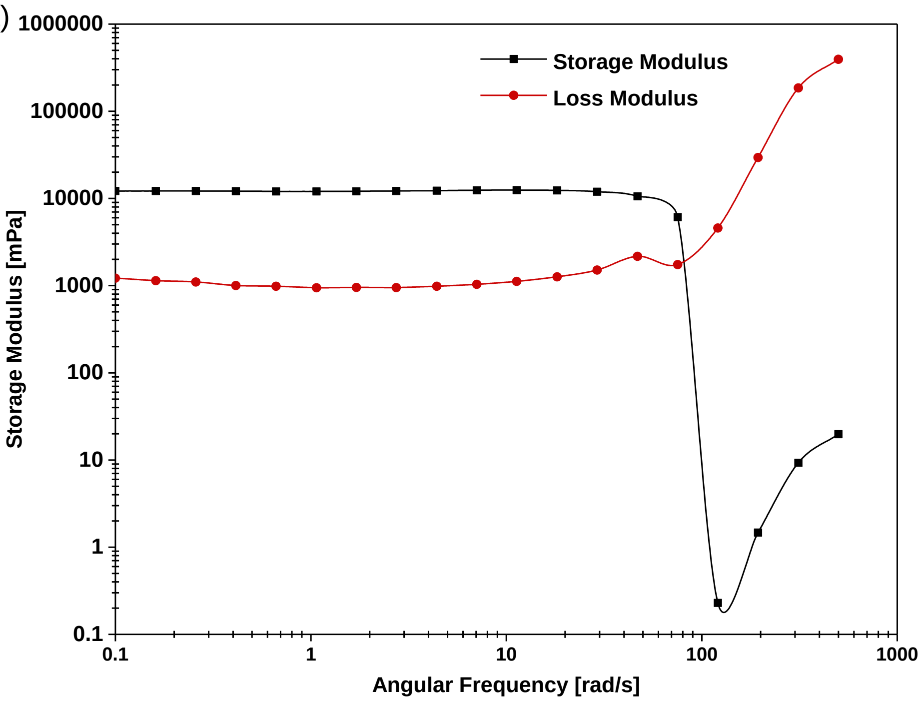
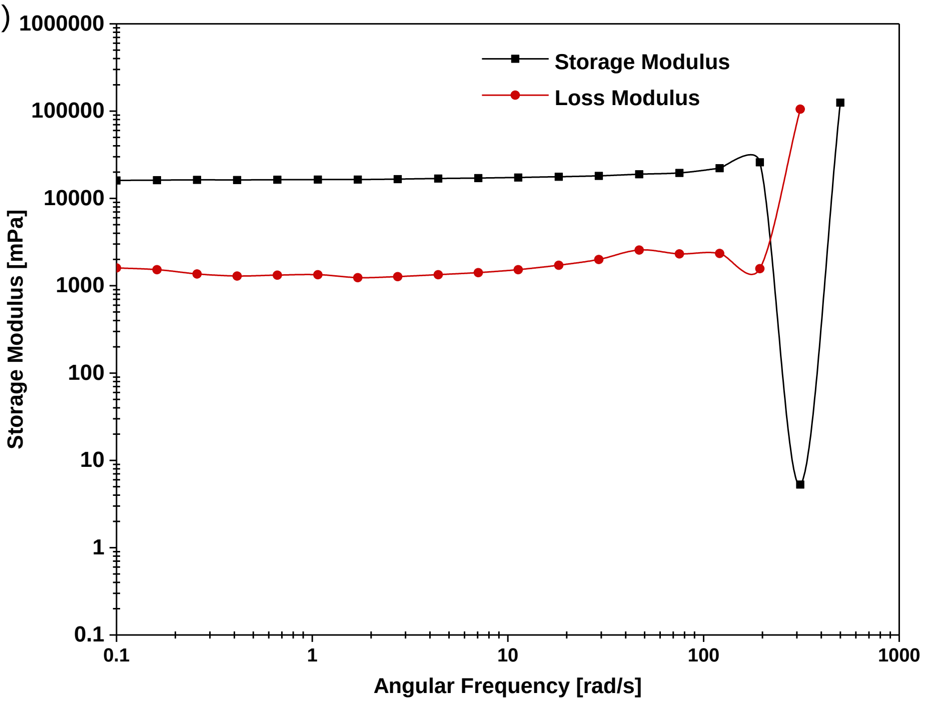
APPENDIX A: STORAGE AND LOSS MODULUS

