

Enhancement of Sludge Dewatering: A look at Polymer Maturation and

Shear Optimization

by

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Abstract

The expected growth in global population and overall development of living standards will inevitably have an impact on wastewater treatment infrastructure. This will in turn put pressure on local wastewater treatment plants to handle greater throughput at a higher efficiency. Sludge treatment is one of the components of a treatment plant that will need to be enhanced as various elements rely heavily on operator empirical experience, or tests that reveal information about sludge after the fact. For example, crystalline polymers are often used for coagulation and flocculation of solids, however, the preparation methodology that is currently employed is typically based on operator judgement. Furthermore, the attempts that have been made to quantify polymer quality in terms of its optimal maturation time, with the use of viscosity and electrical conductivity, have not yielded conclusive results to determine optimal polymer age for application to sludge. In addition, the laboratory tests used measure sludge characteristics (such as total solids) are time consuming and by the time results are generated, sludge characteristics have likely changed.

The first phase of this study was aimed at developing a new methodology to determine the optimal polymer maturation time which would yield the highest quality of dewatering. With the use of spectrophotometry, the optimal maturation time was estimated and corroborated by spiking anaerobically digested sludge with polymers of different age. A significant difference ($p < 0.05$) was found between the filtration volume of sludge spiked with polymer that was aged for three hours compared to six hours. In addition, the spectrophotometer had the sensitivity to detect changes to polymer temperature, pH, chlorine content, and mixing method. Temperature, pH, and mixing regime had the greatest influence on maturation. In the second phase of the study

the rheological properties of conditioned sludge were used to determine a relationship between the degree of shear and the resulting sludge dewaterability. The rheometer used for measuring sludge network strength was also able to capture the optimal polymer dose range.

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List of Abbreviations

ACM (Acrylamide)

ADS (Anaerobically Digested Sludge)

AETAC (acryloyloxyethyltrimethyl ammonium chloride)

COD (Chemical Oxygen Demand)

DS (Dried Solids)

DI Water (Deionized Water)

Diclofenac (DFC)

G (Velocity Gradient/Shear Rate, s^{-1})

ROPEC (Robert O. Pickard Environmental Center)

TS (Total Solids)

TTQ (Totalized Torque)

UV-vis (Ultraviolet-Visible electromagnetic spectrum)

1 Introduction

Polymers and other conditioning agents are an important part of the wastewater and sludge residuals treatment process. They are the primer that facilitates coagulation of particles, leading to enhanced dewatering during the final stage of sludge treatment. Due to growing concerns about climate change and the overall influence societies have on their surrounding environment, there is increased public pressure to enhance treatment standards. This trend is likely to continue as demonstrated by the updated and more stringent *Canadian Wastewater Treatment Standards, 2012*. Coupled with the fact that metropolitan populations are generally rising, and current polymer applications result in only about 30-40% water removal from sludge, the research completed was aimed at applying currently used technologies of spectrophotometry and rheology to monitor and enhance the polymer application process for dewatering sludge.

In the first phase of this study, a crystalline polyacrylamide based organic polymer with ultra-high molecular weight, and cationic charge, was investigated to develop a model that describes polymer maturation, also known as aging. During the aging process, increased sites become activated through unwinding polymer chains, which facilitate the coagulation process. This implies that polymer dosing should only take place once a sufficient amount of aging has been reached. Crystalline polymers are typically used by relatively large wastewater treatment plants, and are prepared at the plant, thus, monitoring the maturation of polymer can help develop a timeline of when the polymer should be applied to sludge after preparation. The time frame required for maturation is likely to vary between different polymers of various ionic nature or monomer structure and environmental conditions. Nonetheless, improved analysis and understanding of this process can help treatment plants maximize the dewatering that results

from polymers, ultimately leading to a savings of the bottom line, as theoretically, less polymer can be used to achieve the same treatment quality.

The second phase of experiments focused on the application of rheological measurements to sludge and polymer mixtures. This was done to establish a relationship between the shear exposed to sludge and the resulting treatment quality when dosed with polymer. Rheology is the study of the deformation and flow of matter. The long-term application of rheology as it relates to sludge treatment is through in-line (real-time) monitoring of sludge physical characteristics and relating this data towards polymer dosage quantity. The studies completed were set to understand the rheological characterization of sludge, how it varies with exposure to shear, and how this sludge would behave with the addition of polymer into the overall framework. This is important to understand as each specific dewatering machine will expose the sludge and polymer mixture to a different amount of shear, which will ultimately impact the choice and dosage of polymer. Although research was not completed in-line, the studies provide the framework onto which real-time monitoring and experiments can take place in the future.

To help minimize the overall burden of cost due to polymer purchase at treatment plants, the research objective was to establish methods with the use of UV-vis spectrophotometry and rheology for enhancing the dewatering potential of polymers. The current methods of monitoring the polymer maturation process are via periodic electrical conductivity or dynamic viscosity measurements of the polymer mixture. Neither of these methods, however, have a strong backing consensus from the scientific community. Time periods ranging from several hours to several days have been suggested as ideal for ensuring polymer maturation. To our understanding, there are no previous investigations addressing polymer maturation detection through UV-vis spectrophotometry, meaning that the research undertaken provides a truly novel approach to the

issue. Additionally, the polymer maturation process is largely discussed by industry, and scientific literature on the topic is limited.

During maturation, polymer coils unwind and more surface area becomes available to facilitate coagulation and flocculation of suspended solids in sludge. Polymer is dosed throughout the sludge treatment process, but its application is especially important in the final stage before dewatering, as this will be the last step before a final biosolids product is achieved. Activation of the polymer is generally understood as the time at which the polymer has sufficient binding sites available to maximize sludge dewatering. Nonetheless, given enough time, polymer quality in terms of dewatering potential decreases, which implies there is an ideal timeframe within which polymers should be applied to maximize dewatering results. Thus, if the aging or maturation process can be better understood, an improvement could result in terms of dewatering sludge, as polymer would only be applied once it has achieved full activation. This would lead to a better final product for potential use as compost and other biosolids end applications.

To further enhance the polymer dewatering potential, understanding the sludge rheology into which the polymer will be dosed is also important. Both the choice of polymer and the dosage applied are influenced by the shear exposed to sludge. When considering different types of sludge, such as anaerobically digested or primary sludge, the rheological information about the two different types will be significantly different. The influence of sludge shear history on the dewatering quality once polymer is applied has been studied and it is generally understood that with greater shear being exposed to sludge mixture, the polymer demand also increases (Novak J. T., 1991). This concept was further investigated by analyzing whether the rheological data can give indication towards the optimal polymer dose. Due to the fact that the polymer dose is influenced by the level of shear, completion of Capillary Suction Time (CST) measurements to

anaerobically digested sludge (ADS) sheared at different shear rates and durations (i.e. Gt values) could give indication towards the expected dewatering results. Using multiple combinations of shear rate and shear duration, the goal was to develop a model to describe the resulting sludge dewaterability. Ideally, enough shear should be added to the sludge and polymer mixture to achieve homogeneous distribution of polymer without causing deflocculation. Shear quantity also plays a factor in determining the floc characteristics. For example, a higher shear rate was reported to produce denser floc, decreasing the floc volume (Cornwell & Bishop, 1983). The research completed can be applied towards reducing cost for wastewater treatment plants through more optimal polymer preparation and application. Also, the rheological studies on the sludge and polymer mixtures provide the groundwork onto which the flexibility of in-line, or on-line, monitoring of sludge and polymer application can take place.

2 Literature Review

Assessing the use of polymers in sludge treatment requires understanding several concepts related to sludge. By understanding the physiochemical properties of sludge, polymers may be better used to enhance the treatment process. This will establish a framework for the identification of polymers suitable for domestic sludge treatment. Thereafter, the application of UV-vis spectrophotometry and rheology can be investigated for their potential to enhance the polymer dosage of sludge. These enhancements include assessment of the polymer maturation process via UV-vis spectrophotometry, and establishing the level of shear that a sludge and polymer mixture will experience in a dewatering device, for relation towards the resulting dewatered sludge quality. Rheology can be understood as the study of fluid deformation and its link to sludge history and quality.

2.1 Classification of Sludge

Sludge generally originates from industrial or domestic use and can encompass various characteristics based on the point within the sludge treatment process. Industrial sludge has a characteristically higher heavy metal content and Chemical Oxygen Demand (COD), a measure of the oxidizable species within a mixture, when compared to domestic sludge.

Various classifications of domestic sludge exist in order to identify the type of sludge under consideration. Primary sludge for example, is a result of primary wastewater treatment; waste activated sludge is that which results from secondary (biological) wastewater treatment. The operations at Robert O. Pickard Environmental Center (ROPEC) are such that the sludge generated throughout the wastewater treatment process are all mixed, thickened, and stabilized through anaerobic digestion. At this point, the anaerobically digested sludge physically resembles the viscosity of water, it is generally anionic, it has its pathogens and odour drastically reduced when compared to its initial status upon reception into the plant, and contains lower solids and organic content measured via parameters such as Total Solids (TS) and Carbonic Oxygen Demand (COD).

2.2 Sludge Treatment Framework

The sludge treatment process is generally categorized under the four steps of thickening, stabilizing, conditioning, and dewatering. Initially, the sludge sourced from wastewater treatment is mixed and thickened in a basin similar to those used during primary treatment. Thickening can also be achieved through alternate technologies such as the use of a gravity belt thickener, but the use of a thickening tank similar to the applications of primary treatment is commonplace. Next, stabilization is accomplished through the use of chemical or biological processes.

Biological stabilization consists of exposing sludge to conditions that stimulate growth of aerobic or anaerobic bacteria, helping create an environment that minimizes the presence of pathogens, and also consumes some of the organic matter in sludge. Afterwards, conditioning follows via the application of polymers or other chemical agents such as iron salts or lime. The purpose of this step is to act as a primer for the final step of dewatering that follows. The conditioning agent, polymer in our case, provides a chemically favourable environment for maximization of the dewatering that is achieved. As implied by the name, the goal of dewatering is to separate the solids from water in the sludge slurry.

Cationic polymers help with neutralizing the overall charge of the generally negatively charged domestic wastewater. Because of the net negative charge that exists within the sludge framework, the suspended solids have a net repulsion that prevents coagulation. This phenomenon is known as the zeta potential, or surface charge, on particles and is known to affect the sludge flocculation process (Li, et al., 2016). Polymers balance the net charge of the solution by creating a net neutrally charged mixture because of their cationic nature. This leads to coagulation of solids in the sludge slurry, resulting in the eventual bridging of solids and finalized by the flocculation of solids.

The primary focus of the research completed was with regards to the polymer application stage of sludge treatment. This is an essential step as it directly impacts the final quality of sludge that results from the final dewatering stage that follows. In addition, the use of polymers constitutes a large expense for a wastewater treatment plant, thus, enhancing optimization of polymer use can greatly benefit the cost savings of the plant. The improvement of this process through the use of spectrophotometry and rheology will be discussed in greater detail during the following sections.

2.3 Current Methods for Assessing Sludge Dewatering Performance

Final solids content is highly dependent on the polymer application process. Polymer efficiency can be compared by measuring the solids content of sludge before and after polymer dosage. The methodology used to measure the solids content consists of heating samples in an oven at 105°C for at least 3 hours, to assess the solids remaining after water has evaporated. Taking sludge samples before and after the conditioning and dewatering phase of polymer application and comparing the solids content at these points would provide a means whereby the polymer's capacity to remove water can be quantified. This approach can be used to optimize both the concentration of polymer, and the specific type of polymer that should be used. Although widely practiced, these methods are time-consuming and can take several hours to a day to analyze.

The Capillary Suction Time (CST) is a test that measures the effectiveness of liquid-solid separation. A known quantity of conditioned sludge is placed within a cylindrical column. The column rests on a rectangular piece of absorptive paper. As the separated water becomes gradually absorbed into the underlying paper, a timer measures the time for water to travel a known distance. A lower time indicates better solid-liquid separation.

The filtration test allows comparison of sludge dewatering by measuring the volume of recovered sludge after conditioned sludge has run through a vacuum filter for a known period of time. A greater volume of recovery implies better quality dewatering.

In contrast, if sludge quality could be assessed through in-line or on-line measurement methods, or even through analysis techniques that would reduce the time necessary for testing, the industry could shift towards real-time process control to maximize sludge treatment. The technologies

that can assist with this shift include spectrophotometry and rheology, and will be discussed in greater detail in the following sections.

2.4 Polymer Classification and how Polymer Quality is Measured

Various physical and chemical characteristics can be used to describe polymers. Metrics such as molecular weight and ionic nature (both charge and charge amount) are typically reported. Due to the size of polymer chains, molecular weight is often quoted in terms such as “very-high” or “ultra-high”. Molecular weight represents the length of the polymer, whereby low and medium range molecular weights are considered coagulant polymers, and high/very-high molecular weights are flocculent polymers (Dentel, 2001). The molecular weight of polymers used for wastewater treatment is generally classified as high or very-high. Higher weights would be required in order to form stronger flocs that can withstand the high shear forces that are generated in the dewatering equipment that follows polymer dosage.

The ionic nature of polymers is also important as this will impact the interactions that take place with the receiving sludge mixture. Because particles present in residential wastewater and residuals typically have an anionic charge, the polymers of choice are generally cationic. By neutralizing the electrochemical charge within the sludge suspension, an environment is created which helps facilitate the coagulation and eventual flocculation of suspended solids. This is done by the polymer neutralizing the surface charge, or zeta potential, of the sludge particles. By reducing the net negative charge of the suspended solids, the net repulsive force between particles is reduced, leading to the coagulation of particles.

Among the vast choice of polymers, various monomer groups can be found. Two general categories of polymers exist for application in wastewater sludge, these being Mannich polymers

and copolymers. Mannich polymers are titled as such due to the Mannich reaction that takes place to generate them. This refers to the addition of formaldehyde and dimethylamine to polyacrylamide (Dentel, 2001). This is necessary because the polymers used for sludge residuals treatment are typically made of the acrylamide monomer, which is used to generate various derivatives of polyacrylamide. Nonetheless, both the acrylamide monomer and its polymer form do not contain an ionic charge. Two methods are used to add the desired charge. First, after the polymer is generated, functional groups are added to create the desired charge (i.e. Mannich polymers); the second method is by joining the acrylamide monomer with other positively charged monomers, thus creating a net positive polymer – this refers to copolymers (Dentel, 2001).

An example of a Mannich polymer is seen in the figure below.

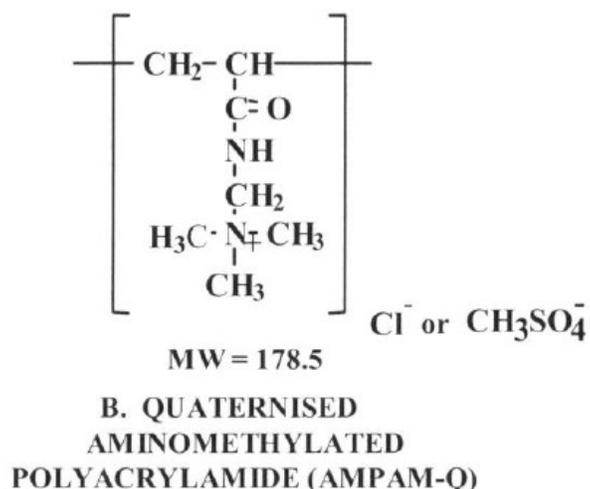


Figure 1. Example of a Mannich monomer unit (Dentel, 2001).

The positive charge for the Mannich polymer above is contributed at the amine site. The polymers generated from Mannich reactions are generally in liquid form, and they require simple

equipment, permitting easy transport and dilution; however, one disadvantage is the relatively low stability of 3 months (Floerger, 2002).

In contrast to Mannich polymers, copolymers are formed by combining various forms of polyacrylamide through the process of copolymerisation. The variations in polymers are used to attain the desired characteristics (whether structurally, or chemically). For example, alteration of a methyl group to an ethyl group would lead to a different level of hydrophobicity, which could impact polymer performance (Dentel, 2001). Copolymers can contain variations in the number of cross-links, molecular weight, and composition, all of which are utilized to achieve a desired effect (Cheremisinoff, 1997). The appropriate combination of monomers can even lead to an enhancement of the polymerisation reaction, generating a product with greater molecular weight, which would be beneficial for wastewater sludge applications (Dentel, 2001). The copolymer ratios can also vary depending on the combination; for example, ratios of copolymers can range from 80:20 to 45:55 (by molecular weight) for acrylamide and acryloyloxyethyltrimethyl ammonium chloride (AETAC) (Dentel, 2001). When compared to Mannich polymers, the use of copolymers allows for additional parameter control for the purpose of achieving subtle variations in the polymer. As opposed to adding functional groups post-polymerization, the desired chemical/physical characteristics are predetermined and the product needs less intervention post-polymerization.

Another important control with regards to the structure of the polymers is the number of cross-linking branches between monomer units. Initially, polymers were primarily linear macromolecules, however, advances in the field have generated the likes of branched polymers and cross-linked polymers. The image below demonstrates the physical differences between the three types of polymer structures.

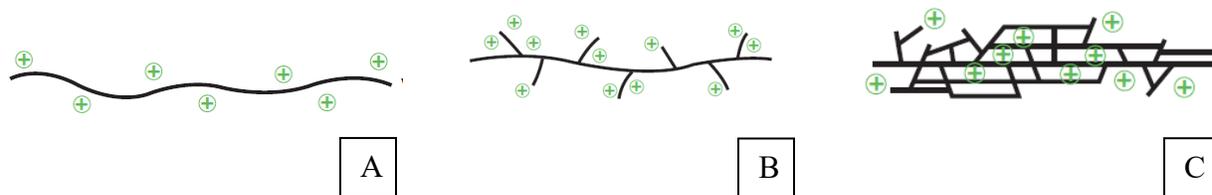


Figure 2. Structural diagram of a linear polymer (A), branched polymer (B), and cross-linked polymer (C) (Floerger, 2002).

The choice of structure depends on the intended applications, as these variations possess advantages and drawbacks. For example, linear polymers require less dosage but have a low floc strength; whereas, cross-linked polymers generate relatively stronger floc strength, but require a higher dosage (Floerger, 2002). For the purpose of wastewater sludge treatment, a strong floc strength is essential as the size of suspended solids and the shear forces that the flocs experience is much greater when compared to drinking water treatment; thus, cross-linked polymers are preferred.

Regardless of structure, an important consideration for all cationic polymers is their behaviour at high pH levels. It is well reported that hydrolysis takes place in high pH environments, which leads to dissociation of the hydrogen proton, decreasing the cationic charge of the polymer (Floerger, 2002). As previously mentioned, the efficacy of polymer conditioning is based on the neutralization of the zeta potential of suspended solids, and if the polymer loses the ionic charge necessary to achieve this, greater polymer consumption results, which leads to the undesired effect of higher cost expenditure. The hydrolysis that takes place can be visualized with the diagram below.

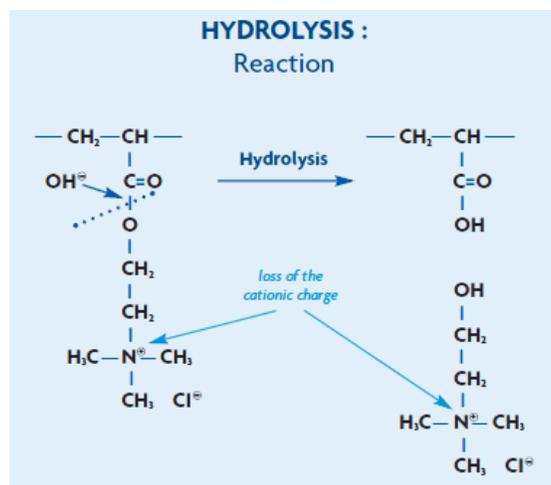


Figure 3. Hydrolysis of polymer which takes place at high pH due to the hydroxyl group (Floerger, 2002).

This problem can be overcome by the addition of methyl chloride or dimethyl sulfate, which substitutes a methyl group in place of the hydrogen proton, resulting in a product that maintains its positive charge at all pH levels (Dentel, 2001).

