

A STUDY ON POLYMER-INDUCED FLOCCULATION IN INDUSTRIAL
WASTEWATER TREATMENT VIA A HIGH-THROUGHPUT METHOD

By,

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Descriptive Notes

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TITLE: A STUDY ON POLYMER-INDUCED FLOCCULATION IN INDUSTRIAL
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LAY ABSTRACT

Since some industrial facilities do not possess the capability of treating wastewater generated throughout their processes, they ship it to a specialized wastewater treatment facility, which treats it to a level safe enough for discharge into the sewage system. Accordingly, specialized wastewater treatment facilities receive dynamically varying wastewater loads from various industries on a daily basis. Thus, it is essential to have a method to run rapid tests for identifying optimum treatment conditions and cost savings opportunities while meeting the discharge limits set by the municipality.

Polymer flocculation is a common procedure in industrial wastewater treatment. In this work, a high-throughput method was used to run rapid polymer flocculation experiments using minimal wastewater volumes, and its capability to be used in optimizing the polymer flocculation process was investigated. In addition, methods that could be used for in-line monitoring of floc formation and for residual polymer concentration detection were tested. All of this work was done on industrial wastewater samples that varied in composition and were obtained from a specialized industrial wastewater treatment facility.

ABSTRACT

The main purpose of specialized industrial wastewater treatment facilities is to treat incoming wastewater loads from various industries which do not have the capability of treating their wastewater on site. Accordingly, specialized industrial wastewater treatment facilities face a challenge in quickly identifying optimal treatment options for the varying incoming wastewater loads they receive. With the new discharge limits set by the federal Wastewater System Effluent Regulations (WSER) and a compliance deadline by 2020, it became crucial for such facilities to optimize their processes and ensure having a method to determine optimal treatment options and conditions to meet the new discharge limits. One such limit is the Chemical Oxygen Demand (COD), which is representative of the amount of organic matter present in a solution.

Polymer flocculation is a common mechanism used for solid-liquid separation in industrial wastewater treatment. While many previous research studies have been previously conducted on polymer flocculation and industrial wastewater treatment, there seems to be a lack in studies that focus on running experiments in a rapid high-throughput manner and using samples that vary in composition and come from different generators/sources.

In this work, a high-throughput method was implemented to investigate several aspects in the polymer flocculation area on various wastewater samples obtained from a specialized industrial wastewater treatment facility. Using this method, the optimum polymer flocculant type, dosage and concentration were successfully identified for several wastewater samples. In addition to that, scale-up experiments were done in the

facility on various wastewater tanks to compare the performance of undiluted and diluted polymer flocculant. Diluted polymer flocculant was proven to successfully treat wastewater tanks to a level safe enough for discharge and just as good as undiluted polymer flocculant while using less “neat” polymer flocculant volumes. Moreover, possible cost savings and a better treated water quality were also achieved by implementing multi-staged polymer flocculation concept for industrial wastewater on a small scale.

This work also focused on testing the FBRM as an in-line method for particle size distribution measurements in industrial wastewater. However, even after an optimization attempt, it did not work well on the samples tested. Another in-line method that was also tested was UV spectroscopy. This method was proven to successfully work as a method to determine optimum polymer flocculant dose and could be a promising in-line tool.

Finally, bentonite was used as a flocculation aid along with polymer flocculants and design of experiments (DOE) methods were implemented to almost successfully reduce the COD, which as mentioned is an important water quality parameter, in automotive industrial wastewater samples with initial average COD of 77,000 ppm to the safe discharge limit (i.e. 600 ppm)

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List of Abbreviations

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
CST	Capillary Suction Time
DOE	Design of Experiments
FBRM	Focused Beam Reflectance Measurement
MDL	Method Detection Limit
MS	Multi-stage
NTU	Nephelometric Turbidity Units
RPM	Revolutions Per Minute
TOC	Total Organic Carbon
TS	Total Solids
UV	Ultraviolet

Chapter 1: Introduction

Industrial wastewater is defined as “liquid waste discharged from industrial activities such as manufacturing, mining, and power generation” [1]. In Canada, 29.9 billion cubic meters of the treated water discharged in 2009 into rivers, lakes and marine areas was from such industries [1].

Industrial wastewater cannot be discharged directly from the source of generation into the environment as it would be contaminated. Each industry is likely to produce wastewater, whether it was generated from the process itself, or from using water for some necessary practices in the process such as washing and cooling. For example, in the iron and steel industry, water is needed for cooling and as part of the separation of by-products. Thus, the wastewater produced from such an industry is usually contaminated with ammonia, cyanide, and several polycyclic aromatic hydrocarbons [2]. In the mining industry, wastewater could be produced from rock washing, coal washing and extraction of metals. The contamination in such an industry is mainly caused by the minerals present in the formations [2]. Industrial wastewater could either be treated for direct discharge into the environment, or to be used again in a process. In both cases, it has to undergo treatment.

If not treated well before discharge, industrial wastewater can have several negative impacts on the environment, especially on aquatic life and humans when they get in contact with it. Untreated industrial wastewater contains several contaminants such as nutrients, metals and organic matter. When industrial wastewater is not treated properly and is disposed into water bodies, one of the main negative impacts associated

is depletion of dissolved oxygen due to eutrophication. Eutrophication is basically the presence of excessive amounts of nutrients in water bodies, such as phosphorus and nitrogen, which lead to dissolved oxygen depletion and algal growth [3]. Dissolved oxygen depletion affects aquatic organisms and may contribute to death in some cases. In addition to that, it may also have an impact on the water body characteristics (i.e. the aquatic organisms' habitat), such as temperature [4]. Dissolved oxygen depletion can also be caused by high Chemical Oxygen Demand (COD). Industrial wastewater that contains high amounts of organic matter and oil, such as the ones from automotive industries, tend to have high levels of COD. COD is defined as Chemical Oxygen Demand, which is a measure of the amount of oxygen needed to oxidize mainly organic matter [5]. A high COD level indicates higher amounts of organic matter. This results in greater oxygen consumption, which eventually leads to dissolved oxygen depletion.

Industrial wastewater also contains suspended solids, which constitute mainly of undissolved organic and inorganic matter [6]. Suspended solids also have negative impacts on the environment. When disposed into water bodies, they can hinder the penetration of sunlight, which is needed for photosynthesis. They can also contribute to increasing the water temperature and decreasing dissolved oxygen since they can absorb heat from the sun [6]. In addition, metals in wastewater tend to adsorb onto suspended particles. Thus, suspended solids may contain high amounts of harmful metals as well [7]. These are just some of the examples of the impacts that industrial wastewater may have on the environment if it was discharged without being well treated.

Such impacts can also affect human health as well through the food chain. When aquatic organisms such as fish are exposed to untreated wastewater, the contaminants and toxic compounds that are present in the wastewater begin to accumulate in the organisms. This phenomenon is referred to as bioaccumulation. When humans consume fish that has been exposed and affected, they will also be at risk. The presence of metals and organic matter in water bodies due to discharge of untreated industrial wastewater can also have direct negative impacts on humans either when they drink it or get in contact with it. For example, some of the metals such as aluminum, iron and zinc could cause memory damage, degenerative diseases, and muscular pain [8]. Some organic matter can also cause cancer and damage some organs [8].

Discharging industrial wastewater into water bodies without treating it well has numerous catastrophic effects. Thus, for the sake of minimizing the negative impacts that such discharges have on the environment and humans, it is important to ensure proper treatment before discharge. While it is always preferred to reduce pollution right at the source of generation by altering the process to reduce the number of contaminants, it can be almost impossible to completely have no contaminants in the wastewater that leaves the process. Thus, any wastewater generated or used in a process by an industrial facility has to undergo certain levels of treatments to meet the laws for safe discharge into water bodies and the environment.

1.1. Industrial Wastewater Treatment Routes and Procedures

Industrial wastewater usually goes from the source of generation (i.e. industrial facilities) to the discharge location via three different options or routes, as seen in Figure 1. While some industrial facilities have their own on-site treatment options, others may choose to send their wastewater to specialized industrial wastewater treatment facilities which treat it to a level sufficient enough to be sent to conventional wastewater treatment plants through the sewer system before discharge. Some specialized industrial wastewater treatment facilities may choose to receive wastewater loads from various industrial facilities, and their main focus is to remove any contaminants that may interfere with the conventional wastewater treatment plant operation procedures. However, if the facility produces wastewater with characteristics similar to that of municipal wastewater, a municipal wastewater treatment plant may accept that loads be shipped directly to it instead.



Figure 1: Schematic that illustrates the different routes that wastewater can go through from the generator to the environment

Depending on the industry and the contaminants present in a wastewater load, different unit operations and stages exist for the treatment. Table 1 lists the treatment stages that are present in a conventional wastewater treatment plant.

Table 1: The purpose of the different treatment stages in a conventional wastewater treatment plant along with the unit operations used for each [9].

	Target/purpose	Processes
Preliminary treatment	Removal of large solids to not hinder the movement of water through pipes and tanks throughout the treatment	<ul style="list-style-type: none"> - Screening - Skimming - Filtration - Grit removal
Primary treatment	Removal of suspend solids and colloids	<ul style="list-style-type: none"> - Sedimentation (after coagulation/flocculation) - Flotation
Secondary treatment	Removal of organic matter. Also known as biological treatment	Aerobic/anaerobic suspended growth or fixed film
Tertiary treatment	Removal of nutrients and inorganic or toxic organics	<ul style="list-style-type: none"> - Adsorption - Oxidation
Disinfection	Removal of pathogens	<ul style="list-style-type: none"> - UV - Chlorination - Ozonation
Sludge treatment	Reduce sludge volume and stabilize it	<ul style="list-style-type: none"> - Thickening - Dewatering - Digestion

The level and stages necessary to treat a wastewater load depends on the incoming feed characteristics, treated wastewater discharge limits, and the treatment plant's capability and purpose. For example, some plants might not have the capability of implementing biological or sludge treatment and might have to send their effluents to another plant for that purpose. In addition to that, some wastewater loads may be successfully treated using only some of the treatment stages to meet the discharge limits. Table 2 below highlights some of the previous research studies that have been conducted in industrial wastewater treatment. As can be seen, not all of the aforementioned stages were used for the treatment. Note how these studies, and many others that have been published in this field, focused on just one source/type of wastewater.

Table 2: Previous work done on treating industrial wastewater samples. All of which were done on a single wastewater type/source

Wastewater source/type	Treatment method	Compounds targeted	References
Food oil (from oil and detergent industry)	<ul style="list-style-type: none"> - Zeolite adsorption column - Wastewater and lipase enzyme mixing tank 	COD and organic matter	[10]
Dye-containing wastewater (textile industry)	<ul style="list-style-type: none"> - Adsorption using activated carbon, bentonite and lignite - Coagulation 	<ul style="list-style-type: none"> - COD - Color 	[11] [12]

Wastewater source/type	Treatment method	Compounds targeted	References
Slaughterhouse wastewater	- Anaerobic sludge in batch reactors	- Total and soluble COD	[13]
	- Anaerobic reactor + aerobic activated sludge reactor + UV/H ₂ O ₂ photoreactor	- Total Organic Carbon (TOC)	[14]
Pulp and paper mill	- Anaerobic and aerobic treatment - Coagulation/oxidation /ozonation - Adsorption	- Soluble biodegradable organic compounds - Color - Chlorinated phenolic compounds	[15]
Pharmaceutical wastewater	Ozonation	COD, TOC and Biological Oxygen Demand (BOD)	[16]
Automotive wastewater	- Electrocoagulation - Anaerobic batch reactions	Oil and COD	[17] [18]
Industrial polymer effluent	Coagulation and flocculation	COD, suspended solids and color	[19]
Beverage Industry	Coagulation and flocculation	COD, total phosphorus and total suspended solids	[20]

1.2. Project Background

The work in this project is in collaboration with Aevitas, which is a specialized industrial wastewater treatment plant located in Brantford, Ontario. Each municipality has certain limits and regulations for treated wastewater discharge. In 2014, the City of Brantford set new sewer-use by-laws which wastewater facilities in Brantford had to

adhere to. This was as a result of the new WSER federal law. Under the new by-law, one of the important treated wastewater quality parameters is Chemical Oxygen Demand (COD). The new limit for this parameter is 600 ppm (mg/L), compared to 1000 ppm previously [21]. Thus, any facility discharging its wastewater into the City's sewer system should ensure that the effluent COD does not exceed that limit.

Aevitas receives around 15 to 20 tanker truck wastewater shipments a day from several facilities, mainly industrial and manufacturing ones, as depicted schematically in the figure below. The tanker trucks unload the wastewater in a tank where sometimes the loads in several trucks get blended, before transferring it to the treatment tank.

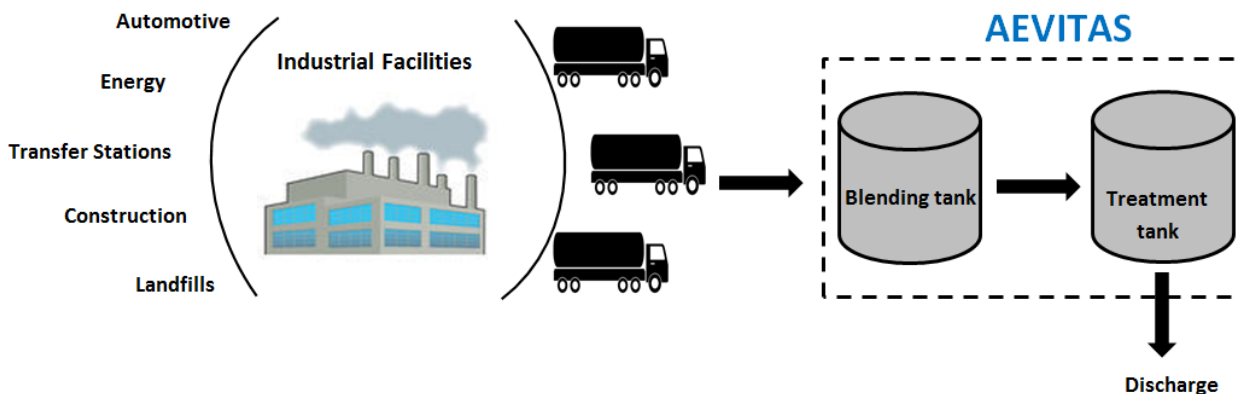


Figure 2: Aevitas receives 15 to 20 tanker trucks that contain wastewater loads from different industries every day

These loads/shipments vary in composition and characteristics. The histogram in Figure 3 shows the variation in COD values of the incoming wastewater loads that Aevitas received in 2014. There is clearly a significant variation in incoming samples. Thus, specialized facilities such as Aevitas have a great responsibility in identifying proper treatment methods for the varying incoming wastewater loads.

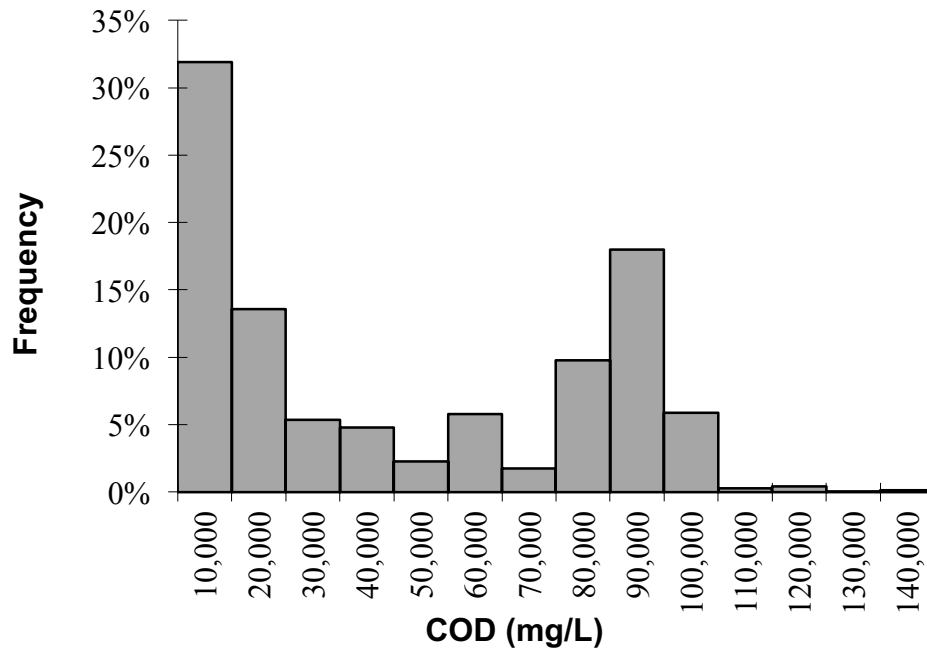


Figure 3: Histogram displaying the variation in COD values of incoming wastewater loads that Aevitas received in 2014. [Source: Kimia Aghasadeghi – personal communications]

Specialized industrial wastewater treatment plants treat incoming wastewater loads to a level sufficient enough to be accepted by a municipal wastewater treatment plant which will later discharge it into the environment. Thus, a specialized wastewater treatment facility does not really require all of the treatment processes mentioned in Table 1 in its plant. For example, the main process that Aevitas uses for their treatment is polymer flocculation, which is a process that will be explained in detail in section 1.5. This process is used to treat wastewater loads to a clarity level and COD value that allows them to discharge it into the sewage system, or ship it to another plant for further treatment. As mentioned earlier, the target COD is 600 ppm. In terms of clarity, turbidity is a common and simple measure. Turbidity is simply a measure of cloudiness of a liquid sample. A more scientific definition can be found in Section 2.5. The range of

turbidity of the effluents that were successfully discharged by Aevitas into the sewer system was 8 - 200 NTU.