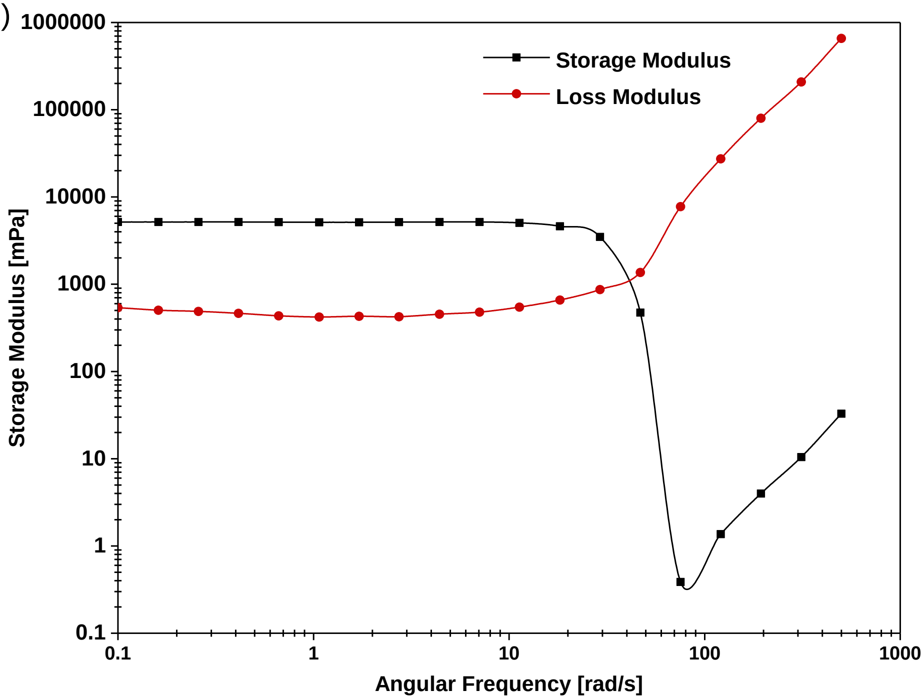
a)



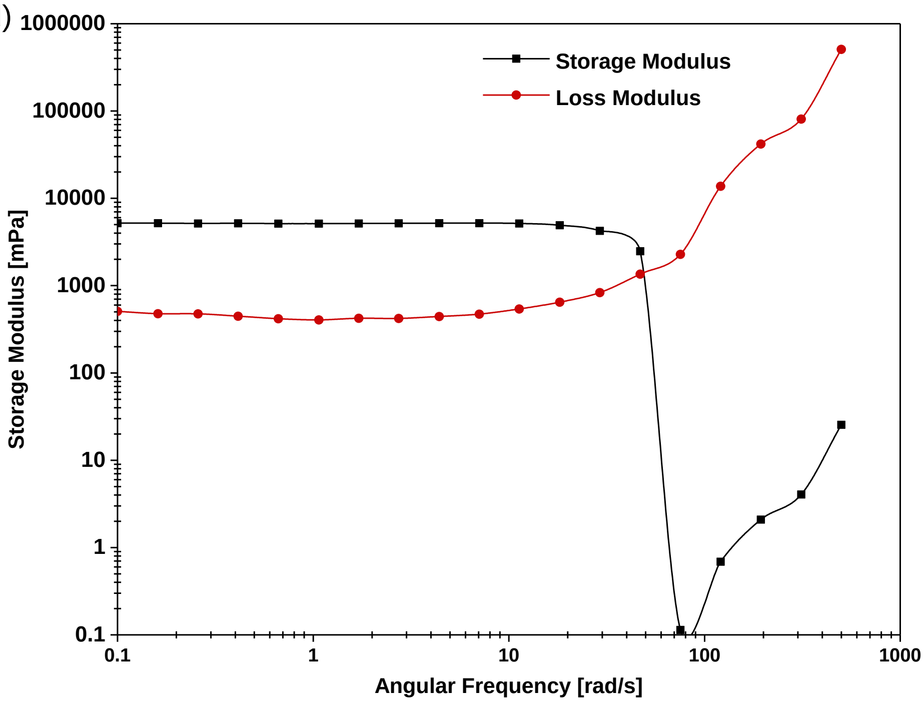
b)



c)


Storage Modulus
Loss Modulus
Storage Modulus [mPa]
1000000
100000
10000
1000
100
10
1
0.1
0.1
1
10
100
1000
Angular Frequency [rad/s]

d)