To describe their physical state, polymers used for coagulation and flocculation are categorized as liquids, emulsions, or dry beads. As previously mentioned, liquid polymers are generally the result of Mannich reactions. They are truly aqueous liquids, which permits easy pumping when the viscosity is limited to relatively low concentrations. Pumping becomes increasingly difficult with higher concentrations (i.e. viscosities), therefore, there is a limit to the polymer concentration that can be used. Emulsion polymers are also considered liquids, however, they are not in an aqueous state, and instead, they are immersed alongside the water particles, similar to common daily emulsions such as milk. The advantage of using emulsions is that higher concentrations of polymer can be used, while still maintaining a low solution viscosity, when compared to liquid polymers of the same concentration (Dentel, 2001). Dry polymers contain the

most active product and provide substantial economic savings during transportation. Because of this, they tend to be favoured by relatively larger wastewater sludge treatment plants. However, this leads to the need for developing an appropriate preparation methodology for the treatment plants upon reception of the dry polymer, as they need to be immersed in water for the chains to uncoil and function as intended. This principle was one of the main considerations for pursuing research in the polymer maturation and activation process.

One of the practical means to compare different polymers is the optimum dosage, which refers to the quantity of polymer necessary – for a specific sludge matrix – to maximize dewatering. The process requires dosing a given mass of sludge with various quantities of polymer, and using current sludge treatment analytical techniques such as Capillary Suction time (CST) or Filtration Test, to establish the dose that results in the best dewatering. In doing so, different polymers can be compared amongst each other by establishing how the optimum dose of a specific polymer with a given sludge matrix, compares to the optimum dose of another polymer with the same sludge matrix. Naturally the polymer that achieves the best dewatering with the same quantity of polymer consumed, will be the ideal choice, assuming equal cost. With the bulk of literature focusing on this one parameter, however, few studies have investigated the impact of polymer maturation period on its efficacy. The maturation period refers to the aging undertaken by the polymer after it has been produced. Part of the research undertaken was aimed at measuring the evolution of the aging process and using this data to understand when the polymer is ready for application in the treatment plant, for the ultimate goal of maximizing the dewatering quality.

Polymers can be purchased in crystalline or liquid form; however, to save on volume during transportation and thus reduce operational costs, they are often bought in bulk in crystalline form by larger treatment plants. Therefore, they must then be appropriately prepared upon reception

by the plant, leading to the question of how can polymer quality be assessed after it has matured in water? An appropriate answer to this question is essential for the purpose of maximizing the dewatering that is achieved. Two current solutions have been explored, which include the use of electrical conductivity and dynamic viscosity of polymer after preparation. These two methods will be compared to our own methodology of using the UV-vis absorbance data measured for the polymer.

2.4.1 Polymer maturation detection via electrical conductivity and viscosity

Immersing polymer crystals into water wets the beads, leading to swelling of polymer chains, and commencing the polymer activation process. The polymer activation that takes place is crucial because the result of good polymer expansion maximizes surface area of exposure, resulting in more sites to facilitate the coagulation and flocculation process. Nonetheless, despite the importance of the maturation stage, the literature that exists to describe this process is very limited and generally comes from industry. Many systems for polymer preparation are described by manufacturers, which typically consist of tanks connected in series with mixers to agitate the polymer expansion (Montan, 2017). It is widely understood that appropriate mixing is required to maximize polymer activation and that over mixing has adverse effects (Owen, et al., 2002). Despite understanding the influence that some environmental conditions have on the polymer quality, there is a lack of understanding regarding the process that takes place after agitation occurs. The factors that may impact the polymer maturation process can be associated with microbial attack, radical attack from residual catalyst, disentanglement, or conformational changes (Owen, et al., 2007). Currently, the age, or maturity of a polymer is often determined with the measurement of dynamic viscosity or conductivity of the polymer after preparation, although studies have shown that flocculant viscosity does not necessarily correlate to flocculant

activity (Owen, et al., 2007). Regarding conductivity, the measurements taken from a polymer solution after preparation are expected to reach an equilibrium maximum over a certain time period, achieving steady-state conditions (Canada Patent No. US 2013/0024132 A1, 2013).

Nonetheless, there is no consensus within the scientific community regarding the time necessary for the polymer to reach its optimal maturation level, and thus the ideal time for application to sludge. Researchers have suggested values ranging from 24 hours (Novak & O'Brien, 1975) to several days (Owen, et al., 2002).

2.5 Rheology and its applications

Rheology describes the deformation and flow of matter (Chhabra & Richardson, 2008) and is often used to analyze the behaviour of non-Newtonian fluids. These are fluids that do not uphold Newton's linear elastic assumptions stating that shear stress is linearly related to the shear rate exposed to a fluid element (Chhabra & Richardson, 2008). Because sludge slurries are considered non-Newtonian fluids, rheological analysis through the use of rheometers has been suggested as a means of understanding fluid behaviour and linking it to parameters related to enhancing sludge treatment quality. Additionally, when sludge slurries are dosed with polymer during the treatment process, the newly developed system exhibits a change in fluid behaviour. Rheology can be a means to quantifiably measure the level of shear being subjected to the sludge system before and after polymer dosage. These studies can be used to understand the different levels of shear that various dewatering devices (i.e. belt filter press, centrifuge) cause, and the dewatering that results.

2.5.1 Parameters used for rheological measurements

The shear rate, or velocity gradient G , is a parameter often reported with rheological measurements. It refers to the change in velocity of a fluid with respect to distance from the encapsulating wall of a container or channel (units of reciprocal seconds are commonly used).

This term originates from Newton's equation for shear stress on a fluid element:

$$\tau = \mu \frac{dv}{dl}$$

Here, dv/dl represents the shear rate G , and describes the differential change in velocity with respect to a differential position from a no-slip surface; μ represents the dynamic viscosity.

Other parameters of interest when discussing sludge rheology include the yield stress and viscosity (Hammadi, et al., 2013). Yield stress refers to the point at which a fluid no longer exhibits a linear elastic response to stress. The dynamic viscosity gives indication towards the ease-of-flow of a fluid. A higher viscosity is indicative of thicker liquids such as honey.

2.5.2 Instruments used for rheological measurements

The instrumentation used for conducting rheological measurements are typically categorized as rotational or capillary rheometers. Both of these devices are discussed in detail below.

2.5.2.1 Capillary Rheometer

The capillary rheometer induces a pressure gradient on the sludge sample, resulting in laminar flow of the sample within a capillary tube of a known length and diameter (Eshtiaghi, et al., 2013). An analysis of these rheometers was completed by (Ratkovich, et al., 2013) and it was concluded that the advantages of capillary rheometers include the relative simplicity, cheap cost, and the control to induce various high levels of shear to the sludge sample. Disadvantages of

these types of rheometers include the inability to measure the time-dependent effects on sludge and the necessity for large sample volumes. There is also higher maintenance concerning capillary rheometers as there is a greater potential for clogging due to the nature of having a small capillary tube design, as purported by (Babbitt & Caldwell, 1939). The capillary rheometer has been used in studies to determine correlations between rheological properties to sludge solids concentration, and also for the characterization of different types of sludge – such as anaerobically digested or thickened sludge (Eshtiaghi, et al., 2013). It has also been used to monitor the effect of temperature and solids concentration on their potential impact on sludge strength (Eshtiaghi, et al., 2013).

Despite the volume of literature that has accumulated as a result of the capillary rheometer, doubts have been raised regarding the capability to scale up these results for industrial application. For example, one concern regarding capillary rheometers claims that stratified bed flow may be ignored in a tubular viscometer, however, this is typically not the case during industrial tubular channel flow (Eshtiaghi, et al., 2013). As a result, it is uncertain whether the rheological data can be used for large-scale process design and control.

2.5.2.2 Rotational Rheometer

One of the main advantages rotational rheometers pose over the capillary counterpart is the ability to measure thixotropic effects on sludge. Thixotropic behaviour refers to the time-dependent nature of sludge. It implies that sludge viscosity decreases over time as it is exposed to shear or flow; however, this impact is reversible when the shear is removed from the system (Travnicek & Junga, 2014). As a result, a sample can be monitored for long periods of time to establish time-dependent variations on sludge behaviour. Rotational rheometers also require relatively less sample volume (when compared to the capillary rheometer), are widely

commercially available, and allow flexible control of the shear rate duration (Ratkovich, et al., 2013). Disadvantages include a generally greater cost, the sedimentation of particles can cause errors within the measurements, and centripetal forces can potentially lead to concentration gradients forming within the measurement gap (Ratkovich, et al., 2013).

It is well understood that rotational rheometers should ensure a base gap size that is at least 10 times larger than the smallest sludge particle (Eshtiaghi, et al., 2013). The gap size refers to the space separating the bottom of the rotating cylinder with the base of the sample container. This is necessary to ensure device sensitivity for detecting low viscosity suspensions.

The function of the rotational rheometer is such that the device measures torque and relates this to shear stress, and the angular velocity applied can be related to shear rate (Eshtiaghi, et al., 2013). Rotational rheometers have been used to monitor the rheological properties of sludge under various environmental conditions (i.e. temperature effects), and also during different stages of the sludge treatment process. Process applications of rotational rheometers have included characterizing anaerobically digested sludge exposed to enzymatic treatment, granular sludge in an up-flow anaerobic reactor, and even the pyrolysis liquid of sewage sludge (Eshtiaghi, et al., 2013). From the aforementioned, it can be seen that rotational rheometers have gained widespread application. For example, through rheological analysis of a membrane bioreactor (Chu, et al., 2007), were able to predict the optimum polymer dose, thus increasing process efficiency. In addition, there are examples where sludge rheological data has been used to develop computational models that have ultimately resulted in full-scale reactor design.

Through the use of on-site sludge characterization, rheological data has also been used to predict sludge residence times and even sedimentation within a secondary clarifier (Weiss, et al., 2007), with models often leading to accurate alignment when compared to empirical measurements.

Due to the vast array of different sludge types that can result from variations in population size, behaviour, sewage network age and quality, the application of rheological data can help capture these site-specific differences. By analyzing the sludge directly under consideration, design changes to enhance the system are likely to be more reliable as they are a direct result of the sludge to be treated.

2.5.3 Rheological characterization of polymers

Analyzing only polymer solutions, (Brown, et al., 2013) demonstrated that rheological measurements can be used to detect changes in oscillation frequency being exposed to a poly(acrylonitrile-*co*-methacrylic acid) polymer. The sensitivity of the rheological equipment also helped with detection of polymer concentration and age. Increasing the solution concentration and aging time led to more elastic behaviour of polymer. It is important to understand the rheological properties of purely polymer solutions so as to have a reference point when comparing polymer-sludge mixtures. Using the rheological data, degradation of the polymer could be determined when comparing the linear energy capacity of polymers aged for long periods of time. However, with regards to polymers used for sludge treatment, polymers are often prepared on a daily basis, thus the short-term aging impacts are of greater concern.

2.5.4 Current applications of rheology in industry

The principles of rheology are applied throughout various industrial processes. The applications extend to the domains of food, pharmaceuticals, and household personal care products. For example, with regards to personal care products such as shampoo, based on past experience, consumers have an expectation regarding shampoo consistency and how it should feel in their hands. As a result, rheological properties of the shampoo can be monitored during production so

as to ensure the final product achieves the parameters necessary for it to be deemed acceptable by the public (Young, 2011). Similarly, within the food industry, rheological characteristics of certain condiments such as ketchup or mustard can be monitored to ensure the appropriate consistency is reached that the consumer has come to expect. For example, if a consumer was in the process of adding ketchup to their fries, they would have a preconceived expectation of how the ketchup should look and feel (i.e. somewhere between water and honey). The use of rheology can help quantify these various physical states so as to consistently produce a product of a desired consistency and nature.

In sludge treatment, (Ruiz-Hernando, et al., 2014) used rheology as a parameter to monitor the effectiveness of various sludge pre-treatment methods. To enhance the biodegradability of waste activated sludge, rheology of the different samples was used as a criterion through assessment of the reduction in steady state viscosity. It provided a quick and simple way to compare the effectiveness of ultrasound, low-temperature thermal, and alkali pre-treatment.

In another study, (Farno, et al., 2015) were able to monitor and optimize the rate of COD solubilisation under various thermal conditions and solids concentrations, through the use of rheology. Their studies revealed a linear relationship between solubilised COD, yield stress and apparent viscosity. This could have important implications for large scale application in a treatment plant. For example, the progress of anaerobic digestion (which involves elevated temperatures) could be monitored through rheology by observing a decrease in yield stress or apparent viscosity, which would correlate with the COD solubilisation.

Another example of how rheology can be used to enhance a manufacturing process, comes from the production of wine gums. Rheology was used to monitor the gelation process occurring with a pectin-additive mixture (Young, 2011). Rheological data can be used to understand the time

during the production process that the wine gum is in a liquid state, thus permitting transport through the system. Also, the rheology can be used to identify when the primary gel formation is taking place, so as to design the process to permit settling and avoid agitation of the product during this relatively sensitive time period. Ultimately, detection of when these phase transformations were taking place was determined through the rheological measurements, and this data was reflected in the process design.

These types of system modifications based on rheological data reflect the types of applications that can be made to enhance sludge treatment systems. From the examples listed above, it is evident that a better understanding of the rheological properties of solutions can be applied for process enhancement in various industries. Sludge residuals treatment is another domain within which the rheology of the fluid can be used for enhancing system design and ultimately the biosolids product that is generated.

2.5.5 Real-time rheological measurements

The potential benefits of using rheology to quantitatively describe sludge and/or polymer mixtures becomes even more appealing when considering the potential to do so with in-line measurements, meaning that measurements can be made on a real-time basis. This allows greater flexibility for operators to make quicker decisions in an industrial setting as adjustments to alter system processes can be made based on information of the current sludge network, as opposed to making decisions based on samples taken from a previous day, whose properties may no longer reflect the current status of the sludge being processed. It should be noted, however, that although studies indicate that there is reasonable agreement between rheological measurements taken in-line and off-line, there are certain instances when there may be deviations between the two (Mazzanti, et al., 2016). For example, (Mazzanti, et al., 2016), found that when analyzing a

polymer polypropylene composite containing various weight percentages of white fir fibers, the in-line and off-line rheological measurements were very close at 30% wt. wood fibers and began to show greater deviation at 70% wt. wood fibers.

There are various benefits associated with in-line measurements compared to off-line measurements. In-line measurements are often less time-consuming and less expensive than off-line measurements (Pinheiro, et al., 2008). In addition, when taking samples off-line, separate sample preparation and quantification are often necessary, which results in potentially adverse alteration of the original state of the material substance to be measured (Pinheiro, et al., 2008). The use of in-line rheological techniques has been suggested in domains ranging from polymer analysis to characterization of food materials (Dogan, et al., 2005). There are also some rheometers in the market that have both lab-scale and full-scale models, such as the Floccky (Koei Industries, Japan) rheometer that was used in this research.

2.6 Spectrophotometry and its applications

Spectrophotometry can be used to establish the presence of chemicals by inducing them to electromagnetic frequencies and measuring the resulting absorbance at particular wavelengths. The use of spectrophotometry has become prevalent in the fields of biology, organic chemistry and medicine. For example, predicting reaction mechanisms that govern biological processes is often done through spectrophotometry as it permits analysis without damage to the cellular membranes (Schmid, 2001). With regards to engineering applications, the use of this technology has been suggested for identification of components within a mixture. For example, determining the presence of organic compounds within mining sludge mixtures is done through gas chromatography and liquid chromatography (Jourdan, et al., 2003). As an alternative, UV-vis spectrophotometry has been suggested as a simple means to determine the presence of organic

compounds within a sludge mixture. Although results from this study indicated that the method of estimating concentration through absorbance spectrophotometry generated a slight underestimation, the predictions of concentration of organic matter within the sludge were in reasonable agreement with the more widely used gravimetric method of analysis (Jourdan, et al., 2003).

Another example of the engineering application of UV-vis spectrophotometry is the detection of cadmium in domestic sewage sludge through UV-vis spectrophotometry at a wavelength of 396 nm (Podgaiskyte & Vaitiekunas, 2009). Concentration of the residual cadmium found within the biosolids generated from municipal sewage is important as this can lead to limitations of the potential land application that is permissible for the treated compost.

In the pharmaceutical industry, use of spectrophotometry has also been proposed in the determination of Diclofenac (DFC), an organic compound, within various matrices (Pebdani, et al., 2015). The shortcomings of spectrophotometry in terms of selectivity, were overcome by a separation and pre-concentration step prior to analysis.

The potential applications of UV-vis spectrophotometry can be used to detect the presence of polymer within a sludge slurry after dosage and dewatering in the treatment process. Analysis in the UV-vis range has demonstrated the capability of detecting the presence of polymer in mixtures, for example, absorbance at a wavelength of 292 nm indicates quantification of styrene in polystyrene (Stuart, 2008). Additionally, acrylamide copolymer concentrations in fiber suspensions and titanium dioxide dispersions have been measured using UV spectroscopy (Howard, et al., 1977). Although spectrophotometry can be used to detect the presence of polymers, the research that was completed herein aimed to go a level deeper and use UV-vis absorbance measurements not simply for detection but also for monitoring the evolution of the

polymer maturation process and changes in residual polymer concentration during shear application.

The accurate analysis and quantification of polymer being released into the receiving environment is important as polymers can exhibit negative health and environmental side-effects. Polyacrylamide, for example, has been shown to behave as a carcinogen and also cause neurotoxic problems (Daughton, 1988). Therefore, optimization of polymer dose during sludge treatment would not only help to reduce the operational costs but also reduce the harmful impacts of polymer to the environment.

3 Materials and Methods

3.1 Monitoring and Optimizing Polymer Maturation

The polyacrylamide crystalline polymer was prepared under various environmental conditions to test whether these changes could be detected with absorbance spectrophotometry. Polymers were prepared by changing ambient temperature, pH, chlorine content of water, and mixing conditions. Stock polymer was then diluted to a concentration that would generate absorbance measurements within the measureable range of the spectrophotometer. After polymer preparation was complete, periodic absorbance measurements were taken. Three replicates were used for the absorbance measurement at each time point.

Maturation was also evaluated with the techniques of electrical conductivity and viscosity. Fresh stock polymer was prepared for each test and the electrical conductivity and viscosity were measured at periodic time increments after preparation. Viscosity was measured once at three different RPM intensities. Electrical conductivity was measured once.

After comparison of the different maturation analysis techniques, anaerobically digested sludge was collected and the optimum dose was established using the Capillary Suction Time (CST) and volumetric filtration. Three replicates were used for determination of the optimum dose.

Next, sludge was dosed with polymer at the optimum dose, however, at different polymer age and dewatering analysis was subsequently completed with CST and volumetric filtration. Three replicates were used for these tests.

3.1.1 Polymer

All tests were completed with the use of Zetag 8160 (BASF) polymer; characterized as polyacrylamide, medium-high cationic charge, high molecular weight, and granular form.

3.1.2 Preparation of Stock Polymer

Stock polymer solutions were prepared daily at concentrations of 0.01% (by wt.), 0.2%, and 0.35%. The 0.2% solution was prepared by the addition of 1.0 g of Zetag 8160 crystals to 500 mL of deionized water (measured with a volumetric flask). Polymer mass was measured with the Sartorius BP221S (Fisher Scientific) balance (precision up to 4 decimal places). The solution was mixed initially at 220 RPM for 5 minutes, and 125 RPM for the next 55 minutes, using a mixing paddle submerged to the middle of the solution. All concentrations of stock polymer were prepared following the same protocol.

3.1.3 Dilution

Dilution of the 0.2% stock solution was completed by the addition of 3.75 mL of stock solution to a volumetric flask of 500 mL, the balance being completed by distilled water. A concentration

of 15 mg/L was chosen based on preliminary testing, as the absorbance at this level led to absorbance being measured within the detectable range of the UV-vis spectrophotometer.

3.1.4 Sludge Sample Analysis

Anaerobically Digested Sludge (ADS) was collected from ROPEC in Ottawa, Canada. The sludge consists of a mixture of primary and secondary sludge, digested under mesophilic temperatures. Samples were stored in a refrigerated environment of 4°C until the day of intended use. The Standard Methods for Examination of Water and Wastewater (21st Edition) was used to determine the total solids present within the sludge.

3.1.5 Evaluation of Optimum Polymer Dose

To determine optimum polymer dose of the ADS, various polymer concentrations were spiked into 500 mL beakers 200 mL sludge samples. Polymer doses were chosen so as to encompass both the under-dose and the over-dose region of the ADS. A jar tester apparatus (PB-700 Jar tester, Phipps & Bird Inc., USA) was used to complete mixing at 200 RPM for 120 s after spiking (jar-tester seen below).