1.3. Project Objectives

Table 2 shown earlier highlighted some of the studies that have been previously done in industrial wastewater treatment. As noted from the studies displayed in that table, most of the research done on treating industrial wastewater focused on a single wastewater source rather than a variety of sources. To the best of my knowledge, there are only a few papers that focused on experimenting with wastewater samples from various sources. Nasr et al. [22] studied COD removal via chemical and biological treatments on wastewater samples from two different industries: building and construction chemicals industry, and a plastic shoes manufacturing industry. It was found that chemical treatment worked better on the wastewater samples obtained from the construction industry and 94% of the COD was removed. However, for the samples obtained from the manufacturing company, biological treatment was a better option and could remove near 93% of the COD. Also, Bianco et al. [23] studied COD removal on various industrial wastewater samples, which varied in the initial COD content, using Fenton's oxidation reaction and a maximum of 80% COD removal was achieved. In another study, Aghasadeghi et al. [24] also used wastewater samples that varied in initial COD while optimizing the advanced oxidation process for COD removal using the design of experiments (DOE) methods and LC-OCD. A maximum of 82% COD removal was achieved [24].

However, unlike most of the previous studies in industrial wastewater treatment, the work presented in this thesis focused on treating wastewater samples that varied in characteristics and were generated by different industries rather than just one.

Aevitas receives up to one million liters of industrial wastewater a day (i.e. 15 to 20 tanker trucks a day, with an average volume of 50,000 L for each). Thus, having a method that allows individuals to run quick and simple tests to optimize the treatment process and to be able to identify the optimum chemicals needed for the treatment along with their dosages is crucial. Accordingly, in this work, a high-throughput technique that allows running several samples all at once was tested as a potential tool for running rapid tests. Using this technique, three main areas were explored and all were done on various industrial wastewater samples that varied in characteristics and were obtained from Aevitas:

- 1) Optimization of polymer-induced flocculation in industrial wastewater treatment
- 2) FBRM and UV absorbance as potential in-line industrial wastewater monitoring tools
- 3) Combination of clay with polymer flocculants for industrial wastewater treatment.

In the first area explored in this work, the main purpose was to test polymer flocculant types, dosages and concentrations that would treat different wastewater samples while lowering the polymer flocculant consumption and to experiment with methods of enhancing the effluent quality in terms of turbidity. The second area of focus in this work was testing the potential of in-line monitoring tools such as the Focused Beam Reflectance Measurement (FBRM) and UV absorbance as methods of optimizing the overall process of industrial wastewater treatment. The third area of focus in this

work was to treat wastewater samples with high COD values to a level low enough to meet the new by-law limit, and also experiment with possible options and alternatives for getting a better effluent quality.

While the work presented in this thesis mainly focused on enhancing and optimizing the treatment process that Aevitas implements, most of the concepts presented can be applied to any specialized industrial wastewater treatment facility that receives a variety of wastewater loads and uses flocculation as part of their process. Aevitas is not the only wastewater treatment facility that faces a challenge in determining optimum treatment options to meet the discharge limits for wastewater loads that vary in characteristics and come from different sources. For example, GFL Environmental and Clean Harbours are companies in Ontario that undergo the same challenge. In addition to that, another specialized wastewater treatment facility located in Brantford had to actually close down after the new discharge laws were set by the City of Brantford in 2014. Thus, it is really essential to focus on the challenges that such plants face and work on optimizing their processes.

In the coming sections, more details are presented on the mechanisms, processes, and tools implemented in this study. In addition to that, some previous studies that have been done in this field are presented in detail, and the main challenges and differences between them and this project are clarified and stated.

1.4. Polymer Flocculation

1.4.1. Purpose and Mechanisms

As mentioned earlier, industrial wastewater usually contains suspended solids and other particles small in size (i.e. 0.01 – 100 μm [25]) that cannot settle easily. This

is one of the main challenges faced in industrial wastewater treatment as it is critical and essential to remove such colloidal particles since they are considered as contaminants [26]. In some cases, being able to remove the suspended solids might be the only treatment required to meet disposal limits as most of the contaminants are usually adsorbed onto these solids, as mentioned earlier. However, in other cases, further treatment might be needed, such as biological treatment. Thus, a process for removing suspended solids from industrial wastewater is an essential part of the treatment.

Several solid-liquid separation methods exist such as gravity settling, drying, filtration, flotation, absorption, adsorption, ion exchange, and many more [26] [27]. In most cases, the method for separation is usually based on the particle size of the solids in the water sample. When it comes to solid-liquid separation in industrial wastewater, the most common technique used is coagulation/flocculation [26]. In coagulation/flocculation, specific chemicals are added into the wastewater tank. These chemicals have the ability to allow small suspended particles to come together to form larger ones and settle down, leaving a clear well-treated supernatant phase.

Coagulation/flocculation as a separation technique is usually chosen over others in industrial wastewater treatment for several reasons. The suspended particles in industrial wastewater are usually not very dense, so settling by gravity can take a really long time. The particles (suspended solids) can also be very small, so filtration can be really challenging. In addition, the chemicals for coagulation/flocculation can just be added into the tank in which the wastewater is stored and the suspended solids can be removed easily, without the need of transporting the water to another tank for flotation

or passing it through a column for adsorption. Thus, coagulation/flocculation is simple, does not require additional tanks or equipment, and does not have any energy costs other than those associated with mixing, which is essential for this technique.

By definition, coagulation is “the effect produced by the addition of a chemical to a colloidal dispersion resulting in particle destabilization by the reduction of the forces tending to keep the particles apart” [28]. Suspended solids or colloids in industrial wastewater are usually stable and repel each other since they are all negatively charged. Since the repulsion force between the colloids is usually greater than the force of gravity, they can never settle [29]. However, when a coagulant is added, it helps in neutralizing the charges on the colloids, which would allow them to start approaching each other rather than repelling. The final result is a group of colloids attached to each other, with clear water around it [29]. Thus, coagulation helps in creating unstable colloids to allow them to stick together. There are several coagulants that can be used, but the most common ones in wastewater treatment are alum and ferric chloride.

Flocculation is the step that usually comes right after coagulation. The main purpose of flocculation is to induce collision of the unstable colloids created via coagulation to bring them together (i.e. for them to aggregate) and form larger particles known as flocs [30]. This is because the particles usually formed after coagulation are fragile and not large enough to be able to settle by themselves [26].

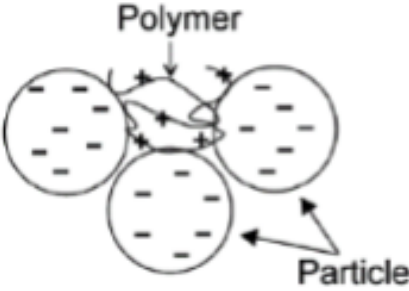
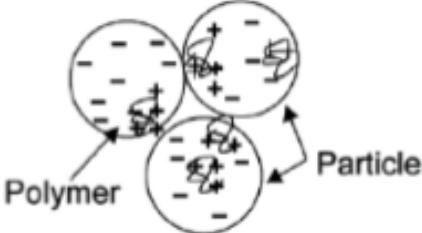
While it could be a common procedure for coagulation to always take place before flocculation, there has been research done on using just flocculation by itself for removing colloids. When performing both coagulation and flocculation for wastewater treatment, a cationic coagulant is first added to neutralize the negatively charged

colloids and bring them together, and then an anionic or non-ionic polymer flocculant is added to aggregate the particles and form large flocs that settle easily [26]. However, when using only flocculation without coagulation (i.e. direct flocculation), a cationic polymer flocculant would be added instead. In one study, various polymer flocculants were screened for treating aqua-cultural effluents without the use of any coagulants, and almost 99% of the total suspended solids were removed by most of the flocculants tested [31]. In another study, a polyacrylamide cationic flocculant was used to treat oily wastewater via direct flocculation and almost 96% of the oil was successfully removed [32]. Moreover, direct flocculation and coagulation-flocculation were also compared in a different study for treating palm oil mill effluent. Results indicated that direct flocculation was able to perform just as well as coagulation-flocculation; sometimes even slightly better. In addition, direct flocculation was proven to be more cost effective [33]. Thus, direct flocculation can indeed be sufficient enough for treating some wastewater samples. Not only does it perform as well as coagulation-flocculation, it also has several other advantages over the latter. Using direct flocculation requires lower dosages and eliminates the need of a coagulant, it forms lower sludge volumes, it does not require any pH adjustments since polymer flocculants are designed to work efficiently at various ranges of pH, it forms stronger and less fragile flocs that can settle easily, and it makes the treatment procedure easier and faster [31] [33]. However, in some cases, the pH still has to be adjusted in some samples, especially those containing emulsions, before the polymer flocculation step. More details about this are presented in Section 2.2.1.

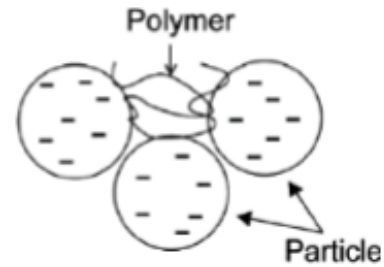
There are several mechanisms by which flocculation of particles via a polymer flocculant addition is believed to happen. The most common mechanisms are charge

neutralization, bridging and patch flocculation. The flocculation mechanism usually depends on the type of polymer flocculant used, its properties, such as molecular weight, as well as the medium in which flocculation is taking place [26]. The schematics in Table 3 below demonstrate each of the mechanisms.

Table 3: Common flocculation mechanisms in wastewater treatment [34].

<p>Charge neutralization: Via adsorption, the cationic polymer flocculant reduces and neutralizes the charge of the colloids. This in return will lower the repulsion force between the colloids and allows them to start approaching each other</p>	
<p>Patch flocculation: Via adsorption, the cationic polymer flocculant attaches to part of the colloid and forms a positively charged side. This positively charged side of one colloid then attracts to a negatively charged side of another colloid to form one particle or floc</p>	

Bridging: As clear from the name of the mechanism, in bridging flocculation, a long polymer flocculant chain acts like a bridge on which several colloids attach. Thus, this chain will end up attracting several colloids to form a large floc



There are many manufacturers that provide polymer flocculants with different characteristics and types. Some common manufacturers and common polymer flocculant types can be found in Section 2.2.2. This makes it challenging for a wastewater treatment plant as there are many options to choose from. Thus, before a treatment plant settles on a specific polymer flocculant, tests should be done on their wastewater to identify the best options, conditions, and methods of optimization.

1.4.2. Previous Wastewater Flocculation Studies

The most common and standard method usually used to screen and optimize polymer flocculants is the jar test [35]. A jar test consists of several square jars that can hold a volume of up to 2 L, with each jar having its own mechanical mixer. The most common jar test apparatus used is the one by Phipps & Bird, which has six 2 L square jars with a paddle in each and a sampling port. The speed of all the paddles is controlled by one motor [31]. The jar test can be used for several purposes such as finding the optimum flocculant dose, optimum pH, and testing several scenarios that could result in a better treated water quality. Thus, most of the research on flocculation was done using the jar test. For example, the jar test was used to screen the

performance of different polymer flocculants in treating aqua-cultural effluents [31], slurries [36] and construction runoff [37] in an attempt to find the optimum flocculant type and dose. It was also implemented to optimize the coagulation conditions for treating drinking water for a treatment plant by varying the alum dose [38]. In the study for treating construction runoff, polymer flocculants of various charges were used for the treatment. Based on turbidity results, an anionic and a non-ionic flocculants were chosen, and further studies were done to identify the better one based on dosage requirements and cost of each. The optimum polymer flocculant chosen in the study was the non-ionic flocculant Flomin 920 MC by SNF since it gave the lowest supernatant turbidity (6.1 NTU) and had a lower cost [37]. The purpose of the other studies was also similar.

Clearly, the jar test is a common procedure in most flocculation experiments and it seems to work just fine. However, when using the jar test, large quantities of wastewater samples are needed (i.e. usually between 1 to 2 L for a single jar). In addition to that, the typical apparatus usually consists of 6 jars only. If one wanted to test just a single polymer flocculant at 4 different dosages, and assuming the experiments have to be done in triplicates, he would need 12 jars, and around 12 L of wastewater. Thus, it is obvious that if a person wanted to test several polymer flocculants at several dosages, several sets of the apparatus and a few buckets of wastewater would be needed, and it would be very time consuming. In 2016, a study was done on a high-throughput method, which was referred to as a “Microscale Flocculation Test”, which was used to screen various polymer flocculants and dosages for treating municipal digestate [39]. Using this technique, various polymer flocculants

were tested at different dosages and the results were based on the Capillary Suction Time (CST), which is the time it takes a liquid sample to pass between two electrodes, of each of the supernatant phases after the treatment [39]. In this method, several flocculation tests could be done all at once and using smaller wastewater samples.

To the best of my knowledge, the majority of the previous experiments that focused on industrial wastewater polymer flocculation, if not all, were done at large scales (> 500 mL). In addition to that, in most of the studies on wastewater flocculation in general, including the ones mentioned earlier where a jar test was used, the focus of the experiments was usually on optimizing the polymer flocculant dose or finding the best polymer flocculant out of a selection of flocculants. Some papers did focus on other aspects in flocculation such as multi-stage flocculation, which involves the addition of the flocculant dose at several stages rather than all at once. In a study by Gregory and Guibai [40], the dosage for a cationic polymer flocculant was split and added at different stages rather than at once to treat a clay suspension at a 1 L scale. In this study, it was reported that using staged polymer flocculant addition produced flocs that were larger than those produced via a single addition [40]. Since larger flocs settle more easily and faster, the supernatant phase quality would be better. In another study, multi-staged polymer flocculation was also used to treat clay samples at a 300 mL scale [41]. A palygorskite suspension, which is a type of clay minerals, was also treated using multi-stage addition of the polymer flocculant [42]. In this study, half the polymer flocculant dosage (1.25 kg/t) added at several stages was able to achieve the same extent of flocculation to that using 2.5 kg/t of the polymer flocculant at a single stage [42]. These results were based on the settled volume at various dosages added all at once and at

different stages after 24 hours [42]. However, to the best of my knowledge, there have been no similar studies to date done on industrial wastewater. Most of the multi-stage flocculation studies were in fact done with clay suspensions and at large scale rather than in a high-throughput manner.

1.5. Polymer Flocculation In-line Monitoring Tools

Having an in-line monitoring system that could detect changes in particle size could be a beneficial tool in optimizing the flocculation process in industrial wastewater treatment. During flocculation, after addition of the polymer flocculant, small particles start aggregating to form larger particles. Thus, an in-line monitoring system would show a sudden increase in particle size when the flocculant is first added, and then a decrease as the flocs start to settle and a clear supernatant phase begins to appear. One of the tools that have been previously used to monitor floc size is the Focused Beam Reflectance Measurement (FBRM). The FBRM has a probe that has a rotating laser within it that detects the chord length distributions of particles and suspensions [43]. FBRM was originally developed and intended for studying crystallization processes but it has been used for other applications as well, especially in the mining industry to study mineral suspensions [43] [44].

In addition to particle size, having a method to also detect polymer concentrations in the wastewater industry can be very useful as it can enable operators and engineers to know if they are overdosing their polymer flocculant or not. Being able to detect an overdose in the polymer flocculant used for wastewater treatment can be beneficial as it can result in cost savings and a better treated water quality that has minimal environmental impacts. There have been several methods investigated for

detection of polymer flocculants in solutions and suspensions. These methods include size exclusion chromatography, N-bromination of amides, fluorescence spectrophotometry and many more [45].

UV absorbance is also another method that is becoming important and common, as it can also be implemented as an in-line monitoring system. It has been previously used in several studies dealing with polymers and has been implemented as a method for in-line monitoring for measuring and detecting polymer concentrations in water and wastewater. It is considered as a sensitive and simple method for that purpose, something that the water and wastewater treatment industry is lacking [46].