Storage Modulus
Loss Modulus
Storage Modulus [mPa]
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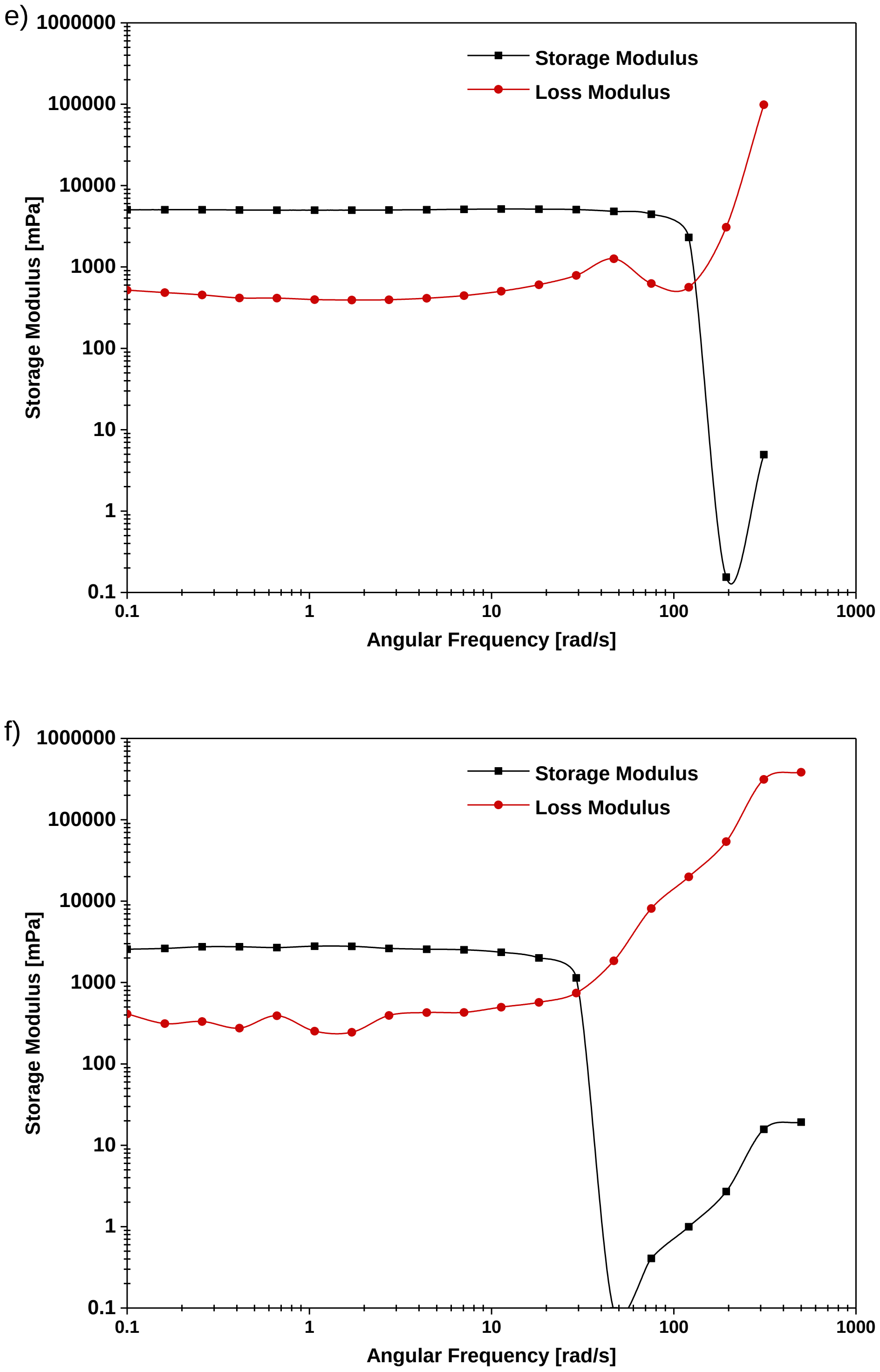
100000
10000
1000
100
10
1
0.1
0.1
1
10
100
1000
Angular Frequency [rad/s]



Storage and loss modulus for sludge conditioned using a) FO 4490 SSH b) FO 4690 SSH c) FO 4498 SSH d) FO 4698 SSH e) FO 4498 XXR f) FO 4698 XXR