Figure 4. Jar tester mixing apparatus used for testing the optimum dose of sludge (Supply, 2017).

After completion of mixing, each beaker had triplicate samples taken to measure the resulting CST and filtrate volume. This process was repeated for each new collection of ADS. Fresh ADS was collected as necessary and samples older than 7 days after collection were not used.

3.1.6 Capillary suction time (CST) test

The Capillary Suction Time (CST) test was used to measure the quality of sludge dewatering after polymer conditioning. A standard volume of conditioned sludge is placed within a small column on top of absorptive paper. Water separated from the flocs absorbs onto the paper and CST is a measure of the time it takes for the water to travel between two sensors of a known distance. A shorter CST time indicates higher quality filtration. The CST apparatus used for testing is seen below.



Figure 5. CST device used for testing the quality of dewatering (Geneq, 2017). The sample of dewatered sludge is placed in a cylindrical column within the center hole of the transparent rectangular section.

The equipment was manufactured by Triton Electronics Ltd., England (Type 319 Multi-CST) was used with CST paper (No. 17 chromatography grade paper cut into 7- × 9- cm, Whatman

PLC), and the protocol outlined in the Standard Methods for Examination of Water and Wastewater (21st Edition) was followed.

3.1.7 Filtration test

Conditioned sludge samples of 200 mL were filtered for 3 minutes using 55 mm-diameter coarse filters (Fisher Scientific Ltd.) and a vacuum pump. Filtrate volume and total solids concentration of the cake remaining on the filter were measured after filtration. Total solids concentration of the cake was determined following the protocol in the Standard Methods for Examination of Water and Wastewater (21st Edition).

3.1.8 Conductivity Measurements

A VWR Bench/Portable Conductivity Meter was used to measure the conductivity of stock polymer solution after preparation. The conductivity meter was calibrated with the standard solutions provided by the manufacturer. A photograph of the conductivity meter is seen below.

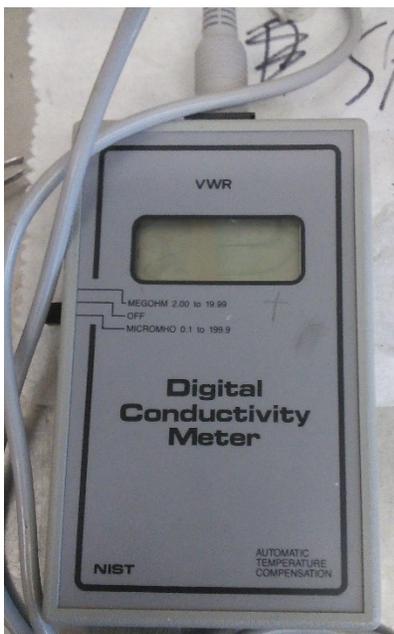


Figure 6. Photograph of the VWR conductivity meter used during experimentation.

3.1.9 Viscosity Measurements

Brookfield LV torque viscometer with Spindle LV-2 (62) was used to measure viscosity. A torque of greater than 10% was achieved, as specified by the manufacturer, in order to have valid results. The viscosity of polymer stock solution was periodically measured after preparation. A photograph of the viscometer is seen below.



Figure 7. Photograph of the Brookfield viscometer used during experimentation.

3.1.10 Absorbance Measurements

With the use of a Cary 100 UV-Vis spectrophotometer (Varian), the absorbance of samples was measured within the range of (190-275) nm using a quartz cuvette. This range was chosen because wavelengths greater than 275 nm yielded no observable changes with regards to absorbance, and 190 nm is where the absorbance peak had been determined by previous research

(Momani & Ormeci, 2014). Absorbance measurements were performed in triplicate. The spectrophotometer used for testing is seen in the image below.



Figure 8. Cary 100 UV-Vis spectrophotometer (Varian) used for measuring absorbance of polymer samples (evisa, 2017).

Samples were placed in a quartz cuvette and analyzed in the spectrophotometer (seen in the above image on the left) and absorbance data was generated with the complimentary software on a desktop computer (seen in the above image on the right).

3.1.11 Measuring the Influence of Temperature

Water to be used for preparation of both stock polymer solution and diluted samples were kept in refrigerators where the temperature was monitored with a red liquid thermometer. The temperatures of 4°C, 10°C, and 23°C (room temperature) were tested, with the water stored at each respective temperature for 24 hours prior to polymer preparation. After preparation of the

diluted samples, the samples were maintained within their respective controlled temperature environments for the full duration of the periodic absorbance measurements.

3.1.12 Measuring the Influence of pH

The pH of the DI water used for polymer preparation was manipulated by creating a buffer solution with Monopotassium Dihydrogen Phosphate (i.e. acid) and Dipotassium Hydrogen Phosphate (i.e. conjugate base).

A 0.05 M solution of the conjugate pair was formed, and with the use of the Henderson-Hasselbach Equation, the respective mass of each component was calculated (see table below).

Table 1. Measurements of pH for DI water used for stock polymer preparation with the use of Monopotassium Dihydrogen Phosphate (KH_2PO_4) and Dipotassium Hydrogen Phosphate (K_2HPO_4).

pH Desired	pH Measured	Mass of KH_2PO_4 (g)	Mass of K_2HPO_4 (g)
5	4.84	3.38	0.0262
6	5.69	3.20	0.261
7	6.74	2.10	1.66
8	8.12	0.197	4.10

The pH of the solutions were confirmed with the use of a Fisher Scientific pH probe.

3.1.13 Measuring the Influence of Chlorine

To observe the impact chlorine may have on polymer maturation, various concentrations of sodium hypochlorite (NaClO) were dosed into the DI water used for polymer preparation. The

NaClO was obtained from a 10.3% stock solution (Lavo Brand). Refer to table 2 below for the various concentrations of chlorine derived and the amount of NaClO added.

Table 2. Volume of NaClO added to 500 mL DI water to generate desired chlorine concentration

[Cl] (mg/L)	Volume of NaClO added (μL)
1	10.2
2	20.4
3	30.6
4	40.8

3.2 Observing the Effect of Shear on ADS dewaterability

The Floccy torque rheometer was used for analysis of the influence of shear on the dewaterability of conditioned sludge. The rheometer was first used to test its capacity to measure the optimum polymer dose. To do this, the 1-Step and 3-Step Floccy cycles were used. As the Floccy rheometer has previously shown the capability to measure the optimum polymer dose range, and this test was a means of corroborating this information, the tests were run once. Prior to running these tests, the optimum polymer dose had been determined by completing CST and filtration volume analysis on the ADS. Three replicate samples were used for the CST and filtration volume tests to determine the optimum polymer dose.

Next, using the 3-Step Floccy cycle by altering the third step, different combinations of shear intensity and duration were exposed to conditioned sludge and the resulting dewaterability was measured with CST. The CST measurements were made with three replicates.

A vacuum filter was then used for dewatering the sludge and collecting the filtrate. The filtrate was diluted with a 100X dilution, and the absorbance was measured with the Cary 100

spectrophotometer to assess the presence of residual polymer. The absorbance measurements were made with three replicates.

3.2.1 Sample Analysis

ADS sample analysis and determination of optimum polymer dose was completed with the same methodology as outlined above. Collection and storage was also completed as outlined above.

3.2.2 Floccky Mixing Cycle (1-Step)

A torque rheometer (Floccky tester, Koei Industries, Japan) was used for rheological analysis of the ADS and polymer mixtures. The benefits of using this instrument are its capacity to showcase the time-dependent influence of shear on sludge network strength, and that sample analysis is relatively quick and easy. The instrument displays the strength of flocs by periodic measurements (every second) of the torque exhibited on the mixture. A photograph of the rheometer is seen below.

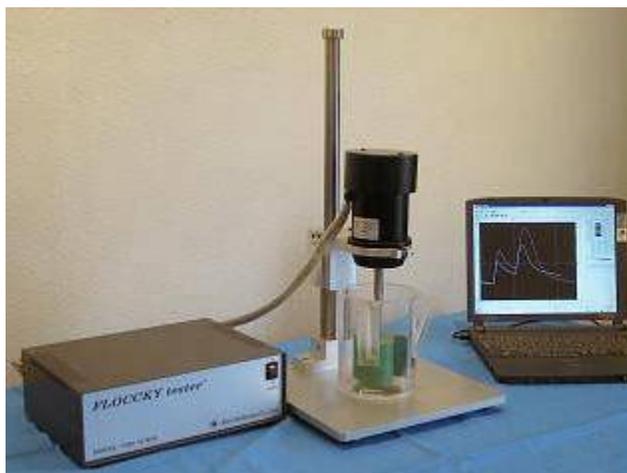


Figure 9. Floccky torque rheometer used for applying shear to conditioned sludge and measuring the resulting torque of the suspension (Researchgate, 2017).

To assess the impact of shear on floc strength, 200 mL ADS samples were initially collected in 500 mL beakers. A PB-700 Jar tester (Phipps & Bird Inc., USA) containing paddle mixers was used to initially mix the polymer into the ADS matrix, after which the mixing intensity was increased to add higher levels of shear to the conditioned ADS. The paddles of the mixer were submerged to the center of the ADS sample, after which a predetermined quantity of polymer was spiked into the ADS. The mixer operated at a low intensity of 100 RPM for 80 s, for the purpose of evenly dispersing the polymer within the sludge mixture to permit formation of flocs. After the initial gradual mixing, the intensity of the paddle mixer was increased to 200 RPM and the mixture was sheared for the desired duration (i.e. 0 s, 15 s, 30 s, 45 s, 60 s, 120 s, 180 s). The samples were then transferred into another container specifically designed for use with the Floccy tester. The Floccy torque rheometer was operated for 120 s at 300 RPM. Triplicate samples were used for each mixing duration.

The totalized torque was calculated as the area under the torque vs. time curve generated by the Floccy rheometer for the entire duration of the Floccy cycle (i.e. 120 s). Peak torque was the maximum torque measured during the 120 s of the Floccy cycle.

It is noted that the polymer used for these tests was prepared according to the same methodology outlined above.

3.2.3 Influence of Polymer volume on the Torque Response (1-Step Floccy Cycle)

To analyze the affect that polymer volume has on the first peak generated by the Floccy torque rheometer, various volumes of polymer were dosed into 200 mL ADS samples, stored in 500 mL beakers. The volumes were chosen based around the optimum dose, previously determined.

Volumes of (8, 8.5, 9, 9.25, 9.5, and 10) mL were spiked into the beakers, after which the

polymer was mixed in the jar-tester apparatus at 100 RPM for 80 s. Once mixing in the jar-tester apparatus was finished, the contents of the beaker were transferred into the container designed to fit the Floccy instrument. A 1-step Floccy cycle at 300 RPM was run for 120 s. The peaks detected were the maximum torque values measured by the rheometer within the entire 120 s duration of the Floccy cycle.

3.2.4 Floccy Mixing Cycle (3-Step)

To monitor the influence that polymer spiked into the ADS mixture has on the torque strength, right at the moment of mixture, a 3-step Floccy cycle was employed. Samples of 200 mL ADS were collected into the container designed for the Floccy torque rheometer. The container designed by Koei Industries contains two injection ports on the side, which permit the easy addition of polymer while mixing is taking place.

The 200 mL ADS samples were initially mixed at 420 RPM for 10 s for the purpose of achieving a homogeneously dispersed sludge mixture. The Floccy rotational intensity was then reduced to 300 RPM for a total of 160 s. The desired quantity of polymer was spiked into the sludge mixture 40 s after the mixing intensity was reduced (i.e. 50 s after the start of the test).

3.2.5 Floccy Mixing Cycle – Assessing Instrument Sensitivity (3-Step)

Samples of 200 mL ADS were collected into the container designed for the Floccy torque rheometer

The 200 mL ADS samples were initially mixed at 420 RPM for 10 s for the purpose of achieving a homogeneously dispersed sludge mixture. The Floccy rotational intensity was then reduced to 300 RPM for 40 s. At the 50 s mark, the Floccy rotational intensity was reduced while polymer at the optimum dose (for all trials) was simultaneously injected. The intensities of (100, 150,

200, 250) RPM were tested. The purpose of this test was to assess the sensitivity of the Floccky instrument to be able to visualize an equivalent volume of polymer addition.

3.2.6 Capillary Suction Time (CST)

After the conditioned samples were sheared in the Floccky torque rheometer, the resulting CST was measured with the same methodology outlined above. Triplicates were used for CST measurements.

3.2.7 Calculation of Shear Rate (G) and Unitless Gt

The shear rate, G , was calculated with the following formula as suggested by (Wang & Dentel, 2011):

$$G = \left[\frac{P}{\mu V} \right]^{1/2}$$

Where μ represents the power output of the torque rheometer (N·m), μ is the dynamic viscosity (Pa·s), V is the suspension volume (m³). The power output of the rheometer can be further represented by the following expression:

$$P = 2\pi NT$$

Where N represents the rotational intensity of the rheometer (revolutions/s), and T represents the torque measured by the rheometer (N·m).

3.2.8 Evaluation of Torque Area and Peak Torque

The area under the torque vs. time curve generated by the rheometer (also known as totalized torque, TTQ) was calculated by taking the sum of all torque values measured throughout the

duration of shear addition. The Floccky rheometer was set to measure the torque (in units of mN·m) periodically, every second.

3.2.9 Absorbance Measurements

After completion of CST, the remaining conditioned ADS samples were filtered through a vacuum filter for the purpose of collecting liquid filtrate. The filtrate was diluted with a dilution factor of 100 using distilled water. This was done to ensure the corresponding absorbance measurements would lie within the measurable range of the spectrophotometer.

4 Results & Discussion

This study had two major phases. The first phase was completed to attain a better understanding of the crystalline polymer maturation process. The second phase of the study focused on the influence of shear on the quality of ADS dewatering.

4.1 Monitoring and Optimizing Polymer maturation

4.1.1 Electrical Conductivity for Determination of Polymer Activation

Electrical conductivity is a measurement currently used to assess the maturation and activation of polymers used in sludge treatment. Figure 10 below shows the periodic conductivity measurements that were taken on 0.2% polyacrylamide polymer sample. The conductivity of the solution continued to steadily rise throughout the two days of monitoring. Polymer aging was monitored upon completion of mixing; thus, a polymer age of zero refers to the time at which mixing was completed. The relatively continuous rise is likely caused by unwinding polymer chains; as the chains begin to open, more branched sections are exposed and can participate in conducting electrons.

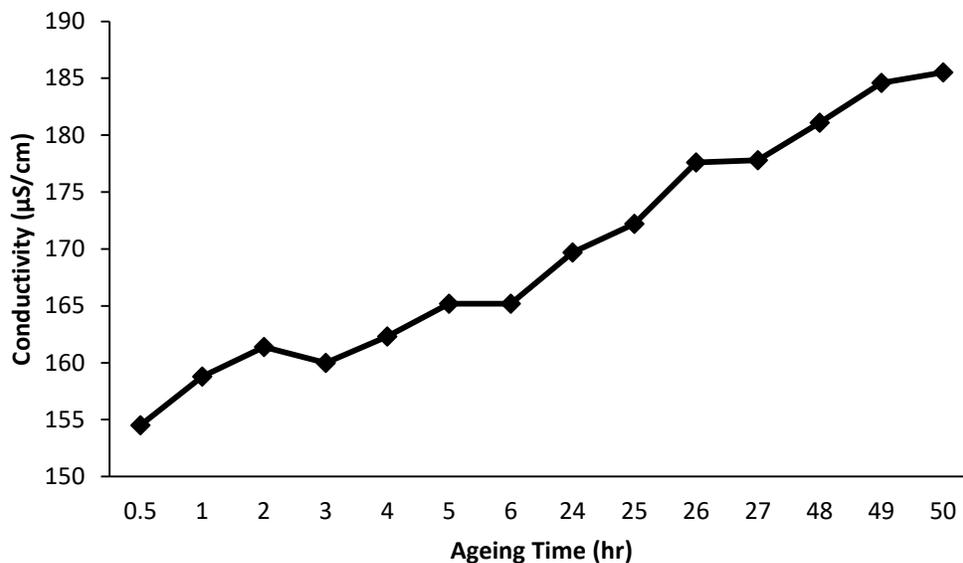


Figure 10. Periodic conductivity measurements of Zetag 8160 polyacrylamide polymer at 0.2% concentration. Time zero is the time at which polymer mixing was completed.

Measuring electrical conductivity is one of the currently used methods for determining polymer maturation in the market, and it is stated in a patent that activation is complete when conductivity reaches steady state (Canada Patent No. US 2013/0024132 A1, 2013). Research regarding electrical conductivity and polymers has primarily focused on determination of the ionic nature of solutions. Very limited data exists in peer-reviewed literature with regards to the use of conductivity measurements for determination of polyacrylamide maturation. It is well-known that increasing the polymer concentration would result in an increase in conductivity measurements. However, for a polymer solution at a given polymer concentration, our data indicates that conductivity measurements may not reach steady-state in two days, and may continue to increase due to the uncoiling of the polymer and continuous change in ionic nature.

4.1.2 Viscosity for Determination of Polymer Activation

Polymer viscosity is another currently used method for analyzing the polymer aging process.

Viscosity measurements carried out for 27 hours after the preparation of 0.2% polymer are seen in Figure 11 below. Multiple mixing speeds were chosen to assess how the viscosity would behave differently under various levels of shear intensity. Figure 11 shows that at a lower shear intensity (RPM), the viscometer had greater detection sensitivity. This is likely because at a higher RPM, the fluid experiences greater shear, and thus a larger vortex is created around the measuring probe. This would lead to a higher differential viscosity amongst adjacent particles and thus a greater drop in the viscosity measurements. In addition, at a higher shear intensity, polymer chains are more likely to rupture as they are exposed to greater stress. Breaking large polymer chains into smaller fragments would likely decrease the viscosity of the solution, as particles could flow past one another with greater ease due to less hindrance from bulky chains.

The same general trend was observed at all RPM levels: a slight drop in viscosity at the first hour, subsequent rise up to hour 5, followed by relatively constant readings until the end of measurements (27 hours after preparation). This is comparable to a study which tested four different polyacrylamide solutions, in which (Gardner, et al., 1978) were able to measure a rise in relative viscosity of the solution up to a maximum around 5-24 hours, followed by a slow subsequent decrease. Also, (Owen, et al., 2002) were able to measure stabilization of solution viscosity to a constant after 7 hr. It has been shown that after weeks, a large drop in the viscosity of polymer occurs (Bolto & Gregory, 2007). This is because a random coil occupies more volume than an equal quantity of monomer units; and as the polymer unwinds, it achieves a more uniform distribution (Bolto & Gregory, 2007).

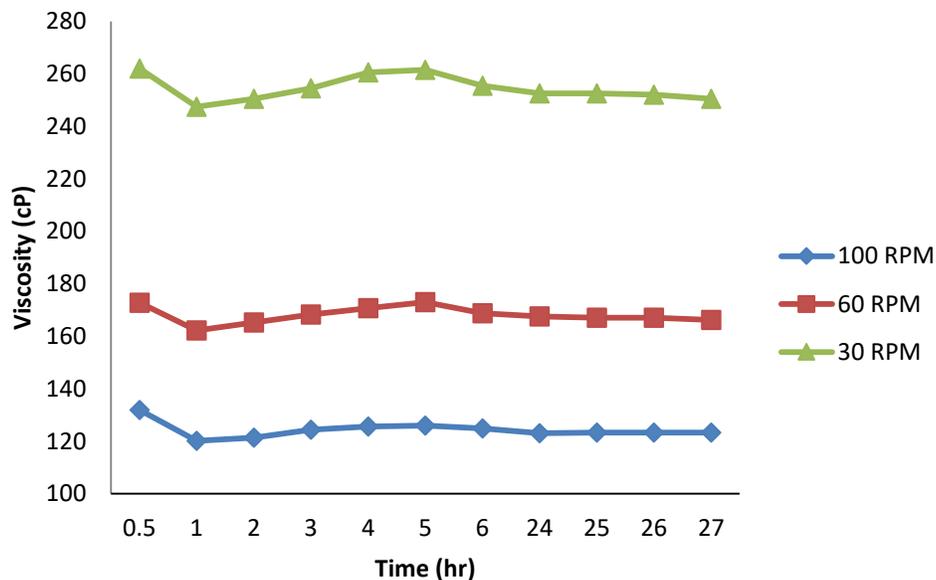


Figure 11. Periodic viscosity measurements over various rates of revolution for Zetag 8160 polymer at 0.2% concentration.