The first study that implemented the use of FBRM in wastewater treatment was in 2004 by De Clercq et al. [47]. It was used to measure particle size in a secondary clarifier of a wastewater treatment plant [47]. In one study, the FBRM was used to measure the flocculation performance of several polymer flocculants on municipal digestate [43]. In this study, the FBRM output results were used to calculate the percent removal of particles less than 50 microns in size, and the polymer flocculant that gave the highest percent removal along with the lowest Capillary Suction Time (CST) was chosen as the optimum one [43]. The FBRM was also used in other studies for real-time monitoring of flocculation performance of clay suspensions [48], ground calcium carbonate (GCC) suspensions [49], dye wastewater [44], oil sand tailings [50], and municipal wastewater [47]. However, to the best of my knowledge, there are no studies that involve using the FBRM for in-line monitoring in industrial wastewater treatment

In one old study, UV spectroscopy was used as a method for determining the concentration of an acrylamide copolymer in suspensions of pulp fiber and titanium

dioxide by building a correlation between the polymer concentration and absorbance at around 200 nm [45]. The first study that focused on detecting and measuring polymer flocculant concentrations in the wastewater industry was in 2013, and it was done on industrial sludge centrate [46]. In this study, a polymer flocculant was added to a treated sludge centrate at different concentrations. The UV absorbance was then measured between 200 and 300 nm for each of the concentrations. Absorbance at lower wavelengths was then plotted against polymer concentration and a linear relationship was observed [46]. Using this plot, one can measure the absorbance of a treated sludge centrate of the same source/generator and be able to determine the amount of residual polymer flocculant present in it. Other similar studies were also performed on different wastewater sources such as raw wastewater and the supernatant phase of a sample obtained after flocculation [51]. A recent thesis was also published that focused on using the UV absorbance as a method of measuring polymer concentration and optimizing sludge dewatering [52]; several aspects were studied such as the effect of pH on the detection of polymers, comparison between different detection methods, and determination of an optimum polymer dose based on absorbance, CST and filtrate volume [52]. Again, to the best of my knowledge, there are no research studies done on using this method specifically for industrial wastewater and on whether UV absorbance can detect that there is a difference between various wastewater sources and actually produce different curves for each of them.

1.6. Clay Materials and Organic Matter

As mentioned earlier, COD is one of the methods used to measure oxygen demand in wastewater samples. COD is an important parameter due to its negative

impact on aquatic life. Other methods to measure oxygen demand include Biological Oxygen Demand (BOD) and Total Organic Carbon (TOC). COD measurement is preferred over the other options for several applications as it is less expensive than TOC measurements and takes less time than BOD measurements [53]. The most common method used for measuring COD is by using dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) as the oxidant. A certain amount of the wastewater sample is heated at 150°C for 2 hours in a vial containing sulphuric acid and potassium dichromate, which reduces the dichromate ion to Cr^{3+} . The vial is then allowed to cool down to room temperature before measuring the concentration of the produced Cr^{3+} , which is representative of COD, using a colorimetric method [54] [55]. There are other methods to measure COD as well such as those involving using photocatalytic and photoelectrocatalytic principles [56], UV spectroscopy [57] and enthalpy changes [58].

There are several methods that can be used to remove COD. Table 2 in “Project Objectives” showed some of the previous methods that have been used for COD removal in industrial wastewater. Clay materials have also been used previously as a method to reduce COD in wastewater. The most commonly used clays in wastewater treatment are bentonite and kaolin. The main advantage of clays is that they have a large surface area, are easily available and are less expensive than activated carbon. Clays are mainly composed of inorganic minerals and other compounds that are capable of absorbing contaminants, suspended solids, and organic and toxic compounds [59]. Thus, they can be beneficial in treating industrial wastewater loads.

Abbood et al. [60] studied COD removal via coagulation and flocculation by using bentonite and alum to treat an oil refinery wastewater with initial oil concentrations up to

136 ppm. Oil removal efficiency of up to 75% was reached in the study, and bentonite was proven to be more efficient than alum [60]. Abdelaal [61] and Abdelaal et al. [62] also successfully treated refinery wastewater with initial oil content of 750 ppm and initial COD of 4800 ppm respectively, only this time, kaolin was used as the clay material rather than bentonite, and a 96.9% removal in COD was achieved. In addition to that, Younis et al. [63] studied COD removal, as well as BOD, for the treatment of sewage wastewater. A 77% total reduction in COD and BOD was obtained, allowing the effluent to meet the discharge limits [63]. Mazumder and Mukherjee [64] studied the effect of using bentonite along with alum as coagulants for treating various automobile service station wastewater samples with initial COD values of up to 445 mg/L. At certain dosages, complete removal of oil and grease was obtained [64]. Thus, there clearly have been previous studies on the use of clay in wastewater treatment. However, to the best of my knowledge, there have been no previous studies that focused on using bentonite along with cationic polymer flocculants to study the effect of clay on polymer-induced flocculation of automotive industrial wastewater with a very high initial COD.

Chapter 2: Materials and Methods

2.1. Wastewater Samples

All the wastewater samples used for the experiments were obtained from Aevitas in Brantford, ON. These were all incoming samples as received by Aevitas and were collected over around 18 months and always stored in a fridge in the lab at 4°C before usage. Since the company receives various loads of wastewater from different sources, there was always some sort of variation in properties of the samples, as stated earlier. Below are some properties of wastewater samples that were used in the experiments present in this thesis. For most of them, the results are based on average values of at least 10 reports provided by Aevitas for each of the samples. The initial turbidity value for all of them was out of range (> 1000 NTU).

Table 4: Properties of Aevitas wastewater samples that were used in the experiments. The asterisk identifies measurements that were taken in the lab.

Wastewater ID	Primary Source	COD (ppm)	pH*	TS (wt%)*	Oil (%)	Solids (%)
1	Automotive	77000	8.37	N/A	2.13	2.29
2	Construction	1500	7.04	N/A	N/A	1.13
3	Energy	N/A	7.03	0.96	N/A	N/A
4	Landfill leachate	8000*	8.70	N/A	N/A	N/A
5	Oily wastewater (Transfer station)	32000	7.65	N/A	2.80	2.42
6	N/A	N/A	8.68	1.2	N/A	N/A
7	Automotive	N/A	7.46	0.15	N/A	N/A

8	Automotive	N/A	7	0.77	N/A	N/A
9	Automotive	N/A	7.57	1.97	N/A	N/A
10	N/A	N/A	6.35	1	N/A	N/A
11	N/A	N/A	6.73	7.23	N/A	N/A

2.2. High-throughput Polymer Flocculation

2.2.1. pH Measurements and Adjustment

pH plays an important role in wastewater flocculation, especially in samples that have a high oil content. Most of the industrial wastewater samples that were received for experiments were automotive industrial wastewater and thus contained high amounts of oils and organic compounds. Breaking down the oil-in-water emulsions can help in increasing the efficiency of flocculation to provide a better treated water quality. In the lab, such emulsions were broken down by lowering the pH of automotive wastewater samples to 4 by using 2M sulphuric acid. The lower the pH, the more the emulsions are broken, but a pH of 4 is the lowest that the plant can have for its treatment and was proven to be low enough to perform good flocculation both in the plant and the lab. The 2M sulphuric acid solution used was prepared in the lab from a 98% liquid sulphuric acid solution from Fisher Scientific. The addition of an acid to such an emulsion helps in converting carboxyl ions in the sample into carboxylic acid, which allows the oil droplets to agglomerate [65]. It also helps in distorting the stability of dissolved solids in the sample, making it easier to form flocs during flocculation [65].

The pH of the wastewater samples from primary sources other than automotive (i.e. samples not containing oil-in-water emulsions) was increased to 9 by using 4M

sodium hydroxide after the treatment. This was to allow the metals to precipitate and have an efficient removal. The sodium hydroxide was prepared by using sodium hydroxide pellets from Fisher Scientific which were dissolved in distilled water. In the lab, pH measurements were done using VWR™ symphony B30PCI bench-top Multi-meter with pH probe.

2.2.2. Polymer Flocculants

Table 5 contains information about the main polymer flocculants, as provided by the manufacturers, used throughout the experiments in this thesis.

Table 5: List of polymer flocculants used in the experiments in this thesis along with their properties

	Manufacturer	Group/solution	Charge	Molecular Weight
Brennfloc CP2845 (P1)	Brenntag	Polyacrylamide	Cationic - high	Very high
Magnasol 4725 G (P2)	BASF	Polyelectrolyte	Cationic	<350 cP (supplied viscosity)
ClearFloc CE5050 (P3)	ClearTech Ind.	Polyacrylamide	Cationic - high	High
Sigma 522376 (P4)	Sigma Aldrich	Poly(diallyldimethylammonium chloride)	Cationic	Low
Sigma 409022 (P5)	Sigma Aldrich	Poly(diallyldimethylammonium chloride)	Cationic	Medium

	Manufacturer	Group/solution	Charge	Molecular Weight
Sigma 409030 (P6)	Sigma Aldrich	Poly(diallyldimethyl ammonium chloride)	Cationic	High
C-1598 (P7)	Kemira	Polyacrylamide	Cationic – Very high	High
A-1883 (P8)	Kemira	Polyacrylamide	Anionic – Medium	High
Flopam 1540 CT (P9)	SNF	Polyacrylamide	Cationic - low	High
Flopam 440 (P10)	SNF	Polyacrylamide	Cationic- High	low

In many experiments, diluted polymer flocculant was used. “Neat”, or undiluted, polymer was converted, or “made-down”, from its given concentration to a specific concentration. This is done by placing a medium size VWR™ magnetic stirrer (1/4” x 3/4”) into a beaker and filling the beaker with distilled water up to a certain level. The beaker is then placed on a VWR™ magnetic hotplate/stirrer and the RPM is set to 600. While the water is mixing, the required amount of “neat” polymer is transferred from the polymer container into the beaker via a pipette, and the RPM is increased to 1000. It is important to have a high mixing speed to allow the “neat” polymer to fully get diluted in the water. After 10 minutes, the mixer is turned off and the diluted polymer flocculant solution is left to sit for 15 - 30 minutes to allow the polymer chains to “relax” before being used. This is also referred to as aging, which is an additional step to ensure that

the polymer flocculant particles are fully dispersed and wetted before usage [66]. For example, a 1 wt% polymer flocculant solution was usually prepared by adding 50 mL of distilled water into an 80 mL glass beaker and letting it mix. Then, 0.5 mL, or 500 μ L, of “neat” polymer was transferred into the beaker via a pipette, allowed to mix for 10 minutes, and then the solution was left to sit for 30 minutes before being used. All other polymer flocculant concentrations were prepared in the same manner. It is important to note that the diluted polymer flocculant solution should be used within 24 hours of making; otherwise it loses its efficiency. In all experiments, unless stated otherwise, the polymer flocculant used was Clearfloc CE 5050.

2.2.3. General Flocculation Procedure

High-throughput flocculation involves running several small-scale flocculation experiments at a time rather than doing it beaker by beaker or using the jar test. After running some preliminary polymer flocculation experiments on samples individually and via the high-throughput, it was proven that the high-throughput method gives more reproducible and rapid results, and uses less wastewater volumes. Thus, it was used to run most of the polymer flocculation experiments in the project. Most of the experiments were done at a 25 mL scale, unless stated otherwise. All of these experiments were done following the same manner after running several preliminary tests to find the suitable conditions for running such experiments. For the 25mL scale, the beakers were first filled with the wastewater sample and small VWR™ magnetic stirrers (3/16” x 1/2”) were put in each. The pH was then usually adjusted via 2M sulphuric acid, and the beakers were then allowed to mix at 900 RPM for a minute. After that, the required polymer flocculant dose was added using a repeater pipette, and 10 seconds later, the

RPM was reduced to 300. The repeated pipette allows dosing multiple times rather than refilling the tip for every dose. The pH was then again adjusted and neutralized with 4M sodium hydroxide, unless mentioned otherwise. After 2 minutes of slow mixing (i.e. mixing at 300 RPM), the beakers were removed and left to settle for 15 minutes before assessing the water quality. This procedure was done for all flocculation experiments using the apparatus seen in Figure 4, which was also used to do the high-throughput studies on municipal digestate by LaRue et al. [39]. Only this time instead of using microplate wells and municipal digestate, 25 mL beakers and various industrial wastewater samples were used. It consists of a tumble stirrer (V&P Scientific) placed vertically. This provides a magnetic field that allows several magnetic stirrers to stir at once. The beakers containing the magnetic stirrers go on the trays fitted horizontally.

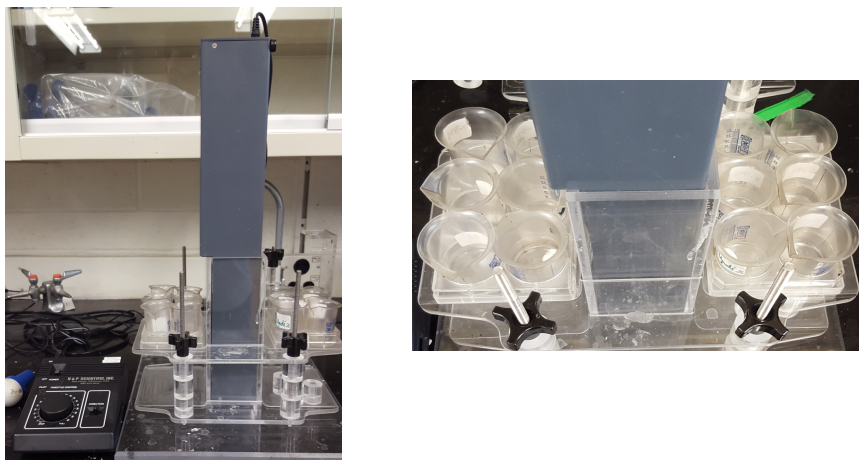


Figure 4: The apparatus used for running high-throughput flocculation experiments. A minimum of 12 25 mL beakers can be used at once. This allows conducting several rapid runs using smaller wastewater volumes compared to conventional techniques

Figure 5 shows a schematic of one of the experiments done to treat samples with different diluted polymer flocculant concentrations using the high-throughput technique. 5.5 μL of polymer flocculant for each 25 mL of wastewater corresponds to 0.22 g/L.

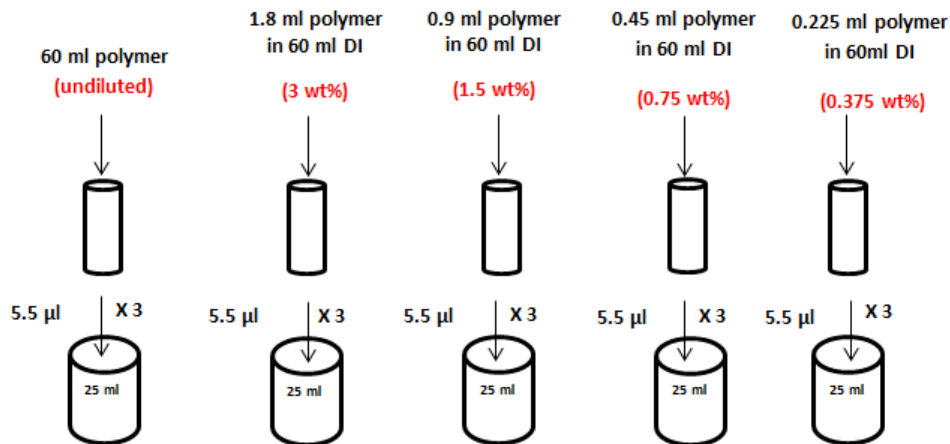


Figure 5: A schematic that demonstrates how the high-throughput experiments were conducted

2.2.4. Multi-stage Polymer Flocculation

The concept of multi-stage polymer flocculation was explained earlier in Section 1.4.2. To test whether splitting the required flocculant dose and adding it at different stages throughout the polymer flocculation step could actually enhance the treated water quality rather than adding it all at once at the same spot, three different sets of experiments were performed:

- 1) In the first set of experiments, 8 beakers were filled with 100 mL of wastewater. The first 4 beakers were treated with a direct dose of 0.2 g/L of the polymer flocculant, and the second 4 beakers were treated with the same dose, but split at 3 points; 0.10 g/L at the first point, and 0.5 g/L at the second and third point. After settling for 15 minutes, the supernatant phase was taken for water quality measurements. This was done using 1 wt% polymer flocculant solution. A schematic of the difference between the two methods is shown in Figure 6. Under this section of experiments, another experiment

was done to test the effect of multi-stage polymer flocculant addition on the total solids (TS) of the supernatant phase. The same procedure was followed. There was only a difference in the polymer dosages used. 0.22 g/L of undiluted polymer flocculant was added in the direct addition, 0.11 g/L of undiluted polymer flocculant was added at two different stages in the 2-staged addition, and 0.09 g/L, 0.067 g/L and another 0.067 g/L were added at three different stages in the 3-staged addition.