The initial drop captured by the viscosity measurements are likely indication of polymer uncoiling, as entangled molecules are considered to increase solution viscosity (Narkis & Rebhun, 1966). It is likely that the majority of uncoiling occurs at the initial stages after polymer preparation, as this is the time at which the most energy is added to initiate the uncoiling process. Our testing was completed on a cationic polymer, however, the ionic characteristics of the polymer would also likely influence the time at which ideal maturation is achieved. For example, using a non-ionic polyacrylamide polymer, (Owen, et al., 2002) were able to conclude that optimal ageing (as measured by flocculation) was achieved after 72 hr. Majority of studies related to the ageing of polymers have focused on changes over several weeks up to months, and more research needs to be completed for shorter time scales (i.e. around 24 hr), as polymer turnover is very quick in a treatment plant. Although the viscosity generated some indication of the polymer uncoiling, there was no clear trend to indicate what the optimum maturation time

would be. In addition, no correlations could be drawn between the results from the viscosity measurements and the electrical conductivity.

4.1.3 Uv-vis Absorbance for Determination of Polymer Maturation

4.1.3.1 Influence of Temperature

The ambient temperature of tap water and process water used for polymer preparation can drastically change throughout the seasons, especially for a country with harsh winters such as Canada; for this reason it was important to understand how temperature affects polymer maturation, and whether UV-vis absorbance measurements can capture these changes. Figure 12 shows the absorbance spectra at periodic time intervals for polymer prepared and stored under different environmental temperatures (23°C, 10°C, and 4°C). A 0.2% stock polymer concentration was prepared, then diluted to 15 mg/L to permit measurement within the tolerable absorbance range of the spectrophotometer. The results show that Zetag 8160, which is a polyacrylamide polymer, strongly absorbs light between (190-210) nm and there is no significant absorbance beyond 270 nm. It was previously reported that polyacrylamide polymers have their peak absorbance around (190-200) nm (Gibbons & Ormeci, 2013; Momani & Ormeci, 2014). Overall, an increase in absorbance measurements was observed with increasing maturation time after polymer preparation. Furthermore, it was also observed that a maxima (at about 201 nm) and a minima (at about 194 nm) gradually develop after a couple of hours (Figure 12-A). The formation of a maxima is likely caused by the unwinding polymer chains. As the polymer uncoils, more surface area becomes exposed, causing more absorbance of the incident light. When comparing this to the absorbance measurements of polymers prepared and stored at the lower temperatures of 10°C (B) and 4°C (C), two major differences are evident. The first is regarding the shape of the absorbance spectra, specifically the absence of the maxima and

minima. The second is regarding the degree of absorbance, as it is much lower at the wavelengths of 201 nm and 194 nm, where the maxima and minima had been observed at room temperature. It should be noted that the polymer prepared at 23°C exhibited a shift in terms of the wavelength at which the maxima and minima formed over time. For example, the measurements at 3, 4, 5, and 6 hours, displayed an absorbance shift towards 202 nm for the maxima. The absence of the maxima and minima for polymers maintained at lower ambient temperatures, suggests that uncoiling of the polymer crystals is being hindered by the lower thermodynamic nature of the colder ambient environment. This implies that the ambient environment that polymer samples were stored in, prevented the excitation of polymer electrons, hindering the formation of a maxima (previously observed at room temperature). This demonstrates the sensitivity of UV-vis absorbance analysis, and its capacity to detect temperature changes made to the polymer solution.

Similarly, the unfolding of proteins, an example of a biological polymer, as a function of temperature, has been demonstrated by observing the change in absorbance at (287-292) nm (Schmid, 2001). This provides support for the use of UV-vis spectrophotometry as a means to measure polymer maturation.

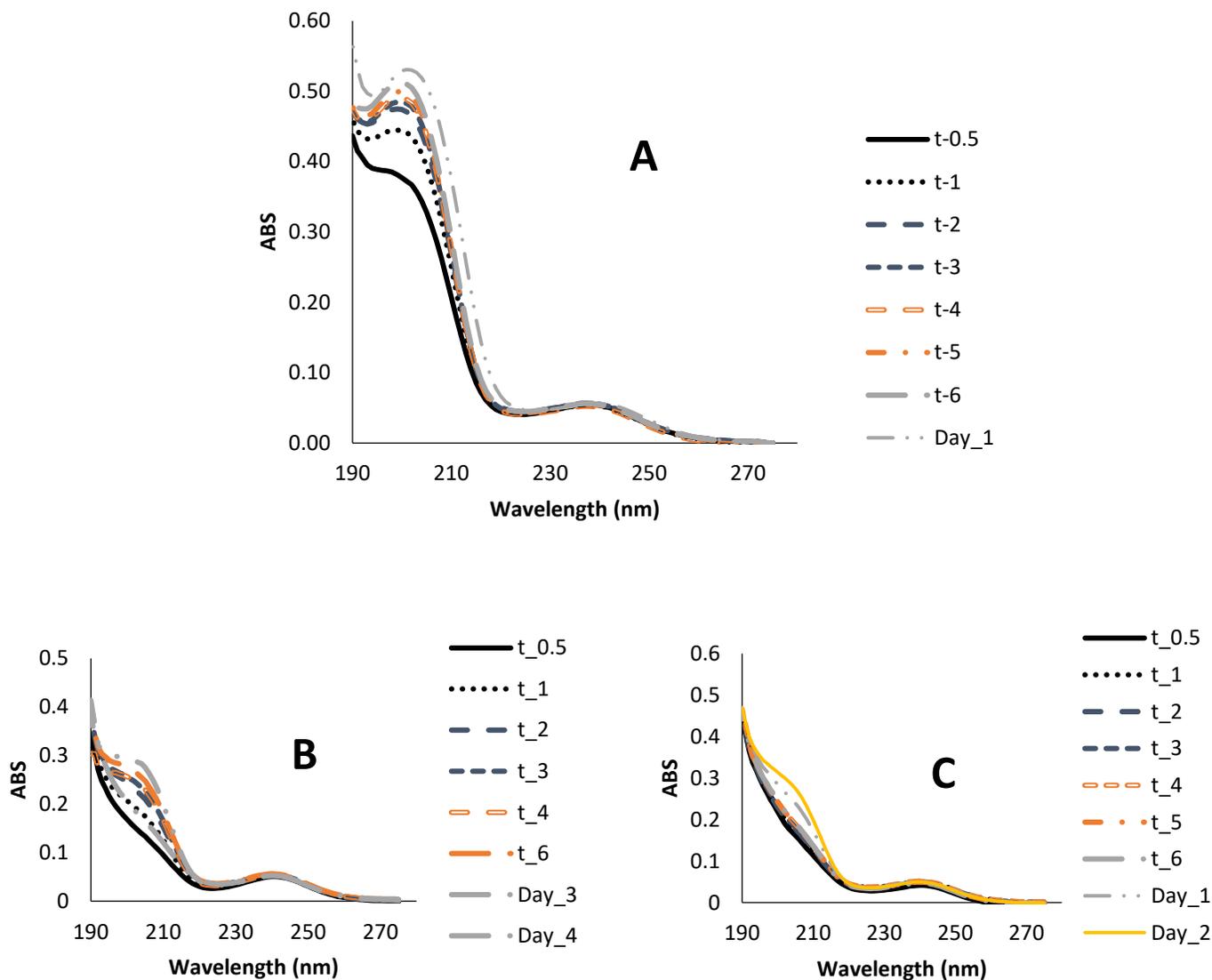


Figure 12. Polymer absorbance over several time periods for a Zetag 8160 polymer, prepared at 0.2% stock concentration, then diluted and aged at 15 mg/L. Day 1 refers to 24 hours after preparation. Ambient temperatures of A - 23°C, B - 10°C, and C - 4°C were used.

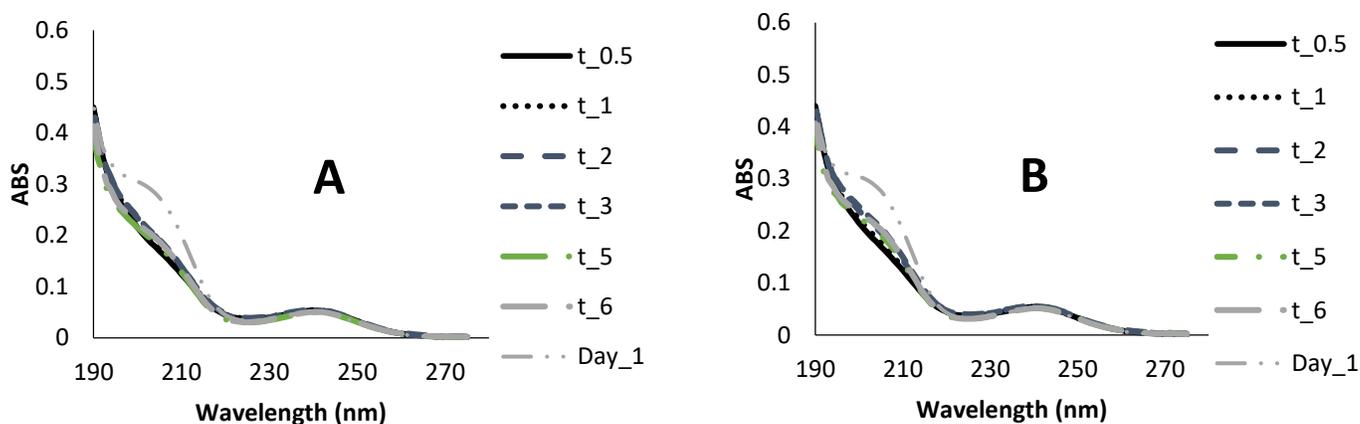
Figure 12-B shows that several days after polymer preparation, the absorbance never forms a maxima and additionally begins to drop in the wavelength range of (194-220) nm. Again, this is indication that the cold environment decreases the polymer molecules' capacity to absorb UV light, hindering their uncoiling and excitation of electrons. The peak observed around 201 nm

(Figure 12-A), was expected as it has been previously reported that polyacrylamide reaches a maximum absorbance in the range of (190-205) nm (Cheng, 2004). Variation with respect to the wavelength at which the absorbance peak is established is likely caused by the multitude of different functional groups and degree of cross-linking. Subsequent tests were all completed at the ambient room temperature of 23°C.

4.1.3.2 Influence of pH

The ambient pH of water can change based on the source of water that is used; for this reason, it was important to analyze the potential influence of pH on polymer maturation. Figure 13 below shows the absorbance measurements at periodic time intervals for polymer prepared at a stock 0.2% concentration, then diluted and aged at 15 mg/L for the duration of the experiment.

Polymer samples were stored at different water pH levels; these were pH of 5 (A), 6 (B), 7 (C), and 8 (D). Observing Figure 13 (A) and (B), the maxima and minima at 201 nm and 194 nm, respectively, did not develop, as previously seen in Figure 12-A.



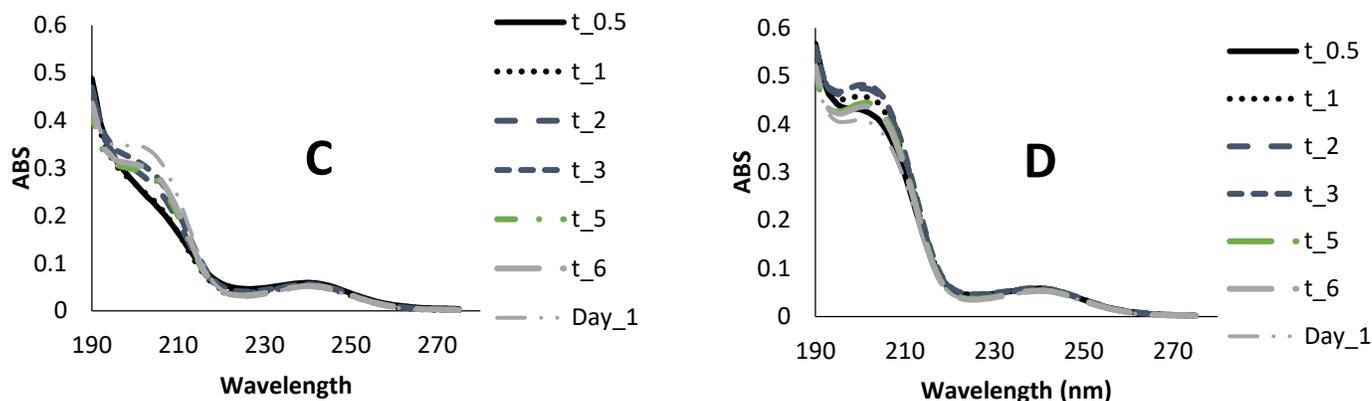


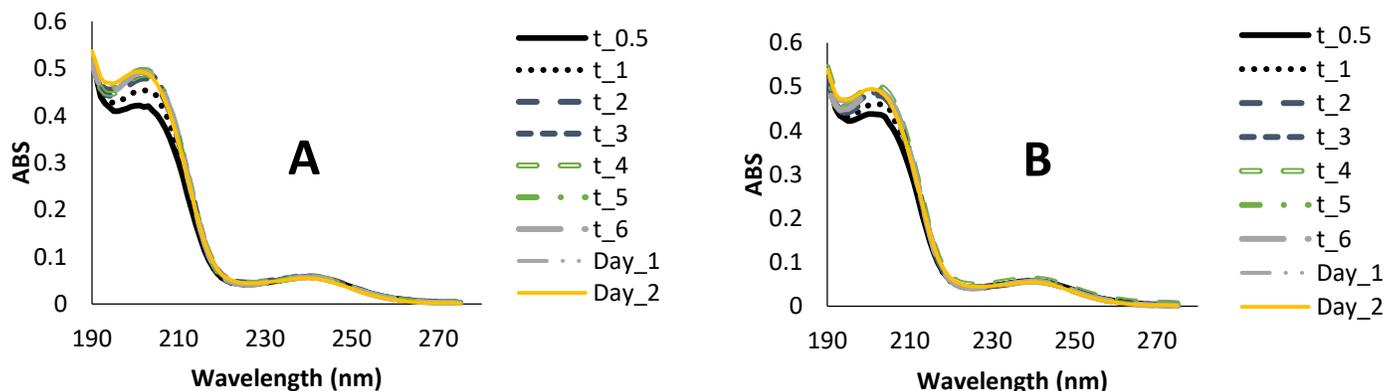
Figure 13. Absorbance was measured over periodic time intervals for Zetag 8160 polymer at A-pH 5, B-pH 6, C-pH 7, and D-pH 8. Polymers were diluted to a final concentration of 15 mg/L from the original stock solutions. A buffer solution of KH_2PO_4 and K_2HPO_4 was used to manipulate pH, at a total concentration of 0.05 M.

Figure 13 shows that polymer uncoiling is hindered at a lower pH, which demonstrates the sensitivity of UV-vis analysis and its capacity to capture maturation of polymer in various environmental conditions. At a low pH, intramolecular catalysis takes place by undissociated COOH groups (formed during initial polymer synthesis), but is negligible for pH greater than 7 (Kheradmand, et al., 1988). This catalysis would cause interference with the molecular structure of the polymer, which could contribute to the reason that the maxima and minima did not form at pH of 5 and 6. It also explains why peaks at pH 8 (Figure 13-D) resembling results for polymers prepared in distilled water, did form. Nonetheless, a high pH (greater than 9) can also increase the degree of polymer hydrolysis, during which amide groups are converted into carboxylate groups (Taylor & Nasr-El-Din, 1994). A high pH should also be avoided when preparing polymers. The above results indicate UV-vis spectrophotometry can capture changes in the ambient pH of the solution used for polymer preparation. A relatively neutral pH around 7-8 appears to be ideal. The sensitivity exists to analyze these changes and their relation to the

polymer maturation process. This is achieved by the periodic absorbance measurements, which capture the development of maxima and minima (seen in Figure 12-A), and also the rate at which they form.

4.1.3.3 Influence of Chlorine

Chloroform has been reported as a by-product of polyacrylamide chlorination in a pH 9 solution (Gehr & Soponkanaporn, 1990). Thus, determining the effects of chlorine ions and the by-products of chlorine on the absorbance measurements was an objective. Also, it is well known that chlorine has the potential to act as a free radical and should generally be minimized from contact with functional macromolecules. Residual chlorine exists in drinking water from the tap, which would be the likely source used for polymer preparation. Below are the absorbance spectra for polymers prepared in DI water (stock 0.2%, diluted and aged to 15 mg/L), with various ambient hypochlorite ion (ClO^-) concentrations of (1, 2, 3, and 4) mg/L.



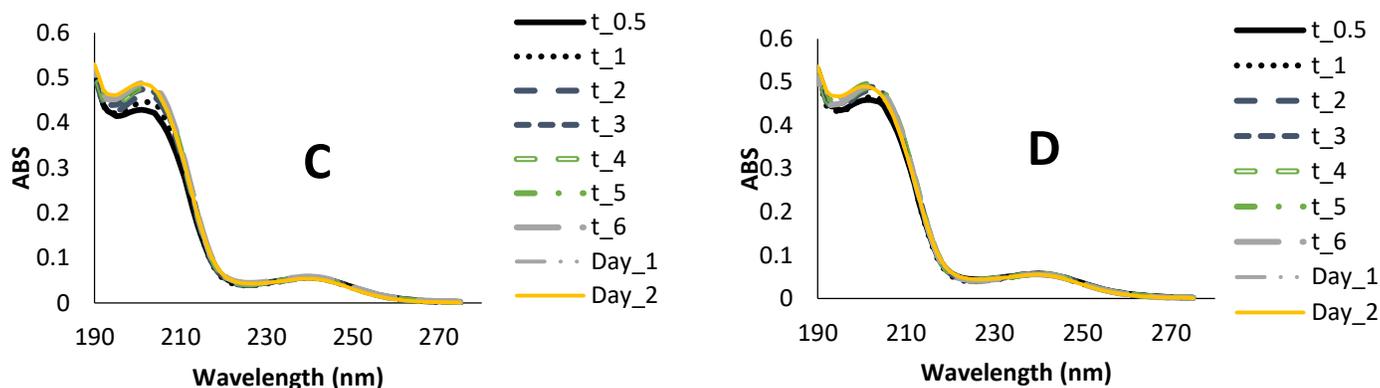
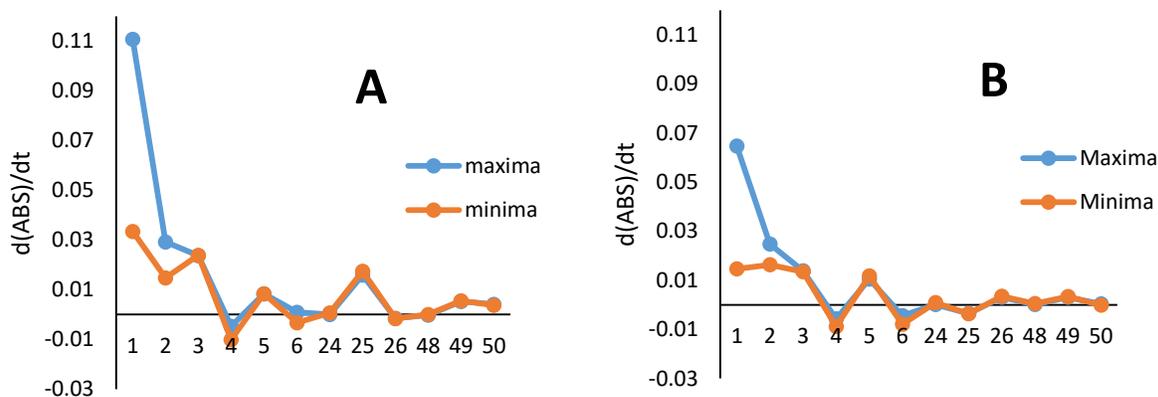


Figure 14. Absorbance measured over several time intervals between the range of (190-275) nm for Zetag 8160 polymer prepared in DI water (stock 0.2%, diluted and aged to 15 mg/L) dosed with various hypochlorite concentrations. A-1 mg/L, B-2 mg/L, C-3 mg/L, D-4 mg/L.

Figure 14 shows the absorbance spectra and that the maxima and minima form around 201 nm and 194 nm as expected. In addition, with increasing hypochlorite concentration, the rate at which absorbance stabilised to a constant value was much quicker. A look at the rate of change of the maxima and minima absorbance at each hypochlorite concentration is seen below. The largest difference is seen when comparing Figure 15A and 15E, where the percent difference between absorbance within the first three hours (of the maxima) dropped from 130% to 67%.



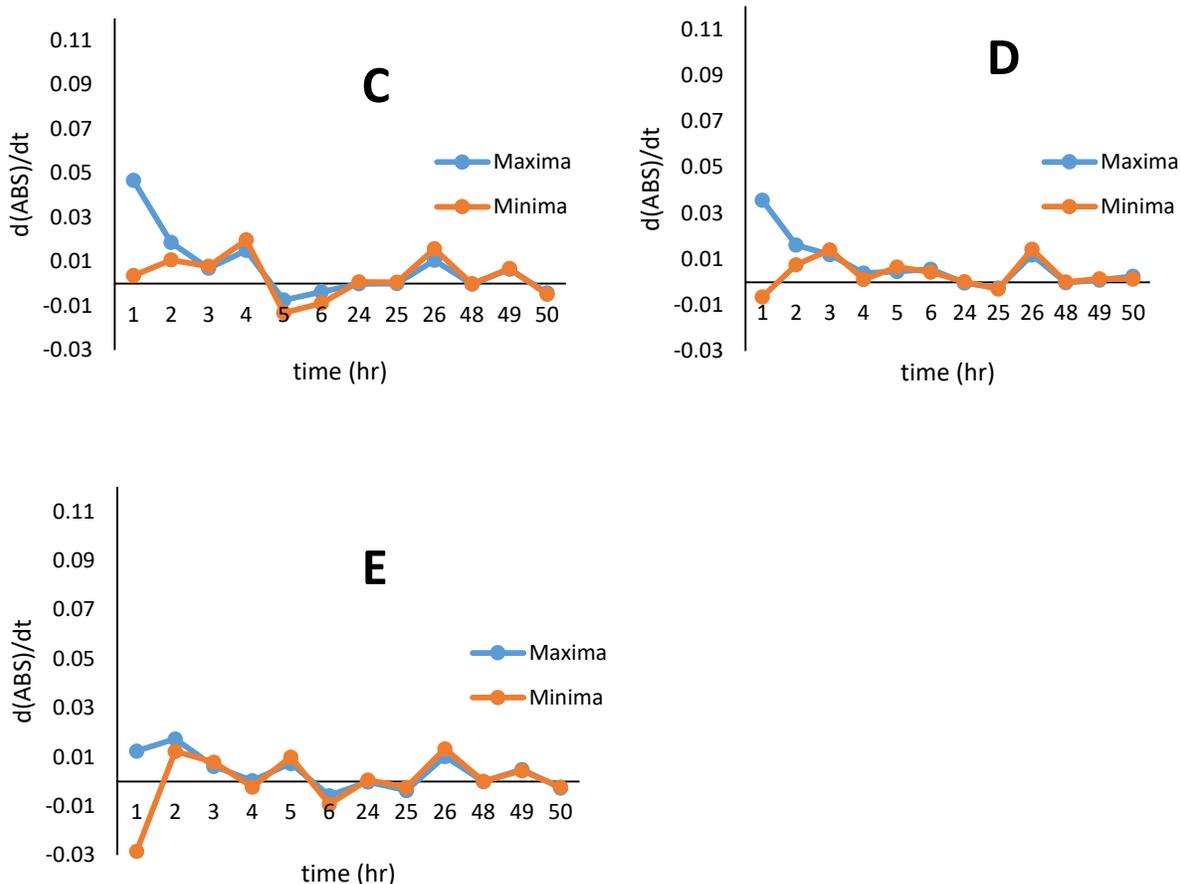


Figure 15. Absorbance rate of change at the maxima and minima for polyacrylamide polymer spiked with various hypochlorite concentrations. A-1 mg/L, B-2 mg/L, C-3 mg/L, D-4 mg/L.

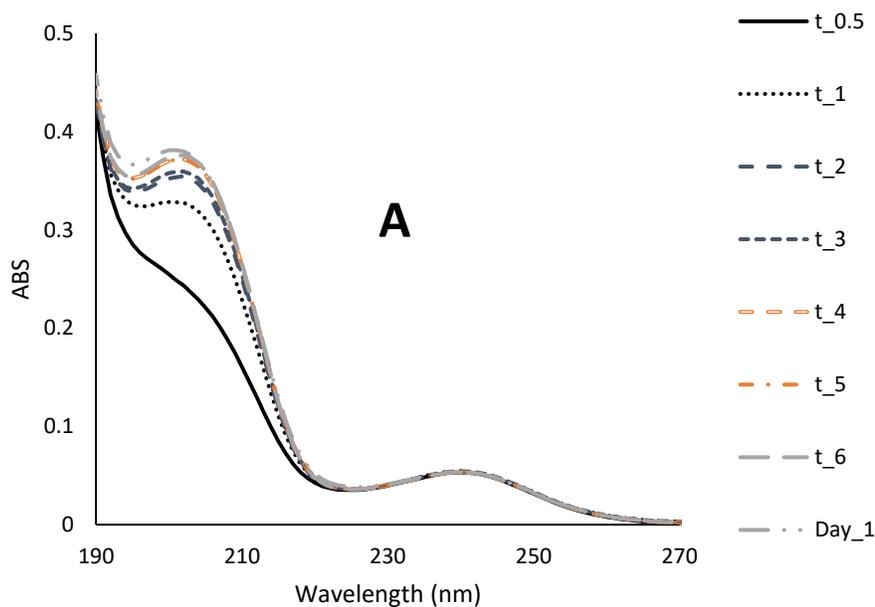
The methodology of using the rate of change of the maxima and minima over time, is discussed further in section 4.1.4. The difference in the rate at which the polymer stabilised at the maxima and minima could be attributed to the increasingly ionic environment. This is not beneficial, however, as it decreases the sensitivity of the instrument for monitoring change in absorbance.

Nonetheless, detection of the maxima and minima suggests that the polyacrylamide was allowed to uncoil without significant damage to the carbon chains. In the presence of chlorine

(concentration of 20 mg/L), polyelectrolytes break down into smaller molecular weight compounds without a significant loss of carbon and nitrogen (Gehr & Soponkanporn, 1990). This would explain why the expected maxima and minima were observed, but at a different rate.

4.1.3.4 Influence of Mixing

The mixing used during polymer preparation is important as too much shear can cause polymer chains to break, whereas not enough can lead to insufficient polymer uncoiling. Figure 16 below shows absorbance spectra of polymers prepared using different levels of shear, achieved by variations in the mixing regime during preparation (high intensity mixing, low intensity mixing, and cyclical high and low mixing were used).



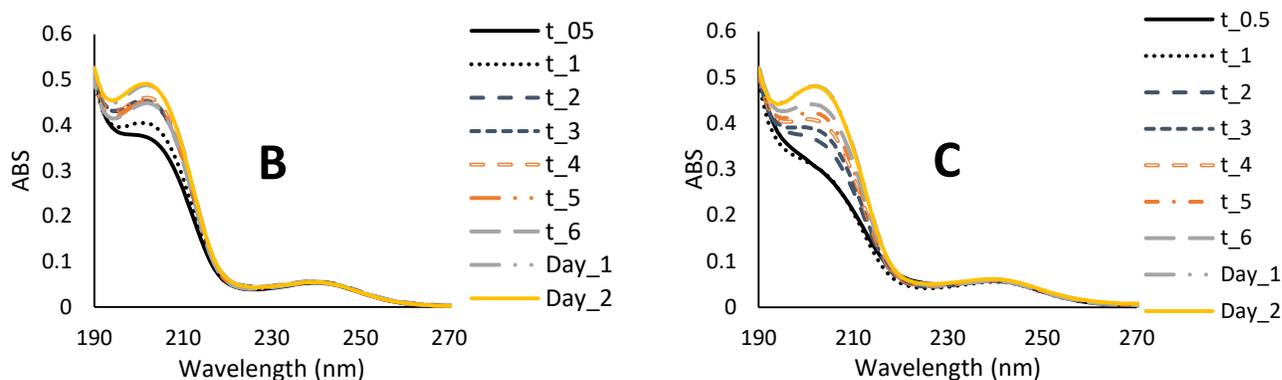


Figure 16. Absorbance spectra at periodic time intervals for Zetag 8160 polymer, prepared using different mixing regimes. A-low mixing (125 RPM); B-High Mixing (290 RPM), C-Cyclical high and low mixing (5 min at 280 RPM, 10 min at 125 RPM for a total of 1 hour).

Figure 16A shows the absorbance measurements resulting from a low degree of mixing (125 RPM). At the lower mixing intensity, a lower absorbance level was reached, when compared to Figure 16B and 16C. This is a result of less energy being added during the mixing phase to stimulate the uncoiling of tightly packed polymer beads. Higher intensity of mixing resulted in higher degrees of absorbance, implying more capacity for the polymer to absorb the UV light due to greater uncoiling. Again, this is an example of how the UV-vis absorbance measurements have the sensitivity necessary to detect changes to the polymer ambient environment and preparation method.

Results from the alternating mixing regime (Figure 16C) show that the rate at which the polymer absorbance increased (at around 201 nm) was much lower when compared to polymer prepared with a continuous level of high mixing (Figure 16B). This suggests that the continuous oscillation from high (280 RPM) to low (125 RPM) levels of mixing causes more stress on the polymer chains when compared to using one continuous level of high mixing. This is likely because the continuous alteration of mixing creates a more turbulent environment, which places

more stress on the polymer, leading to stunted growth. In contrast a continuous level of mixing leads to a system that is more steady state with regards to the internal fluid flow patterns. These results reinforce the notion that a sufficient amount of energy needs to be added to the polymer system to promote uncoiling, however, addition of energy beyond this point will hinder polymer quality and the maturation process.

4.1.4 Analysis of Absorbance Measurements for Maturation Detection

Through the analysis of the periodic absorbance measurements that were gathered during this study, the rate at which the maxima and minima formed was found to be the essential component for detecting polymer maturation. Figure 17 shows the absorbance values measured at these maxima and minima points for 29 hours after the preparation of the polymer (based on the absorbance spectra generated in Figure 12A). It is noted that because the maxima/minima had generally not yet formed within the first measurements, the absorbance at these time points was taken at the wavelength at which the peak did later form. The increasing absorbance values implied that the measurements were capturing the uncoiling of the polymer. This is because as the polymer uncoils, the surface area of the chains increases and becomes more dispersed in the solvent, leading to an increase in the capacity to absorb the UV light.

Initially, the rate of increase was higher but eventually leveled off, and this was observed for both the maxima and the minima points.

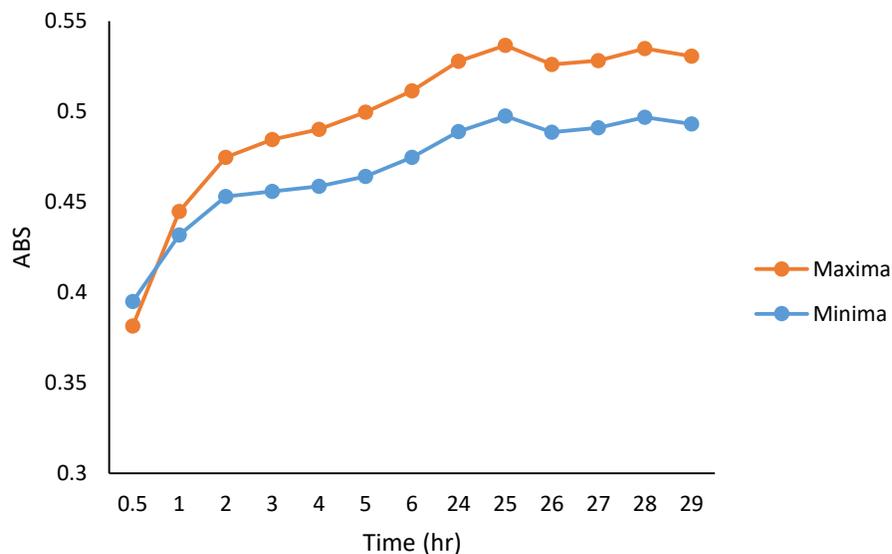


Figure 17. Absorbance measurements at the maxima and minima of Zetag 8160 polyacrylamide polymer prepared at room temperature.

To highlight the differences in the rates of change for the maxima and the minima points, the first derivative of absorbance was calculated with respect to time, and results are shown below in Figure 18.

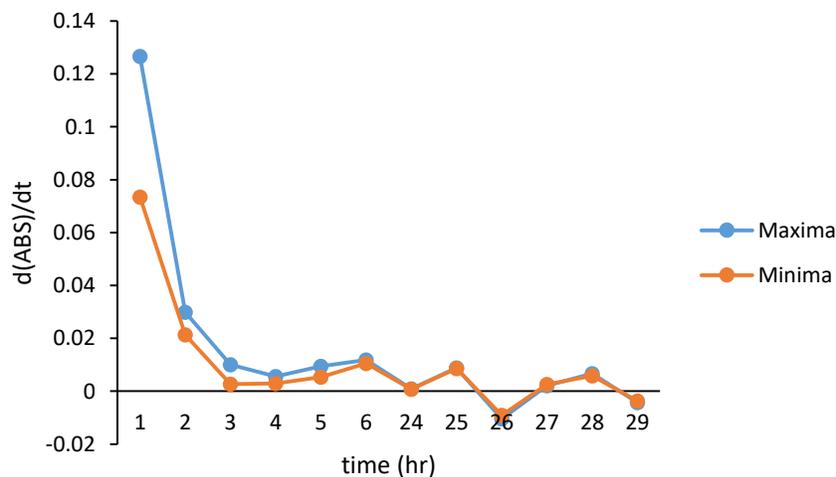


Figure 18. First derivative of absorbance measurements at the maxima and minima of Zetag 8160 polyacrylamide polymer prepared at room temperature.

The greatest rate of change with respect to the absorbance measurements occurs within the first 3 hours. By measuring the rate of change of the absorbance, the uncoiling of polymer can be observed with a higher degree of sensitivity than with the aforementioned methods of electrical conductivity and solution viscosity. Because the greatest rate of change occurred within the first 3 hours, it was concluded that this was the time frame within which the majority of polymer uncoiling occurred and thus indicated the time at which polymer was sufficiently aged and ready for use.

This hypothesis was tested by performing dewatering experiments using polymer solutions that were aged at different times. Anaerobically (mesophilic) digested sludge (total solids concentration of 16.6 g/L) collected from a local wastewater treatment plant was used in the experiments and dewatering of sludge samples were evaluated using capillary suction time test (CST) and filtration tests. The treatment plant uses Zetag 8160 for dewatering. In dewaterability tests, the lowest CST value and the highest filtrate volume indicate the point where optimum filtration is achieved. The optimum polymer dose had been determined through preliminary jar tester analysis, and was found to be 11.25 g/kg DS. All subsequent dewatering analysis for evaluating the influence of polymer ageing time on sludge dewatering was completed at only this dose. The results are illustrated in Figure 19 and validate that the greatest amount of polymer uncoiling occurs within the first 3 hours, thus leading to the highest polymer performance as measured by the CST and filtration volume tests around 3 hours. Higher maturation times quickly decrease the dewatering performance of the polymer. In terms of CST, this is a 19% increase and in terms of filtrate volume, this is a decrease of 51%.

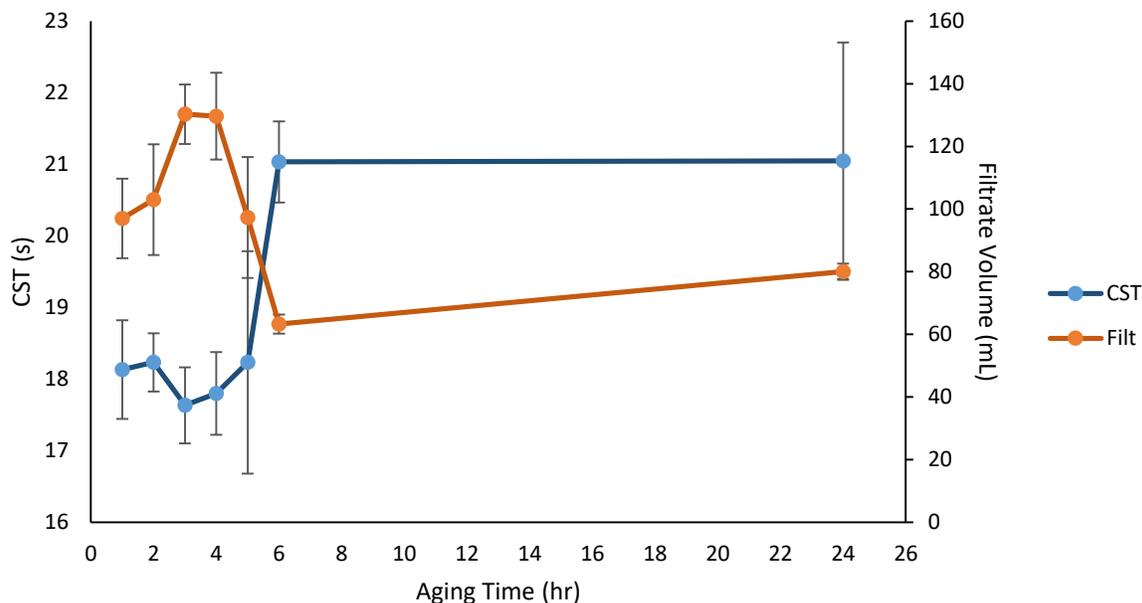


Figure 19. Capillary Suction Time (CST) and volumetric filtration measurements taken periodically on anaerobically digested sludge. Polymer dose was constant (11.25 g/kg DS), and only ageing time was changed.

Increasing the maturation time from 3 to 6 hours resulted in approximately 45% decrease in filtrate volume in this study. A t-test analysis was completed to compare the difference in CST and filtration volume at 3 hr and 6 hr after polymer was prepared. It was found that there was a significant difference between the volumetric filtration tests completed with polymer aged for 6 hr compared to 3 hr ($p < 0.05$). However, comparing the CST between sludge dosed with polymer at these two ages did not generate a significant difference ($0.1 < p < 0.25$).

4.1.5 Interpretation of Polymer Behaviour

Polymer uncoiling can be understood with the Flory-Krigbaum model for polymers. Polymers are separated from the solvent and exist as a uniform distribution about a center of mass (Cowie & Arrighi, 2008). As beads begin to uncoil, their movement is partially a result of Brownian

motion (Cowie & Arrighi, 2008). The process of uncoiling leads to a greater exposure of polymer surface area. Thus, there is an increase in the number of electrons that have the potential to be excited by the incident UV rays. The uncoiling is the likely cause of the rise in the absorbance measured at the maxima and minima of the polyacrylamide polymer.

As beads of polymers unwind and become emulsified in a solution, their shape is often described as a random coil (Cowie & Arrighi, 2008). As the polymer unwinds in the radial direction due to diffusion, it would likely stretch to a point where the polymer would experience a tension force pulling back towards the center of mass. This would lead to collapse and loss of surface area, which would decrease the absorbance measured. Next the collapsed polymer branch would continue to propagate in the radial direction due to Brownian motion. The cycle of collapse and propagation would explain the oscillation that is observed with the absorbance measurements.

4.2 Observing the Effect of Shear on ADS Dewaterability

The optimum polymer dosing range of the collected ADS was determined and all trials were completed at the optimum dose. The optimum dose was measured through the standard tests of CST and filtrate volume, at various polymer doses, as outlined in the Materials & Methods section. Results for determination of optimum polymer range are seen in the figure below.