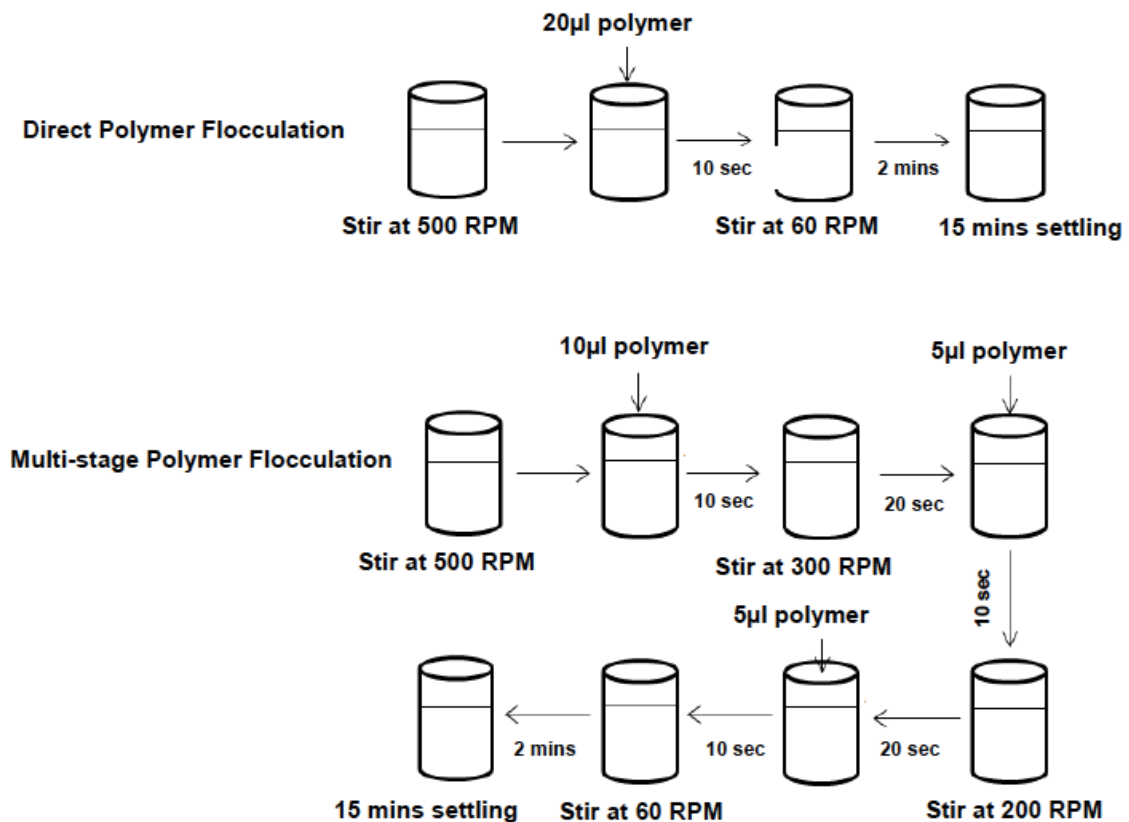


Figure 6: Schematic to demonstrate the difference between direct polymer flocculant addition and multi-stage polymer flocculant addition. In the latter, the dose is split at several points throughout the process.

- 2) In the second set of experiments, the same procedure as above was implemented, only this time the dosage for the multi-stage addition was varied. The direct dose of the polymer flocculant remained at 0.2 g/L, but the multi-stage dose was 0.1 g/L this time, split into 2 points, 0.05 g/L to each. The purpose of this was to see if a lower dose of a polymer flocculant added in a multi-stage manner could give a treated water quality better or at least similar to that treated with a higher direct addition dose. This was done also using 1 wt% polymer flocculant solution.
- 3) The last set of experiments in this section was done to test the effect of multi-stage polymer flocculant addition on the treated water COD value and whether it improves it or not. The procedure here was altered a bit. The first 2 beakers were treated by adding a direct undiluted polymer flocculant dose of 0.22 g/L (stage 1). The supernatant phases of these samples were then taken out after settling, and 0.11 g/L of undiluted polymer flocculant was added to them (stage 2). Again, after settling, the supernatant phases of stage 2 samples were taken, and 0.067 g/L of undiluted polymer flocculant was added to them (stage 3). After settling, the supernatant phase of each beaker was taken and the COD was measured.

2.3. Polymer Flocculation Scale-up Experiments

To reach more conclusive results on whether diluted polymer flocculants work just as well as neat ones, and whether the experiments are scalable or not, experiments were done on larger wastewater volumes.

2.3.1. Lab Scale-up Experiments

Experiments were done at a 25 mL, 200 mL and 1.6 L scale. The 25 mL and 200 mL scale experiments were done using the high-throughput using the procedure mentioned in Section 2.2.3. The 1.6 L scale experiments were done using a Phipps&Bird jar test apparatus. Wastewater was filled up to a 1.6L level and the RPM was set to the maximum (i.e. 300 RPM). 10 seconds after the polymer flocculant addition, the RPM was reduced to 80 for 2 minutes, before allowing the samples to settle for 15 minutes before any water quality measurements. In all of these scale-up experiments, the polymer dose added was 0.22 g/L, whether it was diluted or not.

2.3.2. Plant Scale-up Experiments

After running polymer flocculation experiments at a lab scale, the next scale up was on 45,000 L tanks at Aevitas. This time, large quantities of diluted polymer flocculant were needed. Since the plant did not have a polymer make-down system, the diluted flocculant had to be prepared manually. The polymer concentration tested at the plant was 1 wt%. This was done by filling a tote with 800 L of tap water and inserting an overhead mechanical mixer from the top. 8 L of neat polymer were then slowly added to the tote as the mixer was on. It was allowed to mix for 15 minutes and left to sit for 15 minutes before being used.

Plant scale-up experiments were done on 5 tanks. The main purpose was to test if there will be savings in treatment cost if diluted polymer was used rather than neat polymer. “Wastewater 1” was first treated by adding sulphuric acid to lower the pH to 4. The pH was measured using pH strips, which do not really give the exact pH value compared to a pH meter. After that, 100 L of 1 wt% polymer flocculant was added at a

time and allowed to mix. After each 100 L, a sample was taken out of the tank to check the water clarity. This was done until the treated wastewater looked similar to what the operators used to get while using neat polymer. Base was not added to these samples since the pH was not below the minimum limit for discharge or shipping for further treatment. The other wastewater loads were treated without the acid as they did not contain oil emulsions. 50 L of 1 wt% polymer flocculant was added at a time while mixing. Caustic was also added after the polymer flocculant to increase the pH to near 9 to allow the metals to precipitate and enhance the water clarity. The tanks were mixed for near 10 minutes and allowed to settle for 10 to 15 minutes before quality measurements were done.

2.4. Clay and Polymer Flocculation

As mentioned in Section 1.3, an area of focus in this project was whether clay materials combined with polymer flocculation could help in lowering the COD of industrial wastewater samples with a high initial COD level. The polymer flocculant used in this section was undiluted ClearFloc CE5050, whose properties and information have been specified in Table 5. Unless mentioned otherwise, “polymer flocculant” refers to this polymer. For pH adjustments, 2M sulphuric acid and 4M sodium hydroxide were again used. The filter paper used was “Whatman™ Grade 1 Qualitative Filter Paper Standard Grade, circle, 110mm”. The incubator used in one of the experiments (section 3.10.7) was Fisher Scientific Isotemp and was set at 70°C always.

The wastewater used for the experiments in this section was “wastewater 1” since it has a very high initial COD (77000 ppm on average). Thus, any “wastewater” term in these experiments refers to wastewater of that type.

2.4.1. Clay Properties

The two clays that were tested, kaolin and bentonite, were both purchased from Sigma-Aldrich in 2.5 kg and 500 g bottles respectively. Their properties, as specified by the manufacturer, are provided in the table below:

Table 6: Properties of the clays (bentonite and kaolin) used in the experiments, as specified by the manufacturer.

	Kaolin	Bentonite
Product number	K7375	285234
Color	White to light yellow	White to grey
Form	Powder	Powder
pH	3.5 - 5.5	7 - 10.5

2.4.2. DOE Studies

A Design-Of-Experiments (DOE) approach was performed for each of the clays tested. This is a systematic approach in statistics that is used in planning experiments where several factors can play a role on the experimental output, either individually or by an interaction between the factors. A DOE can help in determining the relationship between these factors and which factors have the most significant impact on the output through a linear model [67]. The most important step in these studies is identifying the factors to be experimented and the levels for each factor. In a DOE, each factor is given either a low level (-1) or a high level (+1). After determining the factors and setting the levels that are of interest, a design table is set and the experiments are done in a random order.

The DOE studies performed consisted of three factors that are the most likely to affect the treated water quality: pH, clay dose and polymer flocculant dose. The experiments in this section were done using the high-throughput technique at a 25 mL scale that was mentioned in Section 2.2.3, and in duplicates.

2.4.2.1. Kaolin DOE Levels

The low and high (-1 and +1) levels for the adjusted wastewater pH for this DOE were 4 and 9.5 respectively. These were selected based on the pH range at which the wastewater can be discharged, literature review, and bench-top experiments. For the kaolin dose, the low and high (-1 and +1) levels were 3 g/L and 10 g/L respectively. These were also determined based on literature review and bench-top experiments. Finally, for the polymer flocculant dose, the low and high (-1 and +1) levels were 0.2 g/L and 0.4 g/L respectively.

2.4.2.2. Bentonite DOE Levels

The low and high (-1 and +1) levels for the adjusted wastewater pH for this DOE were 4 and 7.5 respectively. These were selected based on the pH range at which the wastewater can be discharged, literature review, and bench-top experiments. For the bentonite dose, the low and high (-1 and +1) levels were 3 g/L and 16 g/L respectively. These were also determined based on literature review and bench-top experiments. Finally, for the polymer flocculant dose, the low and high (-1 and +1) levels were 0 g/L and 0.3 g/L respectively.

2.4.2.3. High-Throughput Experimental Procedure for DOE and Other Experiments

After doing some literature review, bench-top experiments, and setting the low

and high levels for each factor, the two-level design table for the three factors for each DOE was set as follows:

Table 7: Two-level three-factor DOE design table used in the DOE studies for clay and polymer flocculation

Standard order	Actual order	Clay dose	Polymer dose	pH
1	6	-	-	-
2	2	+	-	-
3	5	-	+	-
4	3	+	+	-
5	7	-	-	+
6	1	+	-	+
7	8	-	+	+
8	4	+	+	+

The procedure was similar to that of the high-throughput flocculation mentioned in Section 2.2.3. The only difference is that the predetermined clay dose is added and mixed at 900 RPM for 2 minutes before adding the polymer flocculant (undiluted) and continuing the usual procedure. Experiments were done in duplicates, unless mentioned otherwise. This procedure was used for both the DOE and all other experiments done using clay with polymer flocculation.

For the DOE, “R” software, which is a software used along with DOE rather than using hand calculations, was used to develop the linear model and generate a Pareto plot to identify the interactions and effects of the factors on the treated supernatant COD. This was done by writing a simple code in the software and inputting the output

results (in this case the average COD for each duplicate). The code used in “R” along with the output can be found in Appendix A.

2.4.3. Sludge Recycling

When doing experiments involving the addition of clay (especially at high dosages) before the polymer flocculant, the amount of sludge that forms is usually more than that formed through the addition of just polymer flocculant by itself. The purpose of this part of the experiments was to test if the sludge formed after the bentonite-polymer flocculation in a beaker could be used to treat wastewater in another beaker. The sludge that forms after the treatment of a wastewater sample in a beaker through bentonite and polymer flocculant is likely to still have some “free” polymer sites and bentonite surface area that could be used to treat another beaker without having to add the usual amount of materials/chemicals to it.

Three different scenarios were tested. In each scenario, the first stage was kept constant, which was done using the procedure mentioned in the previous section and using 0.3 g/L polymer flocculant, 16 g/L bentonite and a pH of 4. Samples were just allowed to settle for 15 minutes before the second stage.

- Scenario 1: After the first stage and settling, the sample was passed through a filter paper and the sludge was collected. Before that however, a sample of the supernatant phase was taken for COD measurements. At the same time, the pH of another pair of beakers filled with wastewater was also adjusted to 4 and allowed to mix for a minute at 900 RPM. In the second stage, the sludge collected from stage 1 was then added and allowed to mix for 30 seconds, after which 0.12 g/L of polymer flocculant was added. RPM was

reduced to 300 after 10 seconds for 2 minutes before allowing the samples to settle for 15 minutes, after which a sample of the supernatant phase was taken for COD measurements.

- Scenario 2: The same method as in scenario 1 was applied, except this time instead of adding 0.12 g/L of polymer flocculant in the second stage, 0.3 g/L were added
- Scenario 3: The same method as in scenario 1 was applied, except this time instead of adding 0.12 g/L of polymer flocculant in the second stage, 16 g/L of bentonite were added.

2.5. Turbidity Measurements

Simply put, turbidity is a measure of “cloudiness” of a fluid. It is the degree to which suspended particles in liquid scatter light at 90 degrees from an incident white light [68]. Its units are Nephelometric Turbidity Units (NTU). The lower the NTU, the clearer the water is (i.e. less suspended particles).

Turbidity was one of the main measurements done throughout the project. This is mainly because its results usually correspond to what can be visually noticed. Samples that appear to be clear always have lower turbidities than those that appear hazy. The measurements were done using Hach® 2100Q Portable Turbidimeter kit. Before each set of measurements, the calibration was first verified by using the 10 NTU sample vial that is provided with the kit. After the calibration has been verified, the turbidity of the supernatant phases of treated wastewater was measured by transferring 10 or 15 mL of the supernatant phase into the turbidimeter vials that were also provided with the kit.

Each vial is then placed into the turbidimeter, which gives the turbidity value in NTU within seconds.

2.6. Total Solids Measurement

Total solids (TS) is another parameter that can be simply measured in the field of wastewater treatment. This represents the amount of solids present in a sample, and is usually measured in wt%. This was done using the standard methods for examining water and wastewater quality

2.7. COD Measurements

Chemical Oxygen Demand (COD) has already been defined in Section 1.6. COD measurements were done in several experiments as a measure of treated water quality. This was done by transferring the supernatant phase of a sample into HACH High Range Plus COD digestion vials, which are used to measure COD values between 200 and 1500 ppm. In most cases, the sample had to be diluted at 1:20 or 1:40 ratio with distilled water when added into the vial. After the samples were added to the vial, they were placed in a HACH DRB 200 reactor and allowed to digest for 2 hours at 150°C. It is important to have a blank vial that only contains distilled water as well. After 2 hours, the vials were allowed to cool down to near room temperature and then the COD was measured using the HACH DR 3900 spectrophotometer.

2.8. UV Absorbance Measurement

As mentioned in Section 1.5, UV absorbance could be a potential in-line monitoring tool and could be used to detect polymer concentrations. UV absorbance measurements were done using a UV-Vis spectrophotometer (Beckman Coulter DU

800). Most of the UV absorbance measurements were done after treating a wastewater sample. Thus, after the sample is treated through polymer flocculation, near 3mL of the supernatant is transferred via a pipette into a quartz cuvette, which is then placed into the spectrophotometer and the absorbance at a specific wavelength or over a range of 190 or 200 to 400 nm was measured. This procedure was applied to measure the UV absorbance for all samples. It is important to note that the UV light wavelength is not compatible with most types of cuvettes; thus, a quartz one has to be used for such measurements.

2.9. Focused Beam Reflectance Measurement (FBRM)

Focused Beam Reflectance Measurement (FBRM) as an in-line monitoring tool has been previously investigated, as mentioned in Section 1.5. FBRM measurements in this project were done using an FBRM instrument (Particle Track G400) by Mettler Toledo™ that is available at the Biointerfaces Institute at McMaster University. The general procedure to run these experiments was to fill a 100 mL beaker with 80 mL of wastewater, and place it on a VWR™ magnetic hotplate/stirrer with a medium VWR magnetic stirrer (1/4" x 3/4"), unless stated otherwise in the results. Once the FBRM probe is cleaned with distilled water, it is placed into the beaker and the software connected to the FBRM starts generating the plots. In the experiments in this project, the FBRM was used to monitor specific ranges of particle size (less than 10 microns, 10 - 50 micron, 100 - 300 micron and 50 - 100 micron). The output graph in this case would be the number of counts of particles in each size range versus time.

Chapter 3: Results and Discussion

3.1. Polymer Flocculant Screening Tests on Industrial Wastewater

Two main polymer flocculant screening experiments were done on different samples in an attempt to identify an efficient polymer flocculant for the wastewater loads received by Aevitas. All of these experiments were done again in a high-throughput manner at the 25 mL scale, and the performance measurement used was turbidity.

The first set of screening experiments was done on “wastewater 1”, which is automotive industrial wastewater. Treated samples had to be diluted for turbidity measurements at a 1:9 ratio with distilled water. This was because measuring the turbidity of most of the samples after treatment as is gave a turbidity value that was out of range. The experiments in this first screening study were done in triplicates and using a constant polymer flocculant dose of 0.32 g/L, since the wastewater sample is difficult to treat with the 0.22 g/L dose. The results obtained are displayed in the Figure 7 below. The polymer properties can be found in Table 5.