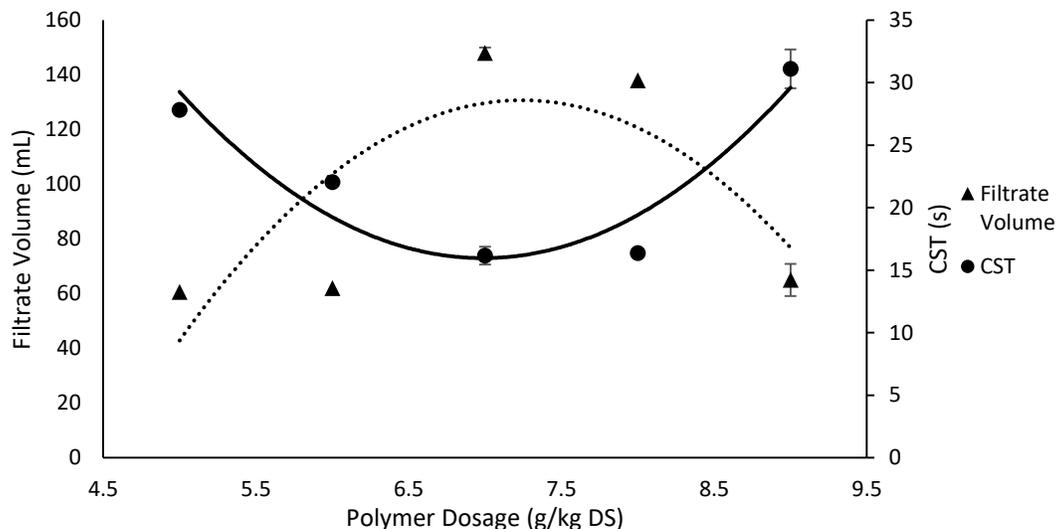


Figure 20. The CST and filtrate volume at each polymer dose with ADS. Data points show the average of triplicate samples.

Using the optimum dose of 7.0 g Polymer/kg DS, subsequent analysis of the influence of shear on sludge dewaterability was completed.

4.2.1 Analyzing the Influence of Shear Duration on ADS Dewaterability (1-Step Floccy Mixing)

This test was designed to capture the strength of conditioned ADS flocs sheared for different durations. The change in torque as a function of shear duration clearly showed an optimum when observing the peak torque and area under the torque time curves generated by the Floccy instrument. The torque measurements make reference to the strength of the conditioned sludge flocs, and as a result, a higher torque value indicates stronger resistance to shear and thus stronger flocs and sludge network. This implies, more energy would be required to break the flocs (Wang & Dentel, 2010). The area under the torque vs. time curve is referred to as the totalized torque (TTQ) and has been shown to be a good measurement of the strength of

conditioned ADS (Abu-Orf & Ormeci, 2005). The figure below demonstrates the torque response of conditioned ADS exposed to shear durations of (0, 15, 30, 45, 60, 120, and 180) s, as measured by the Floccky torque rheometer. Note that the rheograms for the shear durations of 30 s and 120 s have been removed to permit better visual clarity in the figure.

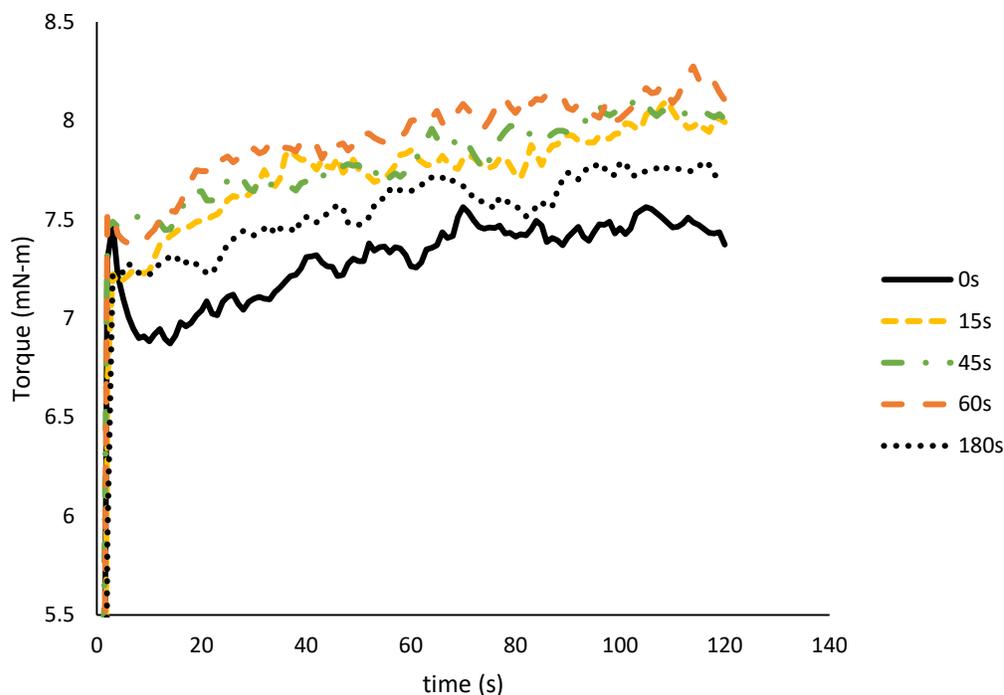


Figure 21. Torque response of conditioned ADS after being sheared in a jar tester at 200 RPM for various durations (i.e. 0, 15, 30, 45, 60, 120, and 180) s. Time points at 30 s and 120 s are removed to permit visual clarity. Triplicate samples were used.

Figure 21 shows the raw torque vs. time curve generated by the Floccky rheometer and it can be seen that as the shear duration increases, the peak torque and TTQ increase up to a maximum, after which, any excessive shear causes weakening of flocs. Some of the rheograms in the figure have been removed to permit better visual clarity of the variation in peak and area torque response. The two lowest torque measurements were generated by the conditioned sludge that

had zero shear added with the paddle mixer, and also the sample that had the maximum shear addition of 180 s with the mixer. This phenomenon is highlighted by the figure below which only displays the change in peak torque and area of the torque data, as a function of the shear duration. An explanation for the decrease in measured torque at the highest shear duration of 180 s is that greater shear leads to greater deflocculation. This is because a greater amount of stress is exerted on the flocs and once a critical level is reached, the flocs break.

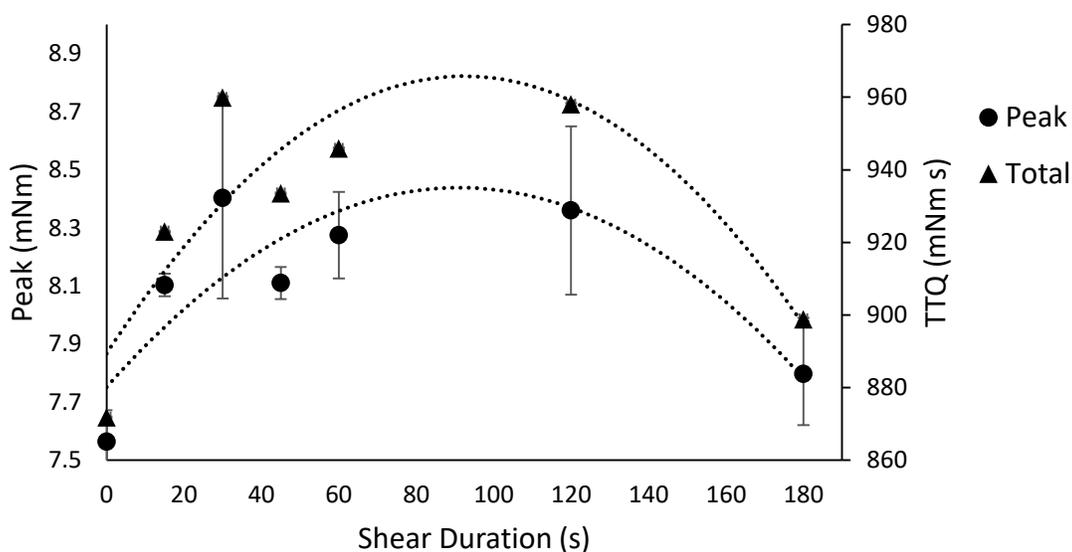


Figure 22. Peak torque and totalized torque (TTQ) for the conditioned ADS sheared by the 1-step Floccy cycle.

The increase in peak torque and TTQ is largely attributed to better polymer mixing with higher shear conditions. As the shear duration is increased, the polymer is more homogeneously dispersed throughout the solution, becoming better incorporated into the sludge matrix, and thus increasing the floc and network strength. Because the torque measurements using TTQ were more consistent and had a lower spread when compared to measuring torque using the peak, it appears that TTQ is a more reliable parameter to gauge sludge network strength. In addition, as

the shear duration increases from 0 s to 120 s, the gradual increase in peak and TTQ can be explained by the fact that greater shear produces denser flocs (Cornwell & Bishop, 1983). Denser flocs would in turn have a higher resistance to the shear forces to which they are being exposed to, generating higher torque measurements. Nonetheless, after the addition of a critical duration of consistent shear, a limit is reached whereby the internal forces holding the flocs are surpassed by the addition of shear forces from the environment. Figure 22 show that as the shear duration increases past this level of shear addition (greater than 120 s) there is a decrease in the strength of the mixture. This can be used to understand the permissible level of shear that the sludge/polymer mixture should be exposed to in dewatering equipment.

It can be seen in Figure 22 that the torque response was not a perfect curve, rather there was a maximum spike at 30 s of shear addition, both in terms of peak torque and TTQ. The subsequent shear at 45 s generated a lower torque response, however, increasing the shear duration past 45 s, raised the torque to a second maximum at 120 s. The spike at 30 s could be due to the differences among the non-uniform nature of flocculated sludge samples which is frequently observed in dewatering studies. It can also be interpreted as the ideal shear duration for generating the strongest flocs. An explanation for why there is a drop in torque and a subsequent increase is that reflocculation is taking place. After the critical point of shear addition, the flocs may weaken and partially or entirely break down. Nonetheless, polymer is still present within the mixture, thus permitting reflocculation of the suspended solids. The additional shear facilitates this reflocculation. However, floc breakage exposes more negative surfaces, which requires more polymer addition for charge neutralization (Abu-Orf & Dentel, 1997); this would also explain why the secondary peak in torque at 120 s was not as high as the peak at 30 s shear duration. This is consistent with the research completed by (Novak & Bandak, 1994) who were also able

to conclude that with increasing shear, the polymer demand would need to increase, although it should be noted that their testing was completed on alum and lime sludge, whereas ADS was used for our tests. In addition, the polymer chains are also being sheared in the process and it can be assumed that they degrade and thus lead to weaker flocs. This can be seen in Figure 22 as the second peak at 120 s, generated a lower torque response than at 30 s of shear. After 120 s of shear addition, the polymer chains likely disintegrate past the point of recovery and functionality, which would explain why the torque response at the maximum shear duration of 180 s generated a much lower torque. The process of flocculation and deflocculation was further investigated with various polymer doses as illustrated below.

4.2.2 Influence of Polymer Dose on the Torque Response of Conditioned ADS (1-Step Floccy Cycle)

The change in torque as a function of polymer dose added showed the potential for determination of optimum dose using torque rheometry. Peak torque shows gradual increase until optimum dose, a local dip at the optimum dose, and then a sharp increase in the over-dosed region. Both peak torque and the area under the torque-time curve (i.e. totalized torque) have been correlated with the energy dissipation into the sludge suspension (Ormeçi & Abu-Orf, Protocol to Measure Network Strength of Sludges and Implications for Dewatering, 2005). Greater energy dissipation into the system implies greater floc and overall network strength. The drop in the torque measurement right around the optimum dose is likely caused by release of the free water from the floc networks. Free water is not bound to the particles and thus requires little energy to dissipate, and the loss of free water would cause a decrease in the measured torque as it contributes to the overall network strength (Abu-Orf & Ormeçi, 2005). In the over-dosed region, the increase in torque is caused by the excess polymer, which contributes more to the network

strength than the loss of free water would decrease network strength; thus, overall, there is an increase in the measured torque.

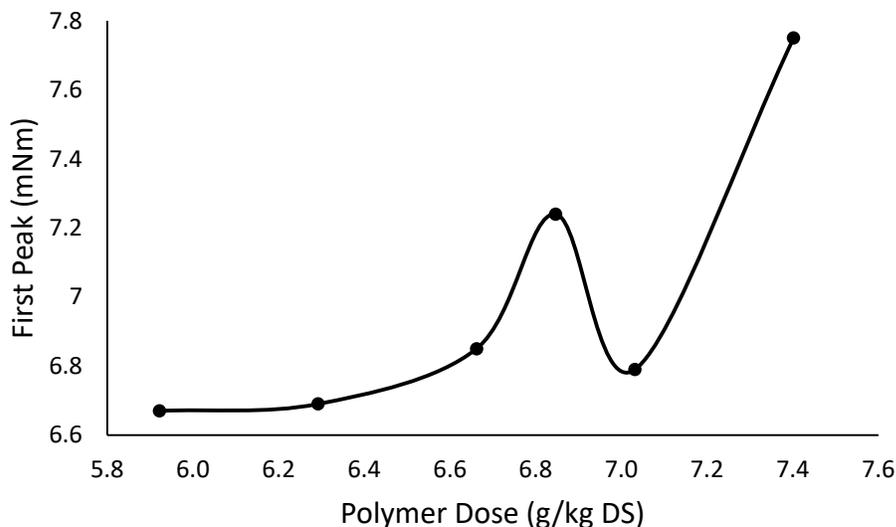


Figure 23. Variation of peak torque as a function of the polymer dosage added to ADS.

Operating in the overdosed region is less economical in terms of cost, and also has the potential for adding more residual polymer to filtrate. As the polymer itself can cause toxicity to aquatic life (Hasegawa, et al., 1990), operation at the optimal dose is essential to minimize the release of polyacrylamide into the environment. The results in Figure 23 demonstrate the potential to evaluate optimum dose in a real-time situation using torque rheology.

The capacity to capture the optimum and over-dosed polymer additions was further investigated by means of a 3-step Floccy cycle, discussed below.

4.2.3 Influence of Polymer Dose (3-Step Floccy Cycle)

Similar to the 1-step Floccy cycle, the 3-step cycle was also able to visually capture the overdosed region of polymer addition into ADS. The benefit of using the 3-step cycle is that the

rheometer can capture the torque response of the floc network right at the point of polymer injection, in contrast to injecting, shearing in a jar tester apparatus, then using the rheometer to measure the torque response. The figure below shows the raw torque output from the floccy rheometer as a function of the polymer dose, which was spiked at 50 s.

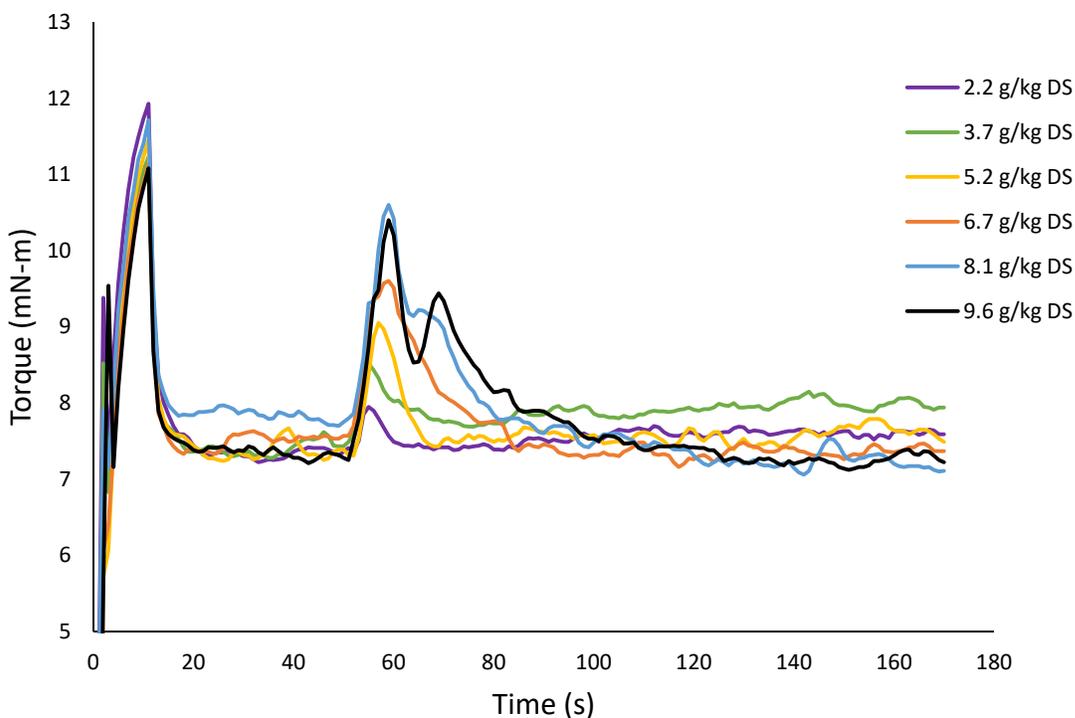


Figure 24. Torque measurements generated by Floccy rheometer as a response to various polymer doses spiked (at 50 s) into ADS, using a 3-Step Floccy cycle.

With increasing polymer dose spiked into the Floccy rheometer, the peak torque after addition also began to rise. The optimum dose had been previously determined to be within the range of 6.7-7.0 g/kg DS and at the over-dosed region (i.e. doses 8.1 g/kg DS and 9.6 g/kg DS), it can be seen in Figure 24 that a secondary, smaller peak formed. The formation of the second peak can again be explained by the fact that after the initial flocs are broken, the excess polymer present within the mixture (due to operating at the over-dosed region) facilitates reflocculation. The

second peak (at 70 s) formed with the 9.6 g/kg DS polymer dose was greater than the secondary peak of the trial using 8.1 g/kg DS polymer dose. This was consistent with expectations, as the additional 2 mL of polymer would assist in generating stronger flocs during the reflocculation process, thus a higher relative peak would form. The excess polymer itself would provide resistance to shear resulting in an increase in torque values.

Figure 24 above shows the ability to detect optimum dose and over-dosed polymer addition with the 3-step Floccy mixing method.

4.2.4 Sensitivity of Torque Measurements

It is important to understand the optimal operational parameters to run the torque rheometer for the purpose of attaining a visual output that captures the peaks generated from floc formations. To do this, the 3-step Floccy cycle was used, with an equivalent volume of polymer added at the end of the second step, while changing the shear intensity in the third step. Figure 25 below, shows the variation of peak output from the Floccy rheometer, as a function of the intensity (i.e. RPM) used in the third step, for the same dose of spiked polymer. It is clear that the floc strength, as measured by torque, is dependent on the mixing intensity. Increasing the mixing intensity caused the rheometer to generate a larger peak relative to the torque output once flocs had been destroyed and peaks had vanished. Among the speeds tested, operation at 250 RPM generated the most symmetrical and visually evident peak.

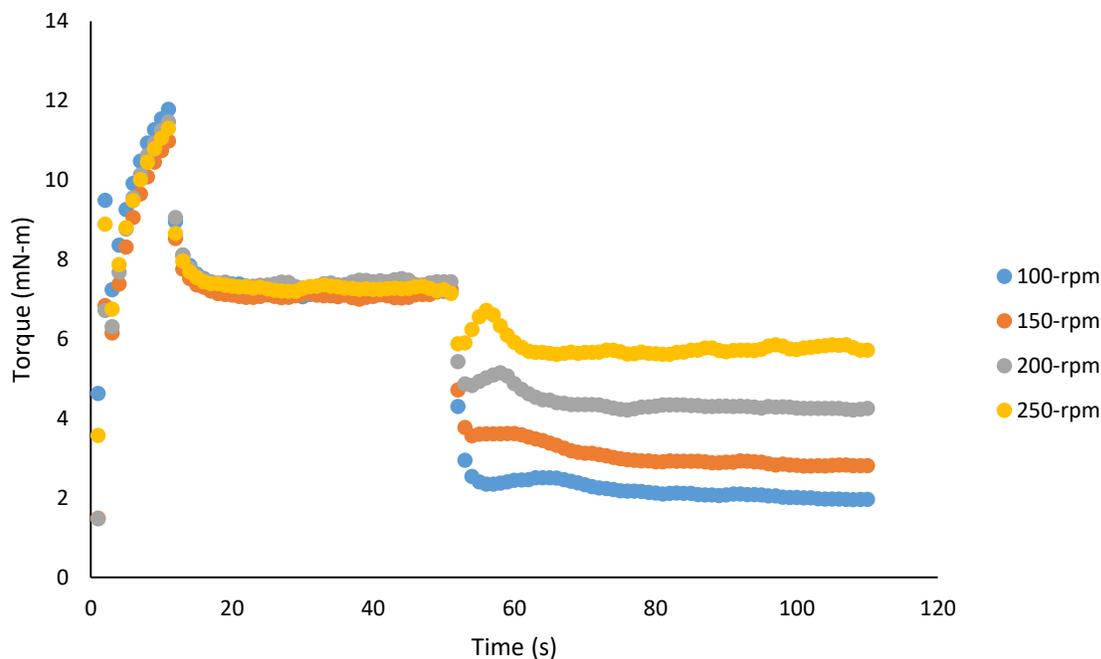


Figure 25. Testing Floccy sensitivity to capture floc formation in the form of peak torque, with the same volume of polymer added, but varied intensity at the third step.

Understanding the ideal instrument operational parameters, such as impeller speed, are important as this will generate torque measurements that are most sensitive to changes in sludge samples and flocculation characteristics.

The increase in relative peak size with higher shear intensity applied to conditioned sludge is explained by the fact that the addition of greater shear, generates more stress at a higher rate on the flocs. Following Newton's third law, this would also cause the flocs to strain, and resist deformation at a proportionally higher rate. In turn, this would lead to a higher measurement of torque resistance by the rheometer. The torque output for conditioned sludge sheared at 250 RPM also formed the most symmetrical peak because a higher shear rate would cause quicker deflocculation and a decreased opportunity for reflocculation to take place, as polymer chains are

exposed to greater stress. Higher stress on polymer chains may also cause more irreparable breakage of chains, which would cause a relatively narrower peak formation as less polymer is available for reflocculation. In contrast, with a lower intensity of shear rate added to the conditioned sludge, it is evident from Figure 25 that a smaller peak with a much larger spread is formed. The figure shows that the breakage of flocs is much slower, likely because of two reasons. The first, as mentioned above, a lower shear rate implies less stress on the flocs, thus a greater time necessary to break flocs. The second being that at the lower operational intensities, there is more opportunity for reflocculation via the polymer chains, as the polymer experiences relatively lower shear, leading to a slower rate of polymer deformation and degradation.

These findings allude to a very important factor concerning shear, which is that the influence of shear is not only a function of the shear rate (i.e. intensity) but also the duration of shear (i.e. how long the shear is being added to the system). The CST results subsequently measured from these sludge samples conditioned at various shear intensities are seen below in Figure 26. It is evident that even though the shear intensity of 250 RPM generated the largest and most symmetrical peak (based on Figure 25), the resulting CST measurements were worse compared to the lower shear rates of 150 RPM and 200 RPM. Had the CST measurements been taken at around 60 s (i.e. right when flocs were formed), the CST at 250 RPM intensity would have likely been the lowest. However, because the measurements were made after the full 110 s of shear in the Floccky rheometer, this would have caused additional shear by the time the samples were collected and had CST measured, thus leading worse dewaterability.

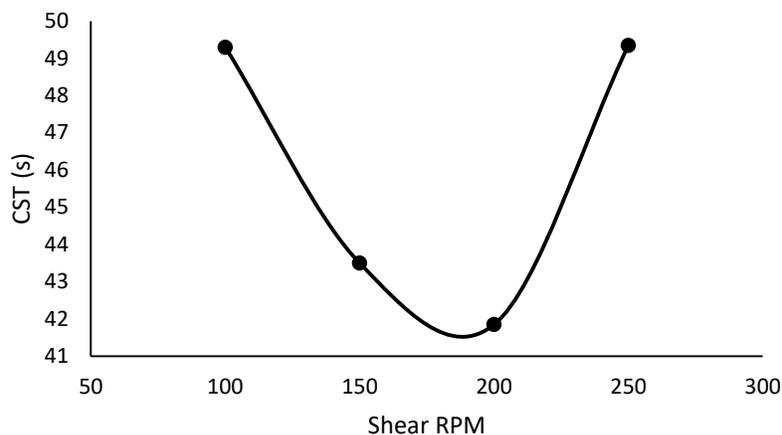


Figure 26. Resulting CST measurements from conditioned ADS sheared at different intensities in the third step of the 3-step Floccy cycle, for the same volume of spiked polymer.

The above suggests that an ideal intensity and duration of shear will result in the best CST response (i.e. minimization), however, any more or less shear is unfavourable for separating the sludge/polymer matrix. This demonstrates how the duration of shear exposed to the system is equally important as the intensity. Our expectation was that since the ADS sheared at 250 RPM generated a more distinct peak, it would generate the lowest CST, however, this was not the case. The trial using 250 RPM generated a more ideal peak, however the duration of exposure was too long and as a result this led to over-shearing the flocs. Over-shearing the flocs also implies over-shearing the polymer, and as a result, minimizing the capacity for reflocculation, ultimately worsening the quality of sludge dewatering. For a better understanding of the influence that both shear intensity and duration have on the quality of ADS dewaterability, a design of experiments was set up to manipulate both these parameters and measure the resulting quality of dewaterability using the CST test. This is discussed in detail in the following section.

4.2.5 ADS Dewaterability Tested at Multiple Shear Intensities and Durations

The 3-step Floccy cycle was used for testing the influence that shear intensity and duration have on the quality of ADS dewaterability. The five intensities of (150, 200, 250, 300, and 350) RPM were used and each applied for the durations of (10, 20, 30, 45, 60, and 120) s. These intensities and durations were applied at the third step of the 3-step Floccy mixing regime. The results from shearing conditioned ADS at these combinations of intensities and durations have been amalgamated into Figure 27 below. Error bars have been omitted from the figure to permit better visual clarity, however they are included in Table B- 3 of Appendix B. The R^2 values seen in the figure represent the best match from comparing the linear and second-order fit to the data.

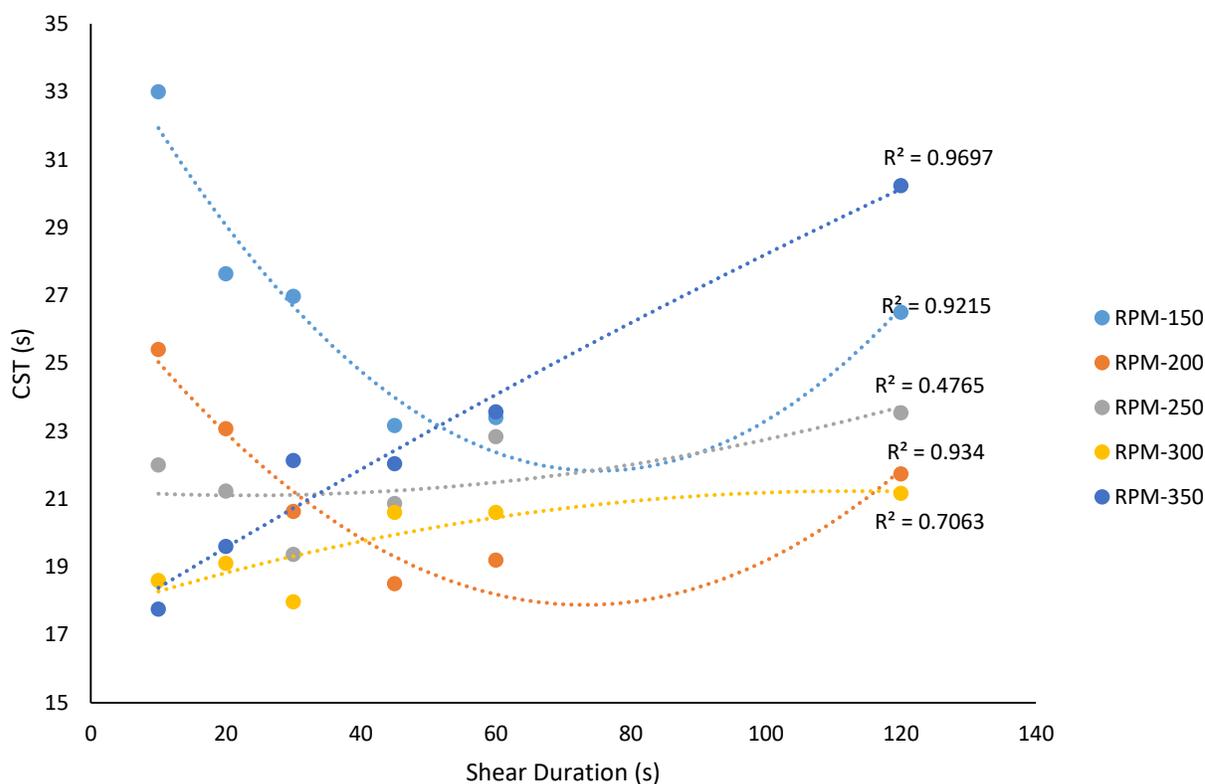


Figure 27. Dewaterability of conditioned ADS exposed to various combinations of shear intensities and durations.

A comparison of the linear and second-order regression coefficients generated for each shear intensity can be found in Table B- 2. Comparison of the linear and second-order regression coefficient linking shear duration to CST, generated at each shear intensity. Table B- 2 (Appendix B). Several important findings can be inferred, with regards to the influence that shear has on the quality of dewatering. First, at the lowest tested duration of 10 s shear applied, the increasing intensities led to a better quality of dewatering. At the lower tested intensities of 150 RPM, 200 RPM, and 250 RPM the increase in shear duration appears to improve the quality of dewatering up to a certain point. After this critical point of shear addition, as measured by the duration of application, any additional shear becomes detrimental to the quality of ADS dewatering, as CST values begin to rise. In addition, this critical point appears to shift towards a lower duration of added shear with increasing intensities. For example, when observing the CST results for the intensities of 150 RPM and 200 RPM, this critical point is at 45 s, after which increased durations of shear lead to a lower quality of sludge dewatering. At the relatively higher intensities of 250 RPM and 300 RPM, this critical point shifted towards a shorter duration of 30 s. This is seen in Figure 27, as CST improves up to 30 s of shear duration, then increases with additional shear duration. The measurements of CST at these shear intensities appear to indicate the presence of an optimum shear addition to the ADS and polymer mixture, for achievement of the highest quality of dewatering. This is explained by the fact that a greater level of shear leads to a denser floc formation. A denser floc would thus generate better dewaterability as more water is intrinsically being squeezed out of the pores. This is the reason that with increased shear duration (at the same shear intensity), there is an increase in the quality of dewatering, as measured by CST. Nonetheless, the flocs have a limit with regards to the stress they are able to sustain until they rupture. Once this point is surpassed, the flocs lose structural integrity which

causes the quality of dewatering to decrease. This appears to provide experimental validation that an optimum exists when considering the shear that is exposed to conditioned ADS.

Results from the dewaterability analysis of ADS sheared at 350 RPM deviated from the results generated at the lower intensities. The deviation came from the fact that quality of dewatering behaved in a linear nature with respect to shear duration. This can be seen in Figure 27 which shows that the best CST measurement came at the lowest shear duration of 10 s, and increasing the duration of shear led to worse dewatering. It appears that the intensity of 350 RPM provides exceedingly high shear, such that only a small addition is required to achieve the best dewatering results. Again, this demonstrates the shift of optimum shear duration towards a smaller duration of exposure as the intensity of the shear rate is increased. This reinforces the interdependent relationship between shear intensity and shear duration and their impact on the quality of ADS dewatering. A balance has to be attained between the two, for the purpose of achieving the highest dewatering performance. A sufficient intensity of shear needs to be applied to maximize floc strength and density, however, only for a limited duration of time as over exposure will cause a loss in sludge dewaterability

To conclude from the results in Figure 27, at a sufficiently low shear intensity, CST behaves in a parabolic nature with respect to shear duration. This implies that increasing shear duration improves ADS dewaterability (as measured by CST), up to a certain critical shear duration, after which the CST begins to rise. However, once the shear rate is raised to a sufficiently high intensity (i.e. 350 RPM), the CST responds in a more linear nature with respect the shear duration. This was seen by the fact that the lowest CST measurement (at 350 RPM) was attained at the lowest shear duration of 10 s, after which CST became progressively worse.

4.2.6 Unitless Measure of the Shear Added to a Suspension

A volume of fluid in the sludge treatment process will not experience shear in the same way as in the laboratory setting. Shear would be added by collision with adjacent fluid elements and with the containing walls, as sludge is carried through the treatment system. Also, spikes of high intensity shear would be added during the dewatering process, added by machines such as the filter press or centrifuge. To allow a unitless comparison between different geometries and methods of shear input, the shear added by the rotational intensity of a torque rheometer can be used to calculate the shear rate (G, s^{-1}) that the suspension is exposed to. In turn, the shear rate can be multiplied by the duration of shear (time, s) to calculate a more holistic, unitless parameter for capturing the overall addition of shear to a liquid suspension (refer to section 3.2.7 for the methodology used to calculate the shear rate, G , from the rheometer torque measurements). The lowest CST of 17.8 s was achieved at the Gt of $7.6E5$ (Figure 28. Torque intensity converted into the unitless form of Gt for all tested intensities. Figure 28 E). Comparing to dewatering equipment used in treatment plants, belt presses have been reported as having Gt intensities ranging from $1E4-3E4$, whereas centrifuges have reported values of $1.0E5-1.2E5$ (Novak J. T., 2006). The data presented in Figure 28 clearly illustrates the importance of shear intensity and duration on sludge dewaterability. Although shear is represented as the unitless Gt , it is evident that under a different shear intensity, the point at which CST is minimized changes. This highlights the importance of shear intensity, as with increasing intensity, the Gt value at which CST is minimized becomes smaller. For large treatment plants, this implies that understanding the shear at the dewatering stage in terms of Gt is not sufficient for maximizing the quality of dewatering.

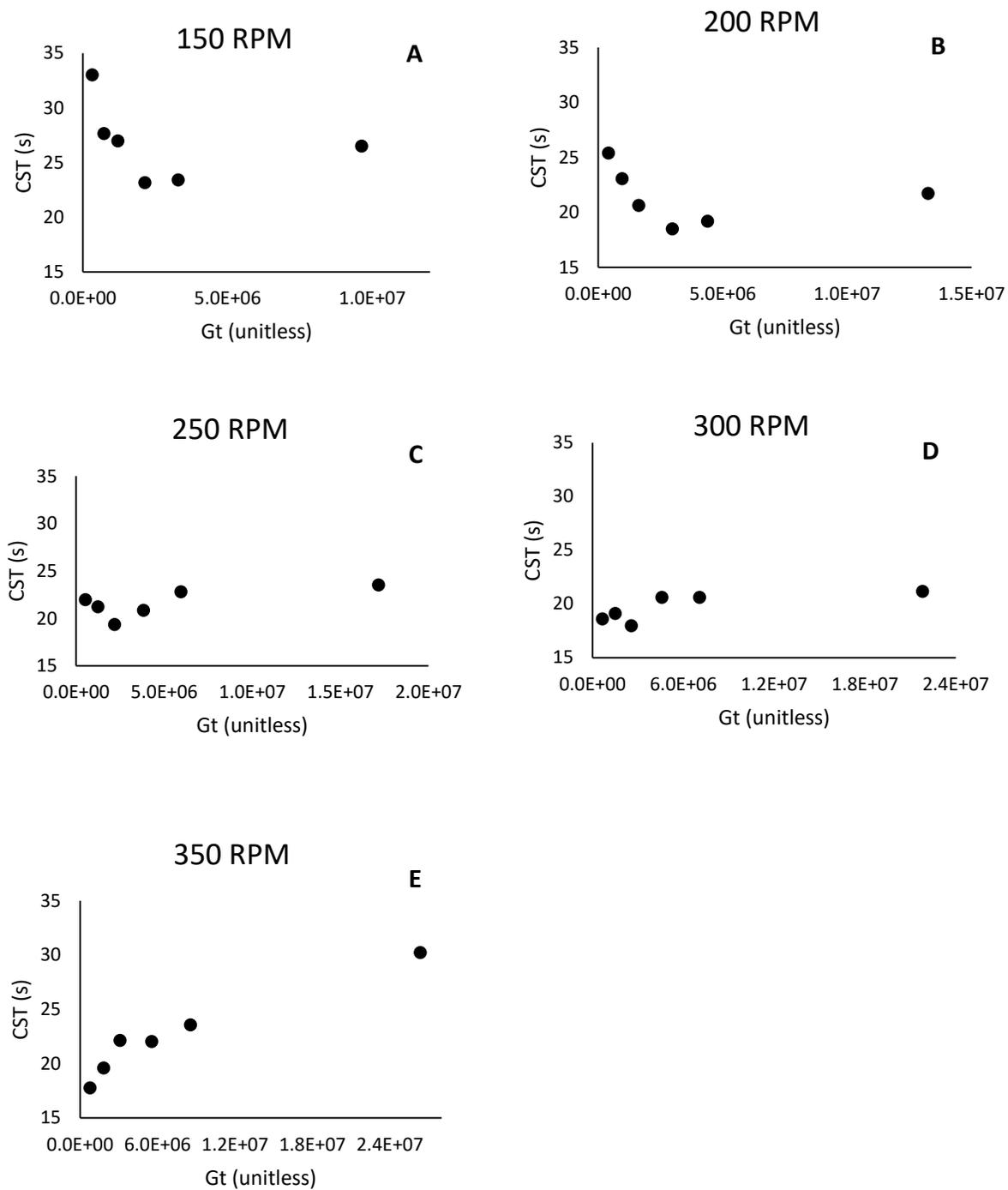


Figure 28. Torque intensity converted into the unitless form of Gt for all tested intensities.

By understanding the shear forces experienced during the dewatering process, the network strength of the incoming sludge can be adjusted by making alterations to the polymer dosage and mixing conditions (i.e. intensity and duration) (Ormeci & Abu-Orf, Protocol to Measure Network Strength of Sludges and Implications for Dewatering, 2005). Ensuring the incoming sludge has sufficient network strength will improve dewatering as flocs will remain unbroken in the dewatering process.

4.2.7 Measuring the Presence of Residual Polymer in ADS

After dewatering ADS with the vacuum filter, the resulting filtrate was collected and analyzed with UV-vis spectrophotometry, for potential detection of residual polymer and investigating the relationship between shear, residual polymer remaining in sludge, and dewaterability performance. Absorbance at the wavelength of 190 nm was specifically observed as previous studies have provided evidence that this wavelength correlates well with polymer concentration (Momani & Ormeci, 2014). Below, Figure 29 shows a summary of the absorbance at 190 nm at all shear intensities tested. At the intensities of 150 RPM and 250 RPM, an absorbance minima was observed, which also coincide with the shear durations at which CST was at a minima for the same intensities (refer to in Figure 28). When CST is at a minimum, this implies good dewatering and thus efficient polymer integration into flocs.

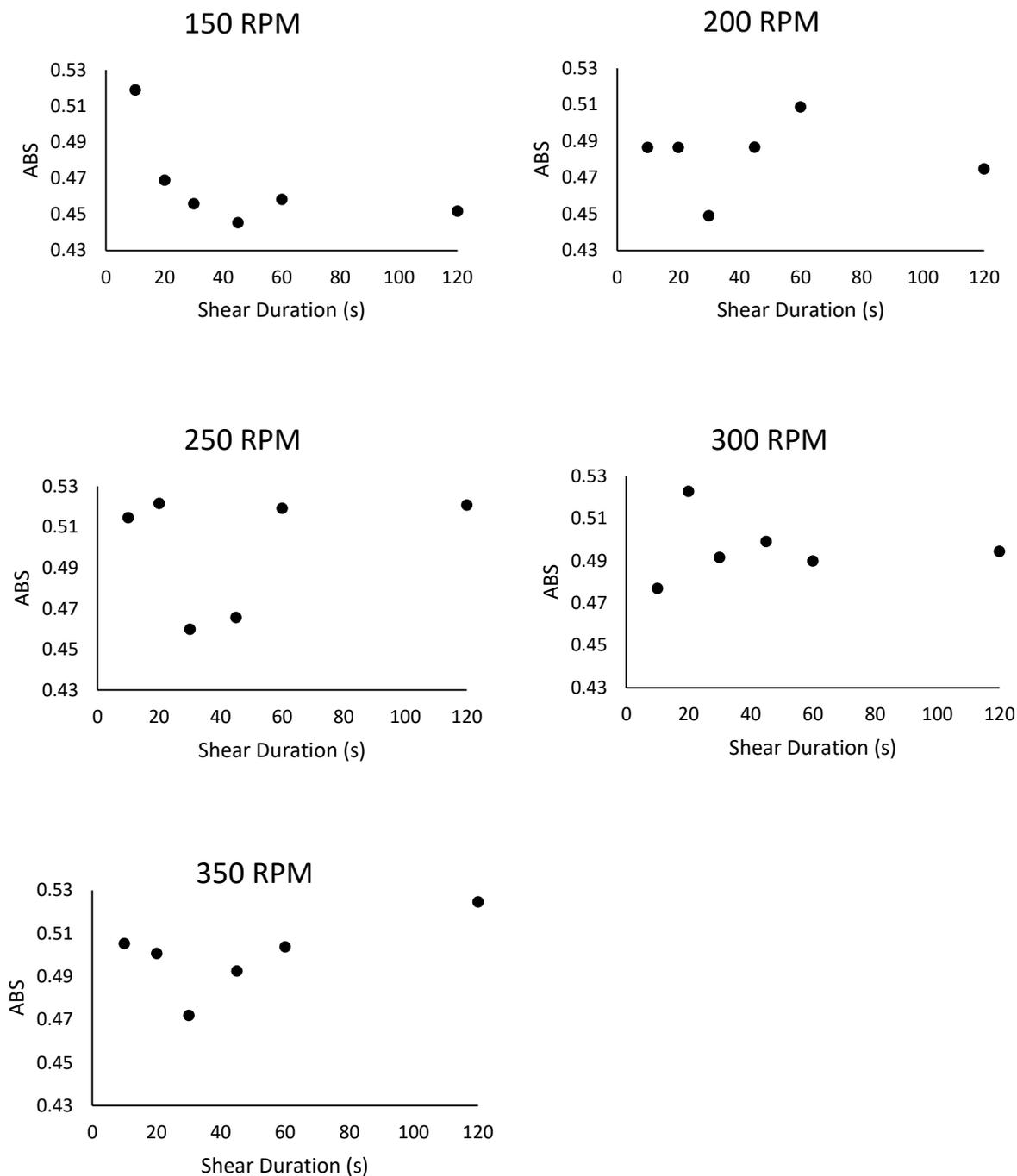


Figure 29. Absorbance measurements of filtrate (at 100X dilution) measured at 190 nm.