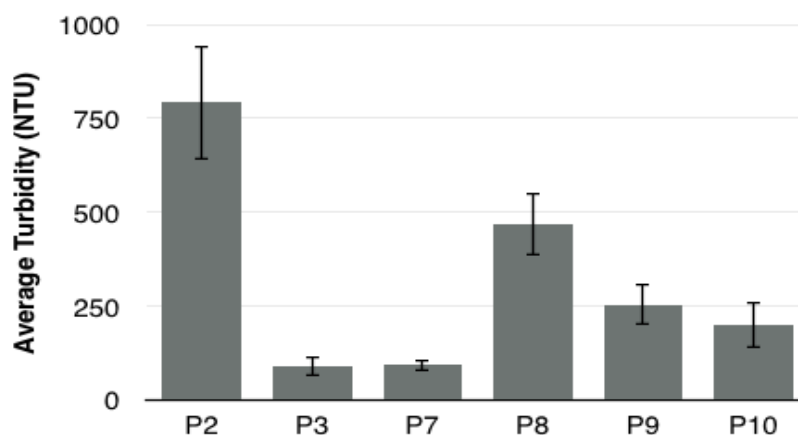


Figure 7: Average turbidity (NTU) of the supernatant phase of "wastewater 1" samples treated using different types of polymer flocculants (labeled P1, P2, etc.) at a constant dose of 0.32 g/L

As seen in the figure, ClearFloc CE5050 (P3) flocculant gave the lowest turbidity. P7 gave a turbidity value close enough, with a % difference of 4, and P9 and P10 were also statistically identical to P3, but the turbidity of the supernatant phase treated with P3 was still lower. Thus, ClearFloc CE5050 seems to be a good polymer flocculant for treating this type of wastewater.

The second set of polymer flocculant screening studies focused more on comparing the performance of P1 with P3 since it was believed by Aevitas that P1 might be able to perform slightly better. Experiments were done using a constant dose of 0.22 g/L of polymer flocculant, whether diluted or not. The figures below show some of the results obtained

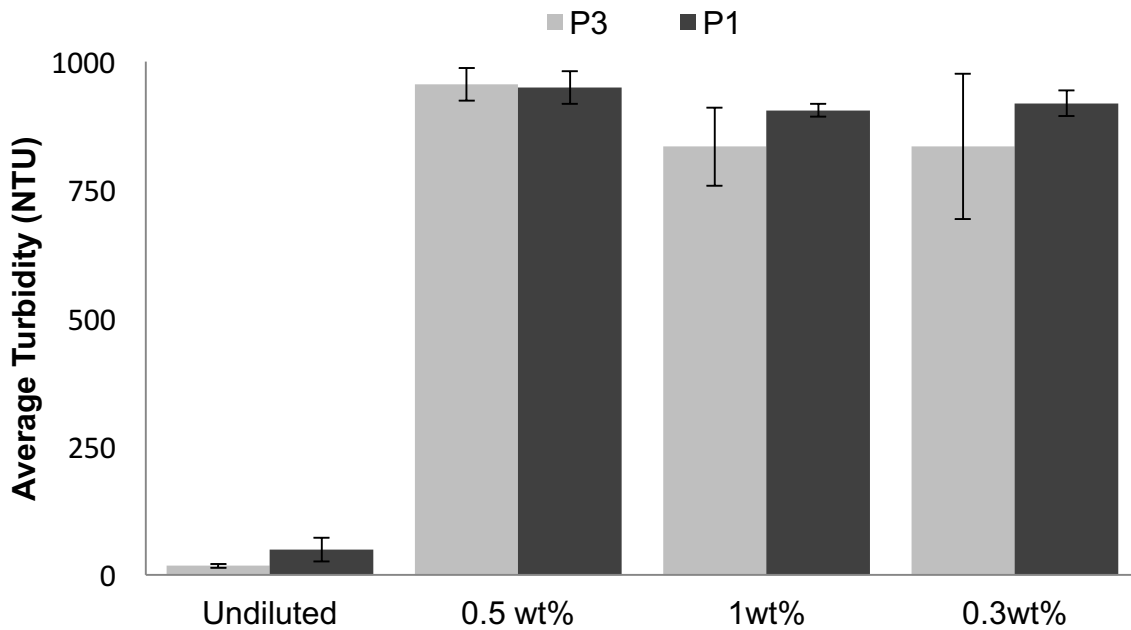


Figure 8: Average turbidity (NTU) versus polymer concentration (wt%) for a wastewater sample (“wastewater 5”) treated with two different polymers (P1 and P3).

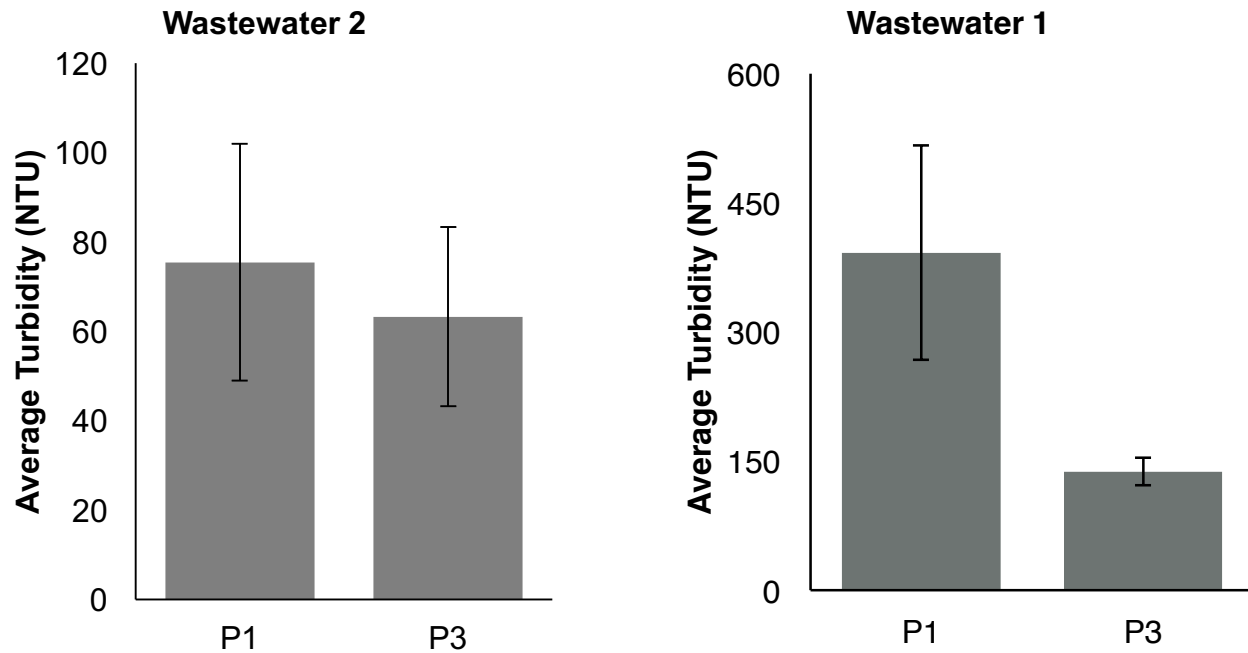


Figure 9: Average turbidity (NTU) for different wastewater samples treated with 2 different polymers (P1 and P3).

T-test analysis for these experiments can be found in Appendix B. In most of the cases presented above, and others that were also done in the lab, there was no significant difference between the two polymer flocculants according to statistical analysis. However, in the plot on the right in Figure 9, there was clearly a significant difference and ClearFloc CE5050 (P3) was better. In all other tests where there was no significant difference, ClearFloc CE5050 still usually gave a supernatant phase with a lower turbidity value than that of the other polymer. Accordingly, ClearFloc CE5050 remains the better option for the various wastewater samples that were tested.

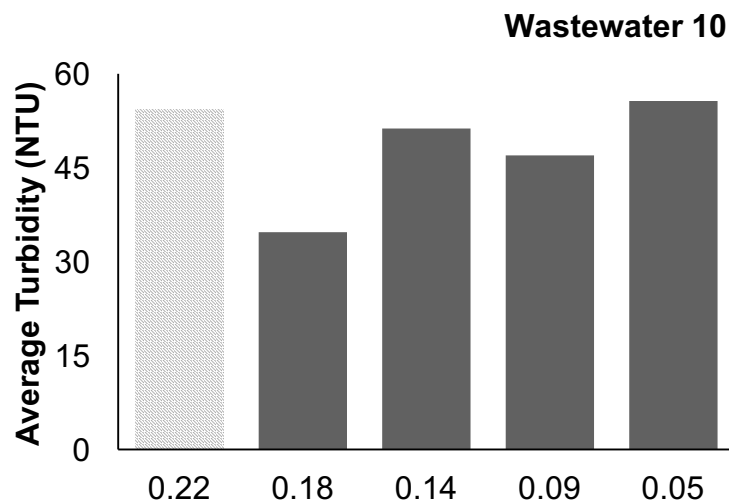
3.2. Industrial Wastewater Treatment at Low Undiluted Polymer Flocculant Dosages and Low Diluted Polymer Flocculant Concentrations

After the polymer flocculant P3 was proven to be a good polymer flocculant for the wastewater samples obtained from Aevitas, experiments were done to find its optimum dosages and concentrations for various wastewater samples.

3.2.1. Treatment at Lower Polymer Flocculant Dose

The experiments done in this section were also on various wastewater samples with different properties. Figure 10 below displays the results of some of the experiments done in this section to study the effect of undiluted polymer flocculant dose on turbidity. The results below are for three wastewater samples from different sources.

As seen in the figure, for all the cases, there was always a lower undiluted polymer flocculant dose that treated the sample to a supernatant phase turbidity value close to that of the normal dosage (0.22 g/L – bar with a pattern in the graphs below).



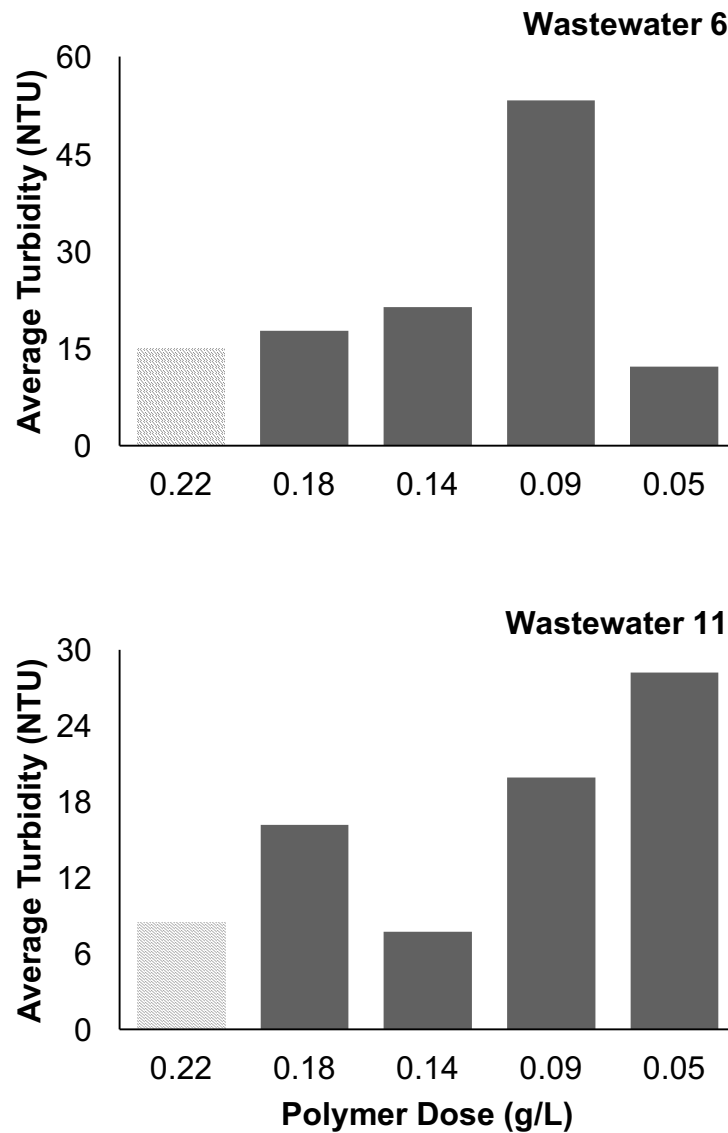


Figure 10: Average turbidity (NTU) plotted against undiluted polymer flocculant dose (g/L) for various wastewater samples. These were done in duplicates.

3.2.2. Treatment at Low Polymer Flocculant Concentrations

This section focused on consuming even less polymer flocculant by diluting it down rather than just lowering the undiluted polymer flocculant dose. The experiments

done in this section were on some of the various samples of wastewater shown earlier in Table 4. All of them were done using the high-throughput technique at a 25 mL scale and at a constant polymer flocculant dose of 0.22 g solution/L, whether diluted or undiluted (i.e. neat).

The results obtained for one of the runs (on “wastewater 3”) are displayed in the Figures below

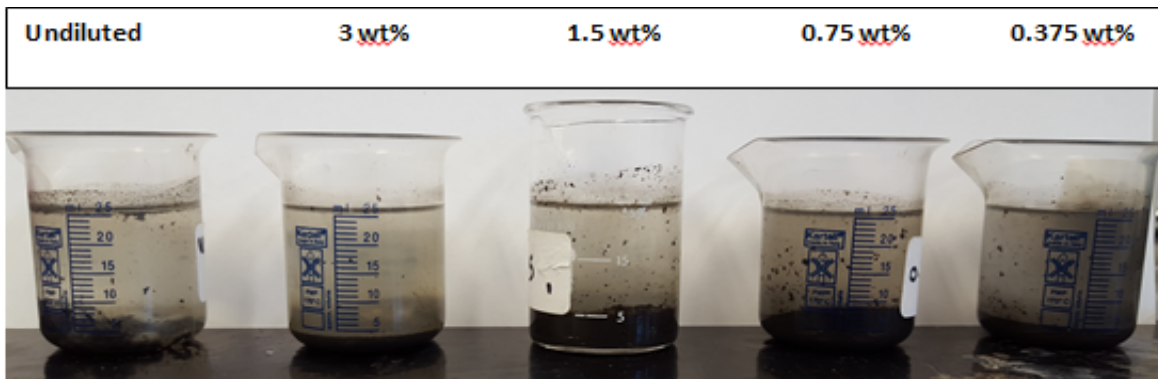


Figure 11: A picture of the wastewater samples that were treated at different polymer concentrations after they were allowed to settle for 15 minutes.

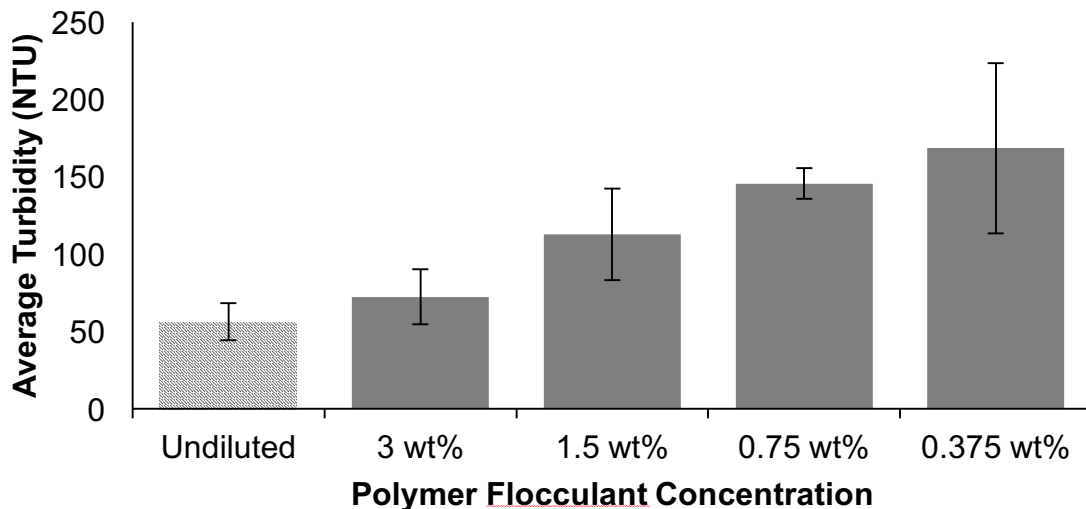


Figure 12: Turbidity (NTU) values of one of the experiments plotted against polymer concentration (wt%).

From Figure 11, it can be noticed that the supernatant phase for the sample treated with undiluted polymer flocculant is as clear as that treated with the 3 wt% polymer flocculant. This was evident in the turbidity results in Figure 12; the turbidity of the supernatant phase of the sample that was treated with 3 wt% polymer flocculant solution was identical to that treated with undiluted polymer flocculant. This means that 97% less polymer flocculant was used, and the sample was treated to a similar clarity level.