With good polymer integration, the polymer is contributing strongly to floc formation meaning that a majority would be found in the flocs, minimizing the amount that escapes into the filtrate;

and thus minimizing the resulting absorbance. At the shear intensity of 200 RPM, the absorbance minima occurs at 30 s, as opposed to the CST minima which occurs at 45 s. Nonetheless, the CST at 30 s and 45 s are relatively close (20.6 s and 18.5 s, respectively), thus the 30 s minima for absorbance is reasonably close to the 45 s minima of the CST. At 300 RPM, absorbance showed a local minima at 30 s, which aligned with the CST minima at the same intensity. At 350 RPM, which was the highest shear intensity, an absorbance minima was observed at 30 s as well. However, as the CST results illustrated this shear was too powerful for mixing and resulted in deflocculation quickly.

To illustrate the raw absorbance data that was collected for Figure 29, the absorbance spectra for conditioned ADS sheared at 150 RPM is seen below. For the purpose of visual clarity, the absorbance spectra at 30 s and 60 s have been omitted. With increasing shear duration, more solids surfaces are exposed to adsorb polymer, and as a result less residual polymer remains in sludge. The decrease in absorbance corresponds to a decrease in residual polymer.

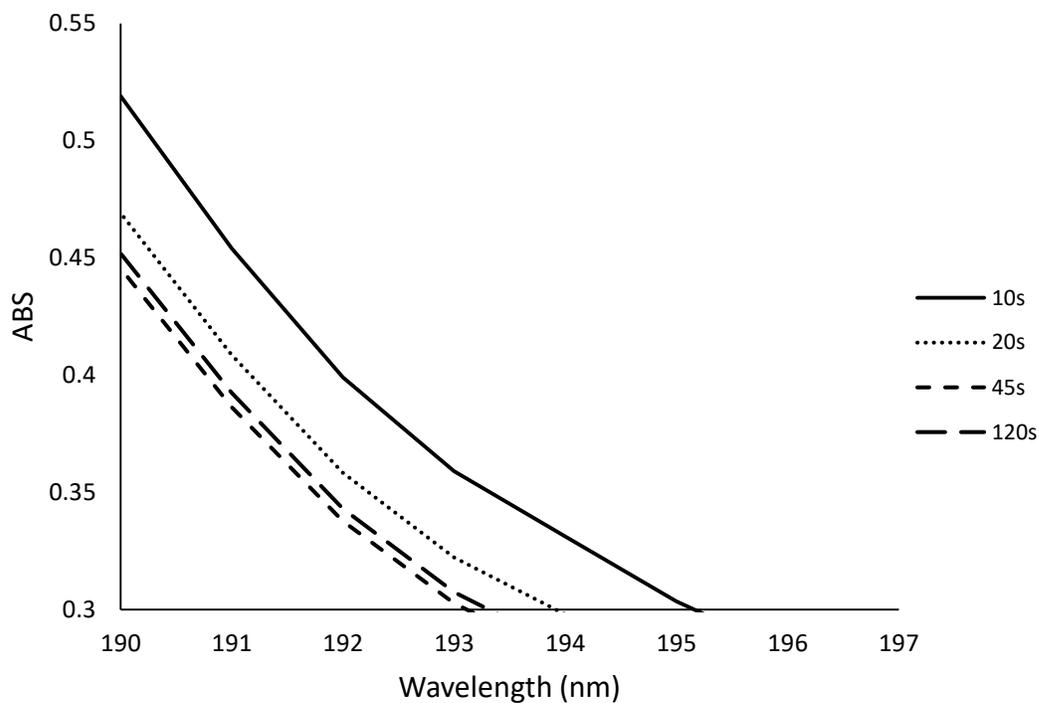


Figure 30. Absorbance spectra for conditioned ADS sheared at 150 RPM for durations of (10, 20, 45, 120) s.

The decrease in absorbance reaches a minima when the shear duration is extended to a point where extended shear negatively influences the ability of solids to adsorb polymer.

5 Conclusion

The results of this study show that UV-vis spectrophotometry can be used to monitor and optimize the preparation of polymers and to determine the optimum maturation time which results in the highest dewaterability performance with ADS. The absorbance of the polymer solution increases gradually over time in the absorbance range of (190-275) nm, due to the uncoiling of the polymer molecules. It is evident that a maxima and minima progressively form within a few hours after polymer preparation, at about 201 nm and 194 nm, respectively. The use of spectrophotometry was able to detect environmental changes made to the polymer. Changes in temperature, pH, mixing methodology, and hypochlorite content were all captured by the periodic absorbance spectra. It was discovered that the ambient temperature, pH, and mixing regime had the greatest effect on the polymer maturation process, whereas the chlorine content had relatively less influence. Increasing the temperature and pH had a positive effect on the polymer maturation process, as seen by the formation of the maxima and minima at about 201 nm and 194 nm, respectively. The mixing regime chosen also influenced the peak to which absorbance rose. For a treatment plant, this implies that the conditions most pertinent to maximize polymer maturation and activation would be temperature (around 23°C), pH (around 8), and mixing (short duration at high intensity, and a longer duration at a lower intensity). Furthermore, it was discovered that the first order rate of change in absorbance at the maxima and minima can be used to determine the optimum maturation time. Taking the first derivative of the absorbance spectra illustrated that the majority of the uncoiling occurred within the first 3-4 hours for the Zetag 8160 polymer, and higher maturation times resulted in a decrease in ADS dewaterability. The volumetric filtration test resulted in a significant difference between polymer aged for 3 hr compared to 6 hr ($p < 0.05$). A significant difference was not however found in the

CST results. Measuring the electrical conductivity and viscosity was not sufficient in producing results from which conclusions could be drawn about polymer maturation.

Regarding rheology, a relationship was established between the intensity and duration of shear, and their influence on the quality of sludge dewatering. At a relatively low shear intensity, the dewatering of ADS with cationic polyacrylamide polymer responds in a parabolic nature, with respect to the shear duration. This indicates the conditioned sludge will improve in dewaterability, up to a certain point of shear addition. Shearing conditioned ADS beyond this point of shear duration results in lower dewaterability. At a sufficiently high shear intensity, there is no longer a parabolic response, as dewatering linearly worsens with shear duration. Using the floccy rheometer, both the 1-step and 3-step cycles were able to capture the optimum polymer dose range reasonably well. After dewatering the sheared ADS, measuring the absorbance spectra of sludge filtrate has the potential to detect the optimum shear conditions to maximize polymer uptake into flocs, thus minimizing the escape of polymer into the environment.

6 Future Work

The in-line UV-vis spectrophotometer should be used to further evaluate the potential to measure residual polymer concentration after sludge dewatering. Filtrate collected from dewatered sludge should be analyzed with the in-line UV-vis spectrophotometer to evaluate and calibrate for potential differences between in-line and off-line absorbance measurements.

The UV-vis spectrophotometer should also be used to monitor the ageing of different polymer types to assess whether the developed method for ageing determination can be applied to multiple polymer types. Polymers with variations in ionic strength, ionic type, and molecular weight could be tested. In addition, different polymer preparation methodologies should be tested to further evaluate how the preparation influences polymer ageing, and whether the spectrophotometer can continue to detect these changes. The most important of these would be to test the method of polymer crystal addition to the water it is to be emulsified in. For example, the polymer crystals can be spiked into the solution, or gradually added. Furthermore, with the gradual addition of crystals, the rate at which the crystals are added to the water should be varied so as to assess the influence on polymer maturation. This is important for the purpose of minimizing the formation of large clumps of polymer during mixing, also known as fish-eyes.

For more rheological analysis, different combinations of shear (i.e. intensity and duration) should be added to ADS prior to conditioning with polymer, then testing sludge dewaterability. This would provide information regarding how different levels of shear experienced by sludge prior to reaching the dewatering stage influence the dewaterability of sludge. This could assist with design of treatment systems such that the sludge experiences a desired amount of shear prior to reaching the dewatering equipment.

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Appendix

Appendix A. Polymer Maturation Evaluation

A1. Sample Calculation for mass of KH_2PO_4 and K_2HPO_4 , using Henderson-Hasselbach equation:

$$pH = pK_a + \log_{10} \left(\frac{[A^-]}{[HA]} \right)$$

Calculating for pH of 6 and $pK_a = 7.21$ for KH_2PO_4 and K_2HPO_4 , the equation is resolved:

$$6 = 7.21 + \log_{10} \left(\frac{[A^-]}{[HA]} \right)$$

$$\log_{10} \left(\frac{[A^-]}{[HA]} \right) = -1.21$$

$$\left(\frac{[A^-]}{[HA]} \right) = 0.063 \quad [\text{equation 1}]$$

Using a total molar concentration of 0.05 M for KH_2PO_4 and K_2HPO_4 :

$$[HA] + [A^-] = 0.05 \text{ M} \quad [\text{equation 2}]$$

Solving with equation 1 and 2:

$$[HA] = 0.047 \text{ M} \Rightarrow \text{KH}_2\text{PO}_4$$

$$[A^-] = 0.003 \text{ M} \Rightarrow \text{K}_2\text{HPO}_4$$

The molecular weight of $\text{KH}_2\text{PO}_4 = 136 \text{ g/mol}$ and $\text{K}_2\text{HPO}_4 = 174 \text{ g/mol}$, and a volume of 500 mL distilled water was used, therefore converting the above to a mass gives:

$$\text{mass KH}_2\text{PO}_4 = 3.2 \text{ g}$$

$$\text{mass K}_2\text{HPO}_4 = 0.26 \text{ g}$$

A2. First order rate of change (ABS vs. time) for various trials:

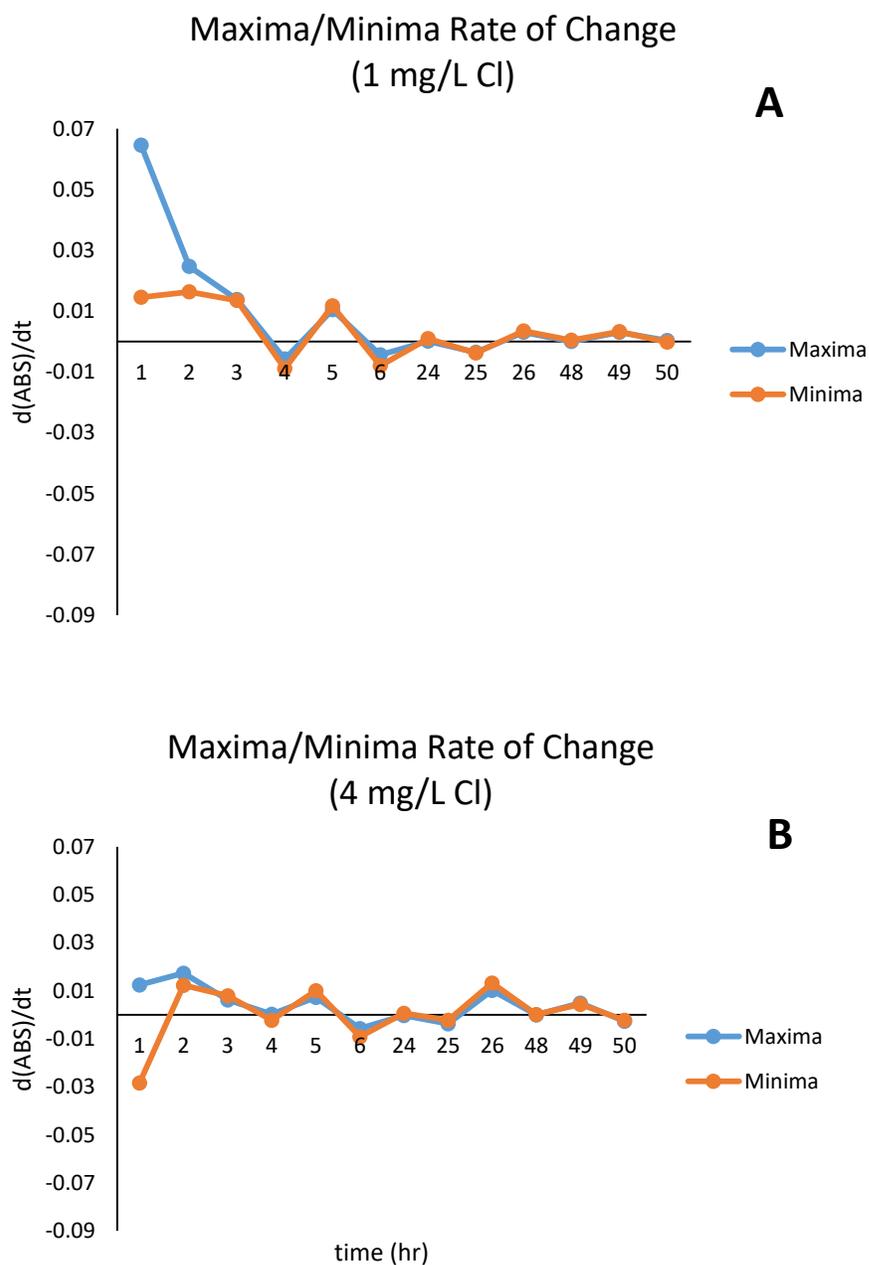


Figure A- 1. First order rate of change at the maxima and minima of polymer stock solution prepared with A-1 mg/L and B-4 mg/L of hypochlorite (ClO^-).

Table A- 1. Solids content of the anaerobically digested sludge used for experimentation was determined using the oven drying technique.

Dish #	Mass of Dish (g)	Mass of Dish+Residue (g)	Difference (g)	C (g/L)	(C-Mean) ²
1	1.5824	2.2452	0.6628	16.57	0.001284
2	1.5974	2.2590	0.6616	16.54	0.004334
3	1.5499	2.2182	0.6683	16.71	0.010336
			Mean	16.61	
			δ	0.089	

Sludge sample volumes of 40 mL were used in each dish. Standard deviation was calculated as:

$$\sigma = \sqrt{\frac{1}{N-1} \sum (C - \text{mean})^2}$$

Appendix B. Rheological Analysis of Shear Impact on ADS Dewaterability

Table B- 1. Solids content of the anaerobically digested sludge used for experimentation was determined using the oven drying technique.

Dish #	Mass of Dish (g)	Mass of Dish+Residue (g)	Difference (g)	C (g/L)	(C-Mean) ²
1	1.9411	2.8872	0.9461	23.6525	0.000117
2	1.9513	2.9016	0.9503	23.7575	0.013417
3	1.9321	2.8727	0.9406	23.5150	0.016044
			Mean	23.642	
			δ	0.122	

Sludge sample volumes of 40 mL were used in each dish. Standard deviation was calculated as:

$$\sigma = \sqrt{\frac{1}{N-1} \sum (C - \text{mean})^2}$$

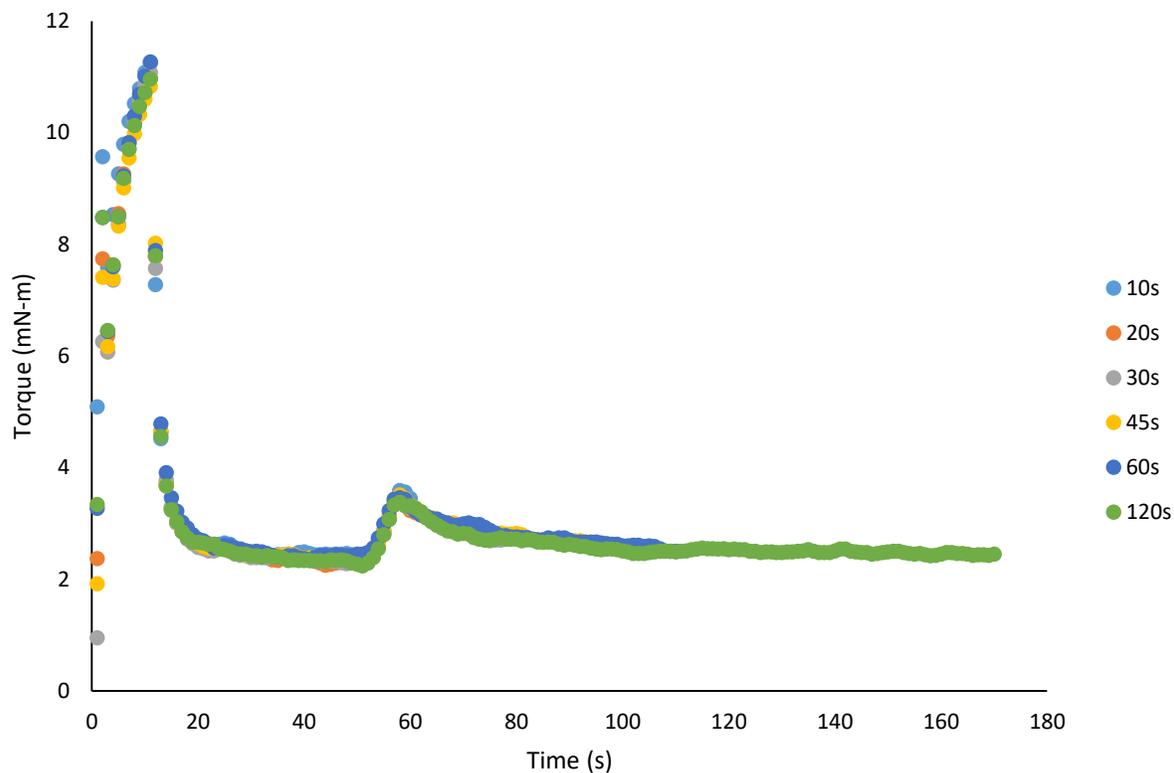


Figure B- 1. Floccky rheometer output for 3-step cycle with varied shear duration in the 3rd step (at 50 s) at the 150 RPM shear intensity.

Table B- 2. Comparison of the linear and second-order regression coefficient linking shear duration to CST, generated at each shear intensity.

Intensity	R²- Linear	R²- Quadratic
150	0.19	0.92
200	0.12	0.93
250	0.42	0.48
300	0.63	0.71
350	0.97	0.97

Table B- 3. Summary of the mean CST and associated standard error for conditioned ADS sheared for multiple combinations of shear intensity and duration. Standard error provided as supplementary info for Figure 27.

Shear Duration (s)	150 RPM		200 RPM		250 RPM		300 RPM		350 RPM	
	Mean CST (s)	Std. Err. (s)								
10	33.0	5.40	25.4	3.23	22.0	0.54	18.6	1.47	17.8	1.12
20	27.6	0.55	23.1	1.01	21.2	1.18	19.1	0.30	19.6	0.10
30	27.0	1.00	20.6	0.99	19.4	1.13	18.0	0.38	22.1	0.98
45	23.2	0.13	18.5	1.16	20.9	0.47	20.6	0.89	22.0	0.45
60	23.4	1.40	19.2	1.11	22.8	0.64	20.6	0.26	23.6	0.62
120	26.5	0.29	21.7	0.87	23.5	0.32	21.2	1.02	30.2	0.62