Using the high-throughput technique, several other wastewater samples (with different characteristics and primary sources) were tested at different polymer flocculant concentrations. After each run, turbidity measurements were done after the samples were allowed to settle. Figure 13 below shows the results obtained for one other sample tested (“wastewater 4”).

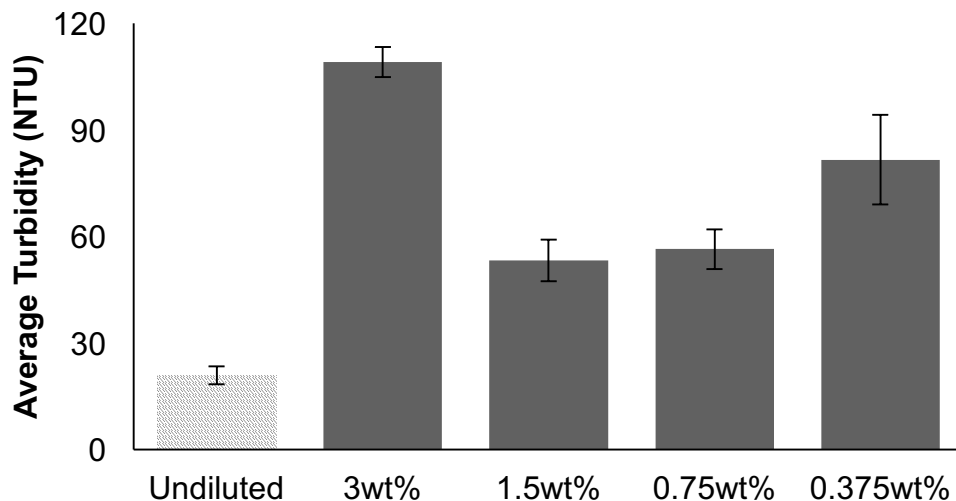


Figure 13: Turbidity (NTU) plotted against polymer concentration (wt%) for “wastewater 4”.

As seen in Figure 13, the supernatant phase of the sample that was treated with undiluted polymer flocculant had the lowest turbidity value, and none of the samples treated with diluted polymer concentrations was able to have a supernatant phase turbidity value close enough to it. The sample treated via the 1.5 wt% polymer flocculant gave the second lowest turbidity value, with a % difference of around 87 compared to that obtained via undiluted polymer flocculant, which is not a minor difference.

All of the experiments done on the various wastewater samples to test whether a diluted polymer flocculant concentration or a lower polymer flocculant dose would perform better than undiluted polymer at the regular dose (i.e. 0.22 g/L) or not, including the ones displayed above, proved that the results vary depending on the wastewater sample properties. However, in most cases, there always seems to be a savings opportunity in polymer flocculant consumption. The various wastewater loads that Aevitas has to treat cannot all be treated using a constant dose or concentration. This is why specialized industrial wastewater treatment facilities face a challenge in identifying the optimum treatment options for the various incoming wastewater loads.

The high-throughput method used for these experiments was able to provide rapid flocculation results for each wastewater sample at various polymer flocculant concentrations and dosages and using low volumes of wastewater. Thus, it could be a beneficial tool in specialized wastewater treatment facilities as it would be necessary to run such tests very often since they receive loads that vary in characteristics on a daily basis. With the high-throughput apparatus, experiments can be done within minutes.

An important observation is while diluted polymer solutions were added at a dosage similar to that usually added using undiluted polymer in the experiments shown

above, this might not be ideal at a large scale. As noticed in Figure 11 earlier, the flocs formed when using diluted polymer were not as well formed as those using undiluted polymer flocculant. Such flocs might be difficult to remove in a large treatment tank. Thus, a higher dosage might have to be added. The actual appropriate dose and concentration for larger scale treatments could be identified better either by experienced operators/engineers or an in-line monitoring tool.

3.3. Effect of Polymer Flocculants on Floc Behavior

The main focus in these experiments was to visually observe whether flocs float or settle under various polymer flocculant dosages and polymer flocculant types/characteristics. While in flocculation flocs are supposed to settle, operators at Aevitas noticed that some flocs tend to float to the top of the tank after treating wastewater loads such as “wastewater 1”. This was also evident in some of the experiments done in the lab.

The experiments were done using the high-throughput method. The behavior observed in all the experiments done was the same. In the first set of experiments, undiluted ClearFloc CE5050 (P3) was used with 0.16 g/L – 0.56 g/L dosage, at a 0.08 g/L increment. This was to test if an overdose in polymer flocculant causes the flocs to float rather than settle. In the second set of experiments, the type of polymer flocculant was varied, and the dose was kept at 0.4 g/L. The polymer flocculants tested were P1, P2, P3, P4, P5 and P6. Both sets were done on “wastewater 1”.

Figure 14 below shows an image one of the samples that were tested at different polymer flocculant dosages. This was taken after allowing the samples to sit for 15 minutes after flocculation.

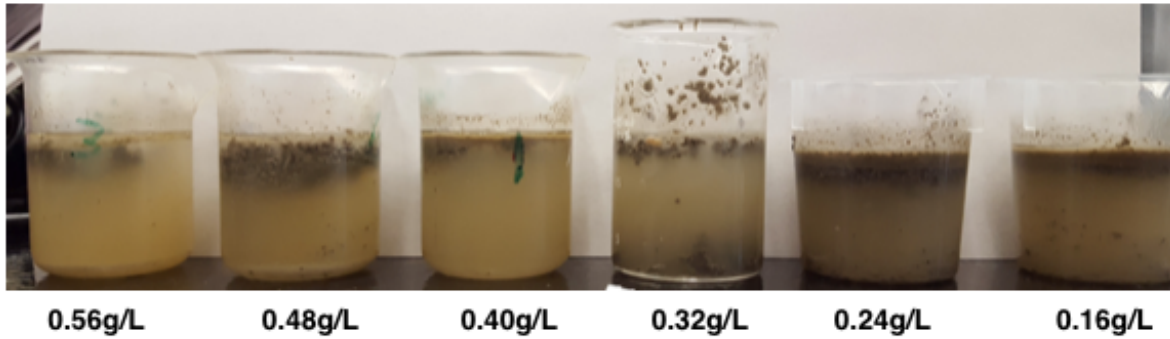


Figure 14: Wastewater samples treated with different polymer flocculant P3 dosages. The picture was taken after the samples were allowed to "settle" for 15 minutes.

As can be seen, whether the polymer flocculant dose was high or low, the flocs still tend to float in such wastewater samples. It was also noticed from previous experiments that diluting the polymer flocculant down to different concentrations also did not change this behavior.

Based on Figure 15 below, using different types of polymer flocculants that vary in characteristics also did not help in allowing the flocs to settle rather than float.

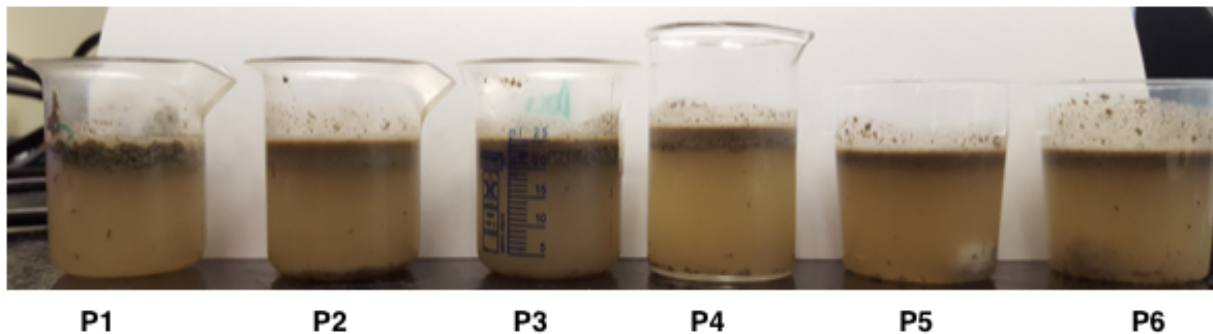


Figure 15: Wastewater samples treated with different polymer flocculant types at a constant dose. The picture was taken after the samples were allowed to "settle" for 15 minutes.

A reasonable explanation as to why this is happening in these samples is that polymer flocculants are not dense, or "heavy", enough. These samples of wastewater are from automotive industries and contain oils and organic compounds. Such

compounds have a low density and always tend to float to the top. If the polymer flocculant added to these samples for flocculation is not highly dense, the flocs that form and contain the oils and organic compounds will not be heavy enough to settle down. Thus, the flocs end up floating. Further discussions and results about this can be found in section 3.10.7.

3.4. Lab Scale-Up Experiments

The high-throughput method was used to run experiments at a small scale (i.e. 25 mL). However, since this project aims to improve the flocculation process at Aevitas, it was important to run experiments at larger scales. All the experiments in this section were done using a P3 flocculant dose of 0.22 g/L, whether diluted or not. Figure 16 below shows the results for treating a “wastewater 2” sample at three different scales, and three different polymer flocculant concentrations.

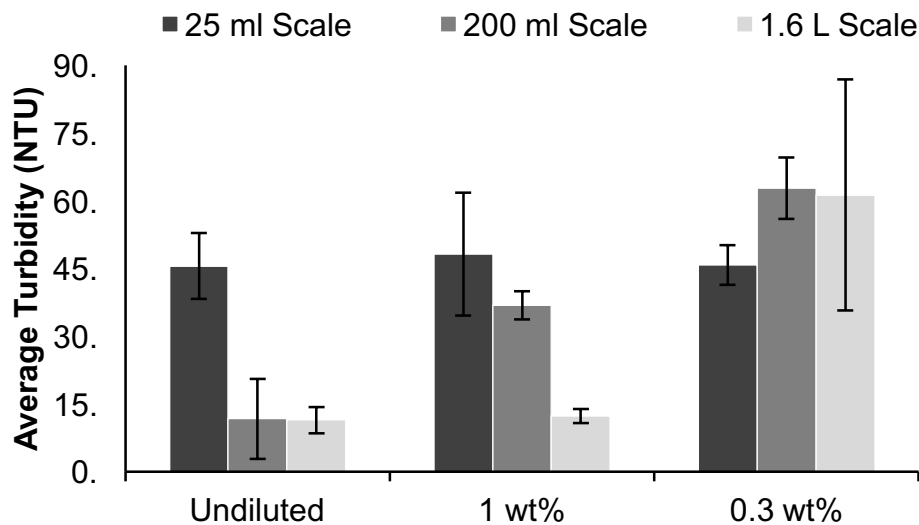


Figure 16: Average turbidity (NTU) obtained for a wastewater sample treated (“wastewater 2”) at three different polymer flocculant concentrations and at three different scales

At the 25 mL scale, all the polymer flocculant solutions were able to treat the sample to a similar turbidity value. However, as the scale increased, a difference between the results was observed. For example, while using undiluted polymer flocculant, the 200 mL and 1.6 L scales produced better results than the 25 mL scale. However, when using 0.3 wt% polymer flocculant solution, the opposite happened.

While the results for each polymer flocculant concentration were not exactly the same throughout the scale up, the supernatant phase of all the treatments was at a low turbidity level. Figure 17 below shows how clear the sample was at the 1.6 L scale at the 3 polymer flocculant concentrations.

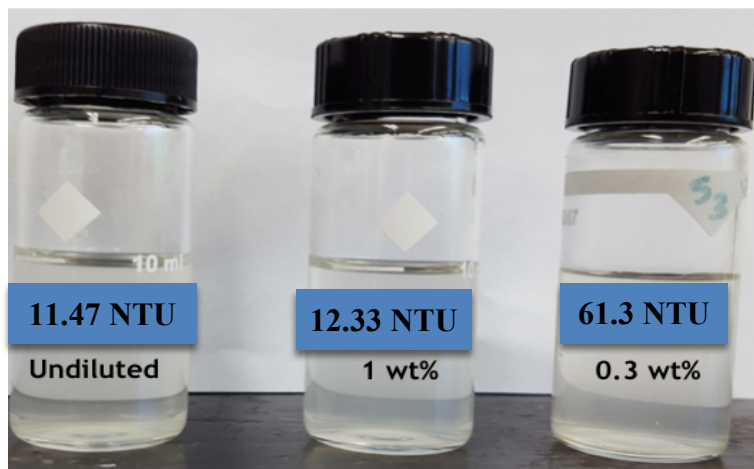


Figure 17: Supernatant phases of a sample treated at a 1.6 L scale using three different polymer flocculant concentrations.

Thus, when scaling up, it was still possible to have a diluted polymer flocculant concentration that was as efficient as undiluted flocculant, proving that using diluted polymer works just as well, and at lower polymer flocculant consumption costs. T-test analysis also proved that there was no significant difference between using undiluted polymer flocculant and 1 wt%. These results can be found in Appendix B.

3.5. Plant Scale-up Experiments

The main focus of these experiments was to test if using 1 wt% polymer flocculant could treat industrial wastewater the same way undiluted polymer flocculant would, but at a large scale (i.e. 45,000 L wastewater tanks). Thus, the main parameter that was being observed was the amount of 1 wt% polymer flocculant added to the tank to treat the wastewater well.

Figure 18 shows the sample jars obtained from the treatment of a tank filled with “wastewater 1” at various 1 wt% polymer flocculant volumes. The volumes of 1 wt% polymer flocculant added to the tank correspond to 0, 1.1, 2.2, 4.4, 6.6, 8.8 and 11.1 g/L respectively.

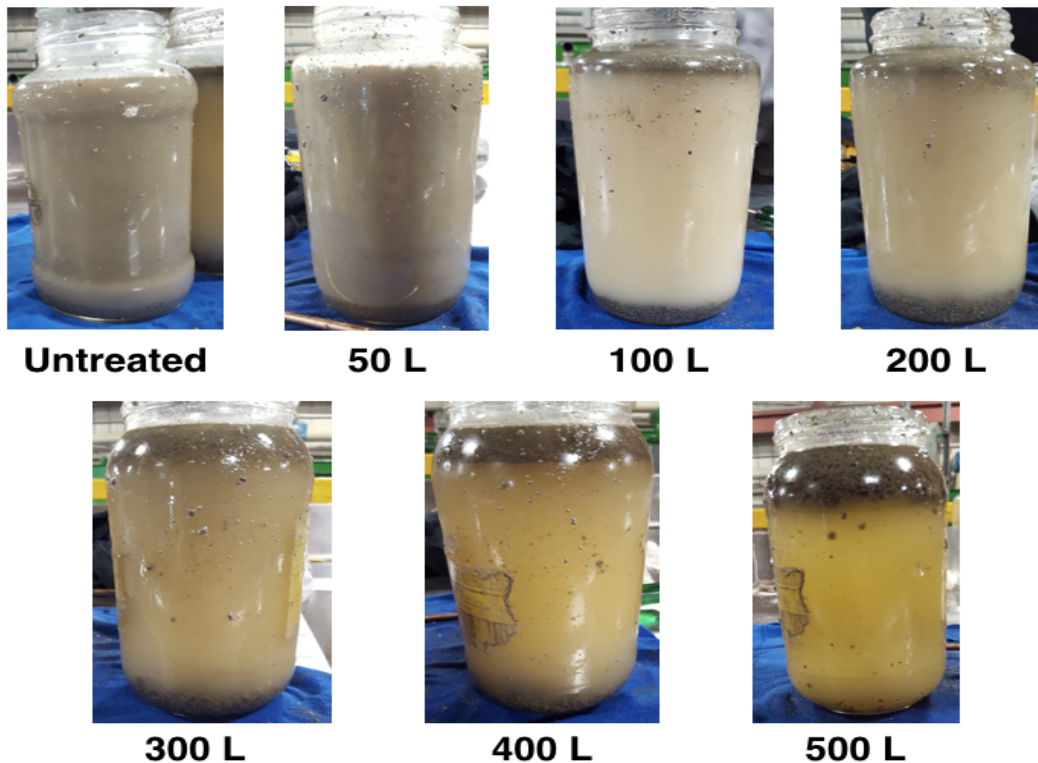


Figure 18: Picture of the sample jars obtained while treating a 45000 L tank filled with "wastewater 1" using 1 wt% polymer flocculant. After each certain amount of the polymer flocculant was added, a sample was taken out for the operators at the plant to examine if it can be safely taken to the next stage

The treated wastewater clarity in the last jar (after 11.1 g/L of 1 wt% polymer flocculant was added to the tank) was what operators usually aim for when treating this sample with undiluted polymer flocculant. Since this is a tough sample to treat via polymer flocculation only, this is as best as it could get. After the treatment was completed, quantitative measurements of the supernatant phases were taken. The results are displayed in Figure 19 below.

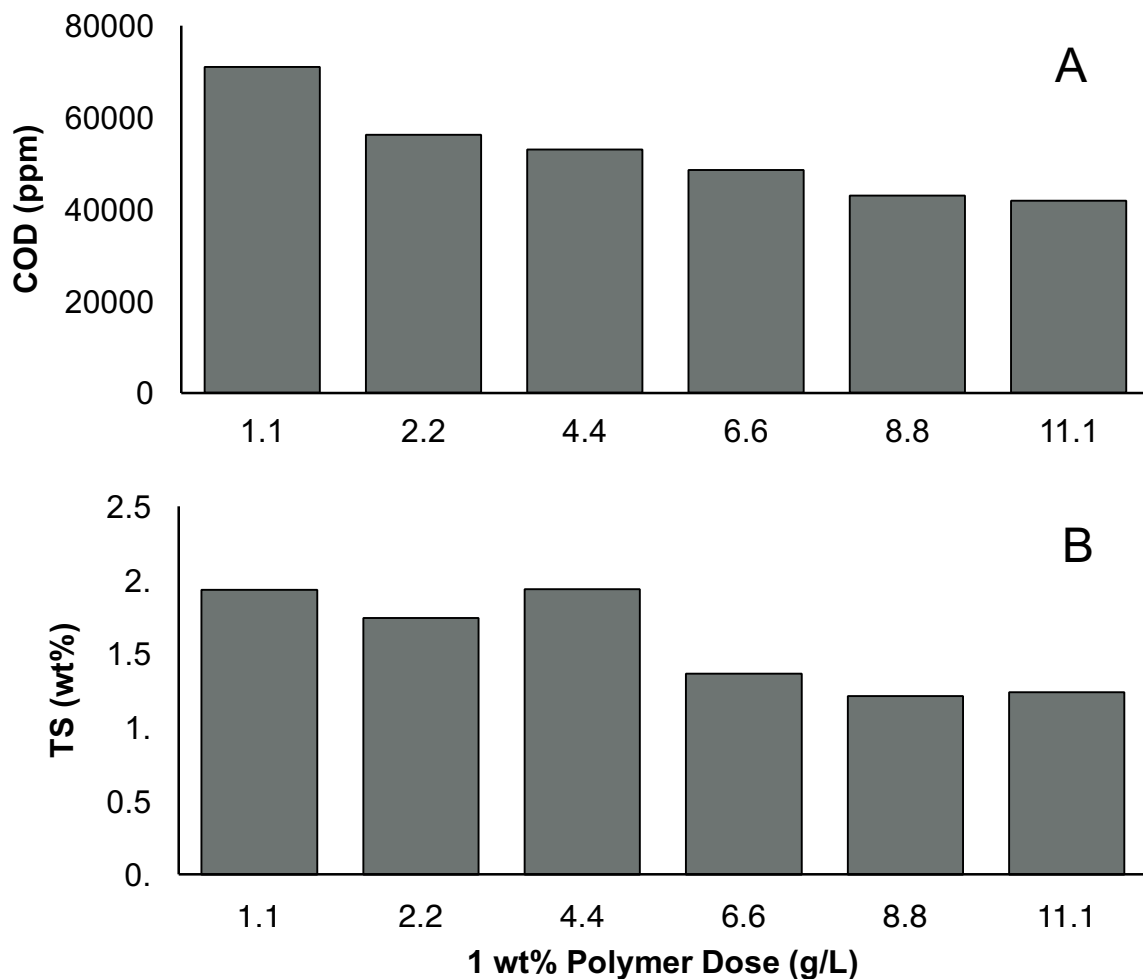


Figure 19: Plot A shows the COD (ppm) values obtained of the supernatant phases at the different 1 wt% polymer flocculant dosages (g/L). Plot B shows the TS (wt%) of the samples whose COD was measured, also at the different 1 wt% polymer flocculant dosages (g/L)

Based on the above results, using 8.8 and 11.1 g/L 1 wt% polymer flocculant gave a similar performance. However, the flocs were not completely well formed at 8.8 g/L dosage, as was seen in Figure 18, and that is why additional flocculant had to be added. Note how the flocs also floated to the top rather than settle, which is a concept that has been explained earlier and will be explained further later on. An unusual observation that was realized in the results of this treatment is the COD level. Treating the same sample in the lab usually resulted in a final average COD of 8000 – 12000 ppm, which is lower than what was achieved in this trial. There might have been a mistake in this trial that resulted in such a high final COD. Thus, another tank with the same sample was again treated with 11.1 g/L of 1 wt% polymer flocculant and the final COD was measured to be 12,629 ppm, which is close to what is achieved usually during lab experiments on this sample

The 45000 L scale-up experiments were also done on other wastewater loads. Figure 23 below shows the sample jars obtained while treating a tank containing “wastewater 4” with 1 wt% polymer flocculant.

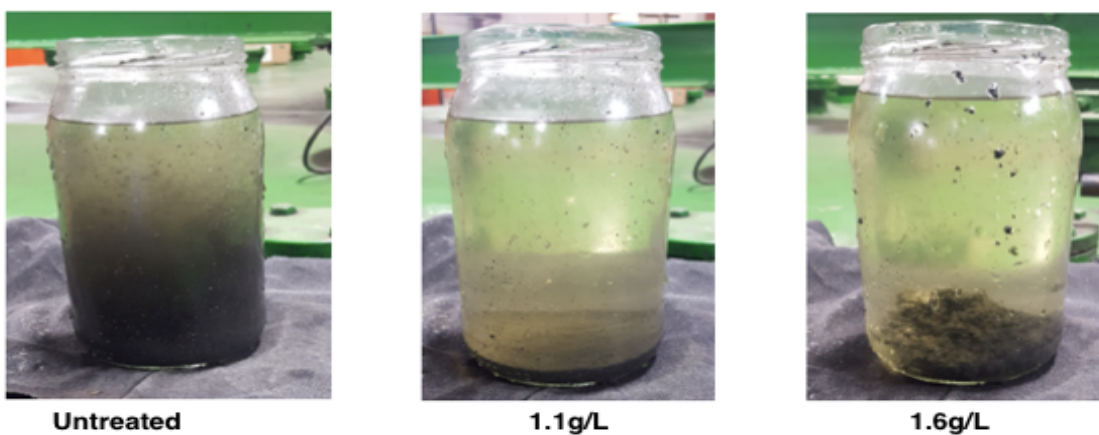


Figure 20: Sample jars obtained while treating "wastewater 4" with 1 wt% polymer flocculant.

After the treatment, quantitative measurements of the supernatant phases were taken. The results are displayed in Figure 21.

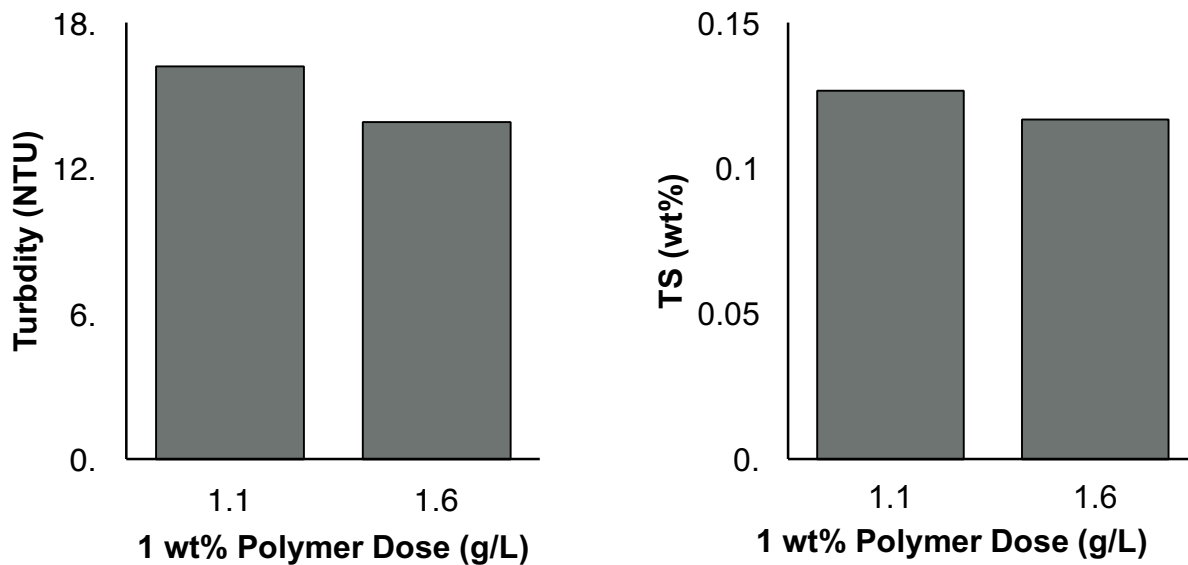


Figure 21: Quantitative measurements (turbidity (NTU) and TS (wt%)) obtained for the treatment of a 45000 L tank filled with "wastewater 4" using 1 wt% polymer flocculant

As seen in Figure 21, there is clearly no significant difference in the turbidity and total solids results obtained at both the polymer flocculant dosages, and accordingly, one might assume the 1.1 g/L is an ideal dosage for the treatment. However, by looking at the flocs formed using both the dosages in Figure 20, the only reason more polymer flocculant was added was to form better flocs to ease the process of removing them from the tank. The treatment done for this sample using 1 wt% polymer flocculant was just as good as what was obtained by the operators using undiluted polymer flocculant.

Table 8 below displays the results shown above, as well as those of other wastewater tanks treated in a similar manner. While some of the wastewater tanks treated are shown to come from the same source, it is not really necessary for the final

results to be 100% consistent as some of the tanks might have been mixed with another wastewater load with similar characteristics or the initial pH for the treatment might have been different. Accordingly, the 1 wt% polymer flocculant dosage that was necessary for the treatment sometimes varied for the same wastewater source.

Table 8: 1 wt% polymer flocculant dosages used to treat 5 wastewater tanks at the plant, along with the actual neat polymer flocculant volume available in each dosage used

Wastewater source	Dosage of 1 wt% polymer flocculant added (g/L)	Volume of neat polymer flocculant in the dose (L)
Wastewater 1 (A)	8.8	4
Wastewater 1 (B)	11.1	5
Wastewater 4 (C)	2.2	1
Wastewater 1 (D)	11.1	5
Wastewater 4 (E)	1.6	0.75

If the above samples were to be treated using undiluted polymer flocculant, which is the method that Aevitas usually uses, the amounts of neat polymer necessary for the treatment would vary. The graph in Figure 22 below shows a comparison between the volumes of neat polymer needed to treat the samples above using undiluted polymer flocculant, compared to what was used while treating them with the 1 wt% polymer flocculant solution.

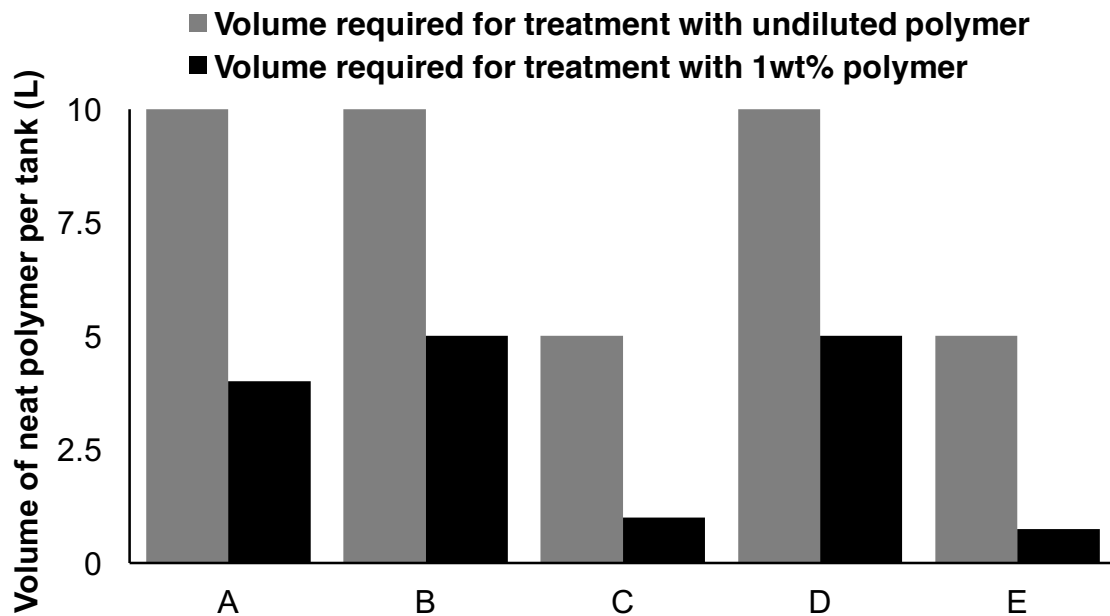


Figure 22: A graph to compare the volumes of neat polymer flocculant that would be needed when using undiluted and 1 wt% polymer flocculant to treat 45000 L tanks filled with certain wastewater samples (labeled alphabetically here. The actual wastewater source can be found using Tables 4 and 8).

As per the figure, depending on the sample, there could be a minimum of 50% savings in polymer consumption for each tank, which in return could result in some money savings. In all these cases, the 1 wt% polymer flocculant solution was prepared manually. Again, this is not an ideal method to prepare large amounts of diluted polymer flocculant. If a proper system was used, the 1 wt% polymer flocculant might have been more effective, and thus fewer quantities would have to be added to achieve similar results as above. However, one has to put into account that switching to using diluted polymer, while it may result in savings in polymer flocculant consumption, has additional costs such as labor cost for preparing the diluted polymer flocculant solution or the cost of a polymer make-down system.

3.6. Effect of Polymer Flocculation on COD

Polymer flocculants are beneficial in reducing COD in industrial wastewater. The polymer flocculation process at Aevitas is capable of reducing the COD of some wastewater loads by up to 90%. However, in some cases, further reduction in the COD value is still necessary for safe discharge.

Since it was proven that diluted polymer flocculant can treat the wastewater loads that Aevitas receives to a clarity level similar to that obtained by using undiluted polymer flocculant, it was important to examine if the use of diluted polymer flocculant affected the treated water COD. The high-throughput method was used to run these experiments, at a 100 mL scale, and using “wastewater 4”. The results can be seen in Figure 23 below.

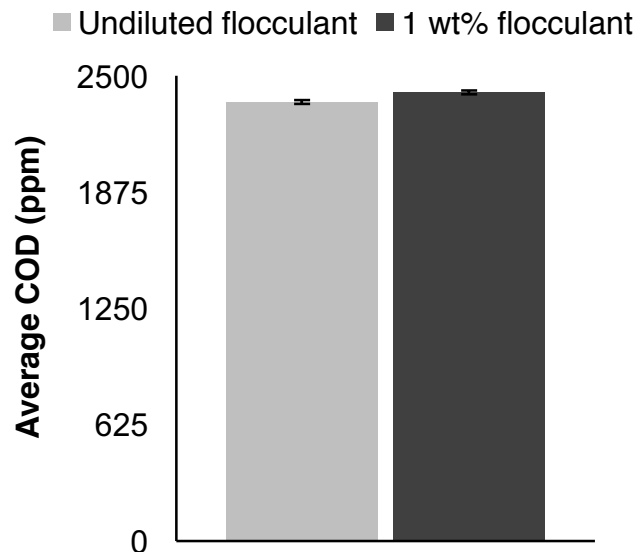


Figure 23: Average COD (ppm) obtained after treating a sample with undiluted polymer flocculant and 1 wt% polymer flocculant.

According to the t-test, there was no significant difference in COD value of the treated wastewater samples, whether diluted or undiluted polymer was used. Thus, in terms of final COD, it does not matter whether or not diluted polymer flocculant is used.

A second set of experiments was done in this section on automotive industrial wastewater (i.e. “wastewater 1”) to test if the removal of the insoluble oil layer in the wastewater before polymer flocculation could result in a lower treated water COD. This experiment was done at least 3 times, and the final results obtained were always the same. Figures 24 and 25 below contain the results for one of the runs. This was also done using the high-throughput method, but at a 25 mL scale.



Figure 24: The picture on the left shows a “wastewater 1” sample after removing the insoluble oil layer from the top. This was done after letting the sample sit for 10 – 15 minutes for the oil to float to the top and be removed. The picture on the right shows “wastewater 1” as received from Aevitas before any treatment.

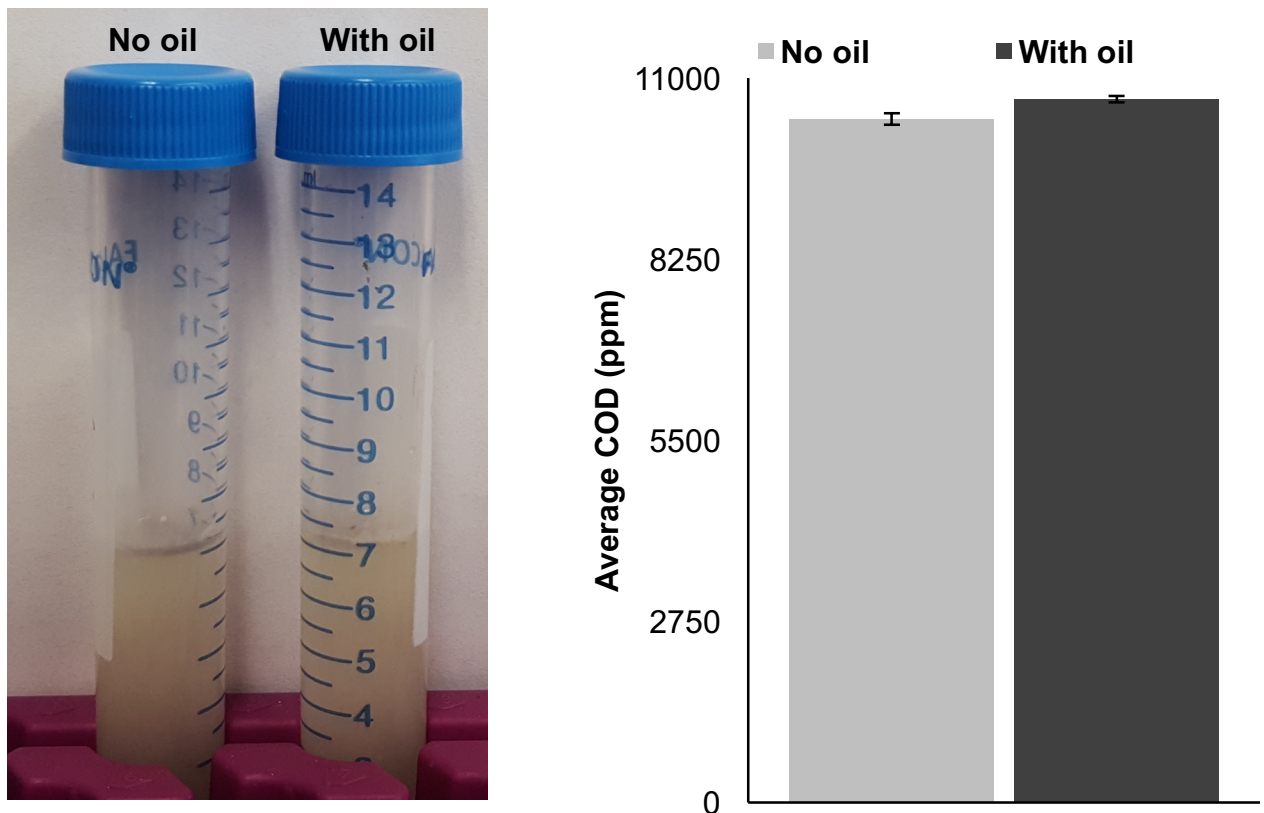


Figure 25: The picture on the left shows the supernatant phases obtained for one of the trials after settling. The graph on the right displays the average COD (ppm) obtained. “No oil” identifies the sample that was treated after removing the insoluble oil layer

Based on the supernatant phases and results above, the COD did not vary greatly when the oil layer was removed before flocculation. While it did slightly decrease, it is still not low enough for safe discharge. Thus, results prove that such samples may not be treated further to a lower COD if the insoluble oil layer was removed, and other options that could actually be more useful in getting these samples to a reasonable COD for discharge have to be considered.

3.7. Multi-Stage Polymer Flocculation

After it was proven that the high-throughput technique works well in polymer flocculation studies and can help in rapidly identifying optimal treatment conditions, it

was used in an attempt to enhance the treated water quality by applying the multi-stage polymer flocculation concept, which has been explained earlier. As mentioned in Section 2.2.4, three main sets of experiments were done in this section.

The results for the first set of experiments, which was to compare the performance of a constant polymer flocculant dose added directly into the wastewater first and then in multi-stage manner, can be seen in Figure 26 below.

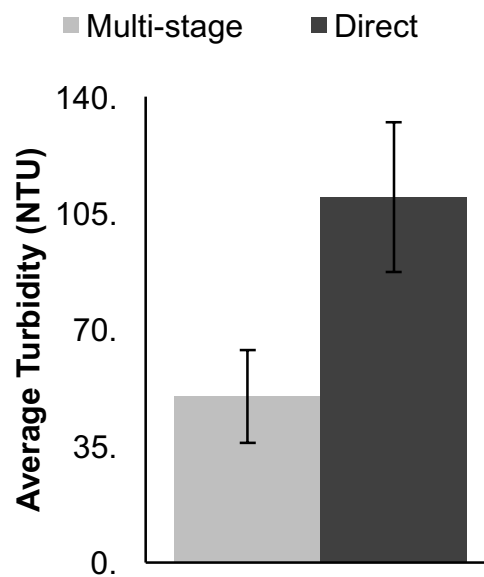


Figure 26: Average turbidity (NTU) obtained after treating a wastewater sample with a constant polymer flocculant dose via direct addition at first, and then via multi-stage addition. This was done on “wastewater 4”

As can be seen in the figure, the multi-stage polymer flocculation gave a treated supernatant phase with turbidity significantly lower than that with direct polymer flocculation. This was evident in both the figure and via t-test analysis. This proves that treating wastewater samples via flocculation by adding the polymer flocculant at different stages throughout the treatment enhances the water quality when compared to adding it all at one stage.

When the polymer flocculant is added in one stage and flocs form and settle, there might be some remaining particles in the supernatant phase that did not get to attach to the polymer chains before settling. However, when the flocculant is added at different stages, it is more likely for particles that remain in the supernatant phase after the first stage to attach to the polymer flocculant in the second stage, resulting eventually in a better water quality. Similar results were achieved for other samples treated in the same manner as well.

This theory was proven in an experiment that compared the total solids of the supernatant phase of a sample treated using direct and multi-staged polymer flocculant addition. The results can be seen below.

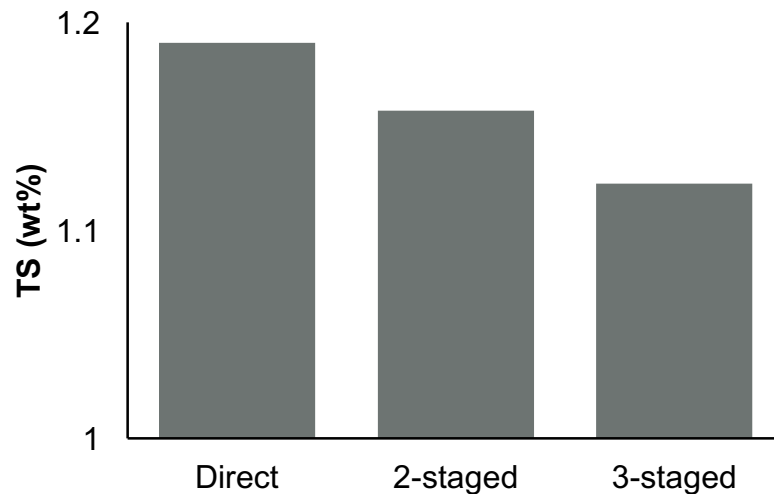


Figure 27: TS (wt%) of the supernatant phase obtained after treating a sample using direct polymer flocculation, 2-staged flocculation, and 3-staged flocculation. This was on “wastewater 5”.

When the polymer flocculant was added over different stages rather than directly, the total solids in the supernatant phase did indeed tend to decrease, proving the theory mentioned earlier.

Figure 28 below shows the results of the second set of experiments done in this section.

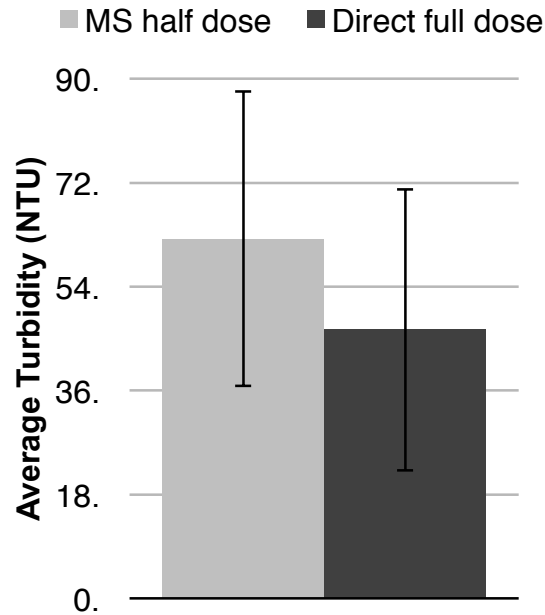


Figure 28: Average turbidity (NTU) of supernatant phase of a sample treated via direct polymer flocculation using a full high dose, and via multi-stage (MS) addition using only half of the dose. This was done on “wastewater 2”

The results of the t-test, found in Appendix B, were able to prove that there was no significant difference between direct polymer flocculant addition and multi-staged polymer flocculant addition at half the dose of that added in the direct addition.

While the turbidity for the supernatant phase of the sample treated with direct polymer flocculant addition was lower than that treated with multi-stage addition, they were both statistically similar to each other.

Thus, multi-stage polymer flocculant addition enhances the water quality when added at the same dose as via direct addition, and can also treat a sample as well as

using direct flocculant addition using half the dose only. Thus, multi-stage polymer flocculation could be implemented to provide a better water quality, or to treat a sample to a similar water quality as that treated by the usual process but at a lower dosage, resulting in some cost savings.

The results for the last set of experiments done in this section can be found in Figure 29 below. This was done on “wastewater 1” to see the effect of multi-stage polymer flocculant addition on the supernatant phase COD, and whether it is helpful in lowering it.

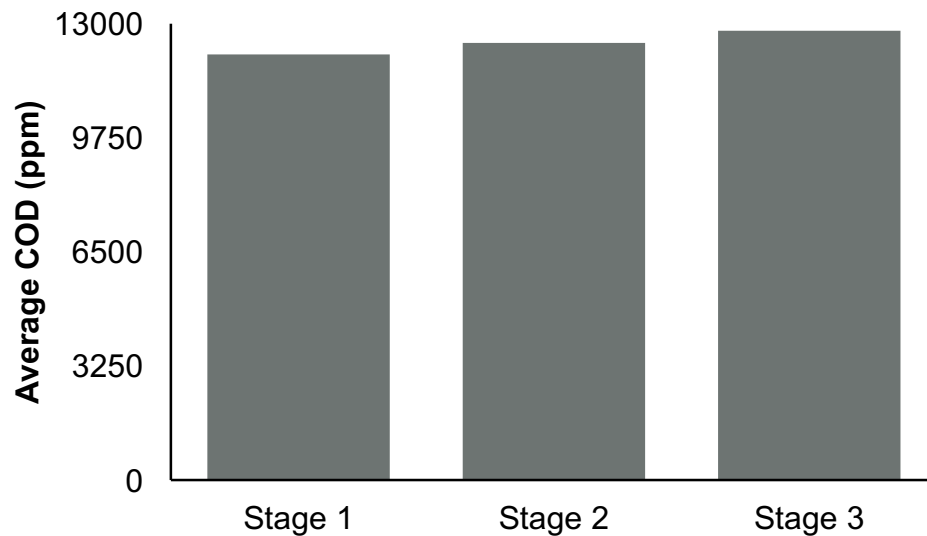


Figure 29: Average COD (ppm) of the supernatant phase of a sample treated in a multi-stage flocculation manner.

The COD value did not undergo any significant changes when multi-stage polymer flocculation was implemented. If anything, the COD actually slightly increased with each stage.

This is reasonable as when more polymer flocculant is added to the supernatant phase to remove additional particles, it is likely that there will be some residual polymer flocculant left. This residual polymer flocculant contributes to the COD value and increases it. Residual polymer flocculant in the supernatant phase is likely to undergo hydrolysis and release some organic materials that would contribute to COD. Thus, multi-staged polymer flocculation does enhance the quality of wastewater in terms of clarity and removal of suspended solids in the supernatant phase. However, when it comes to the supernatant phase COD, it could slightly increase it with more stages. Yet, this increase is statistically insignificant. So, multi-stage polymer flocculation still ends up with more advantages than direct flocculation.

3.8. Polymer Flocculation and UV Absorbance

As mentioned in Section 1.5, UV absorbance has been previously used as a method to detect polymer concentrations. This section includes the studies done with UV absorbance on industrial wastewater samples obtained from Aevitas.

3.8.1. UV Absorbance Method Detection Limit

The first set of studies done with UV absorbance involved finding the Method Detection Limit (MDL), which is basically the minimum/lowest concentration of polymer flocculant that UV absorbance can detect, for the polymer flocculant P3, which was proven to be an efficient polymer flocculant. If UV spectroscopy was to be used as a method of in-line monitoring for polymer flocculation, it is important to first verify that it can detect the polymer flocculant concentration/dosage that is used at the plant.

Assuming a plant uses a polymer flocculant dose of 0.22 g/L, or 220 mg/L to treat their sample, and 99.9% of the dosage gets consumed in the actual flocculation process

(i.e. 0.1% residual polymer flocculant remains in the supernatant phase after the treatment), then there will be 0.22 mg/L residual polymer flocculant in the supernatant phase. Thus, it is important to ensure that UV absorbance can actually detect this concentration first. Accordingly, several polymer flocculant concentrations were prepared in distilled water. These were: 0.001, 0.01, 0.1, 0.2, 0.5, 1, 2, 4 and 10 mg/L. These were prepared as mentioned in Section 2.2.2. After that, the UV absorbance over a wavelength range of 200 to 400 nm was measured. Figure 30 below shows the plots obtained at the lower polymer flocculant concentrations, since these are the main focus.

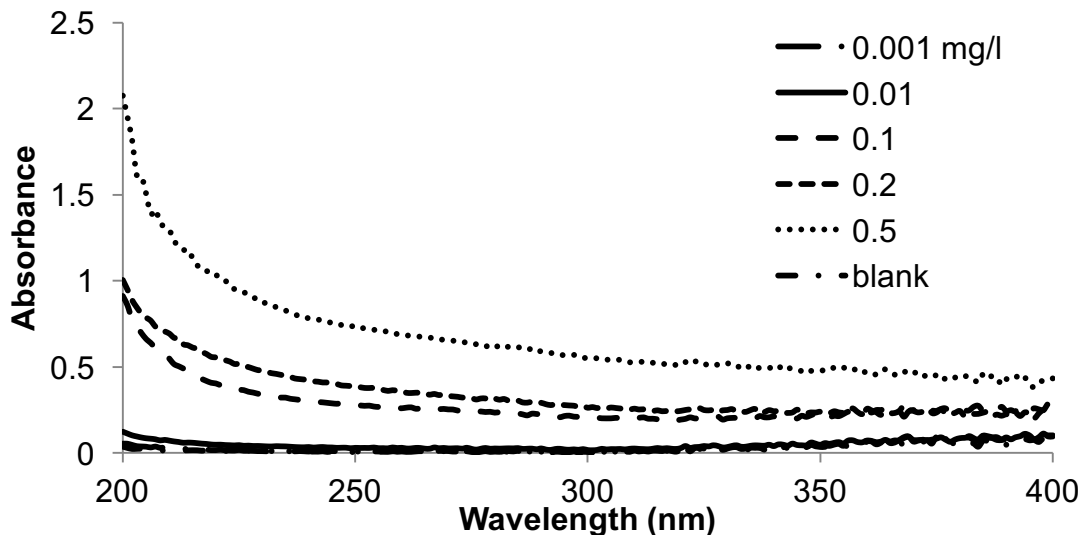


Figure 30: UV absorbance curves obtained for low polymer flocculant (P3) concentrations over a wavelength range of 200 - 400 nm.

As seen in the figure, UV absorbance seems to be able to easily detect any polymer flocculant concentration that is above 0.1 mg/L. When the concentration is lower than that, the UV absorbance cannot really differentiate between it and a blank sample. The MDL for a polymer flocculant usually varies depending on the medium that it is placed in. However, when using UV absorbance, it was concluded in a study that the MDL for a polymer flocculant does not really vary significantly when placed in different mediums

[51]. Accordingly, the MDL for polymer flocculant ClearFloc CE5050 (P3), which was used for the majority of the experiments in this thesis, in the supernatant phases of treated industrial wastewater samples should be around 0.1 mg/L. Thus, assuming 0.1% of the polymer flocculant dosage used by a plant using P3 remains in the supernatant phase after a treatment, UV absorbance would easily be able to detect it.

3.8.2. UV Absorbance for Polymer Flocculant Overdose Detection

Before running experiments to test the ability of UV absorbance to detect polymer flocculant overdose in different supernatant phases of treated samples, it was important to first do a wavelength scan of the absorbance of the centrate of different centrifuged wastewater samples. This was to verify that UV absorbance can differentiate between the different characteristics and compositions of industrial wastewater samples and does not give the same absorbance curve for varying samples. Several centrifugation conditions were first tested on one of the samples to identify the conditions that will give the best water quality. This was done using Beckman Coulter Allegra™ 25R Centrifuge

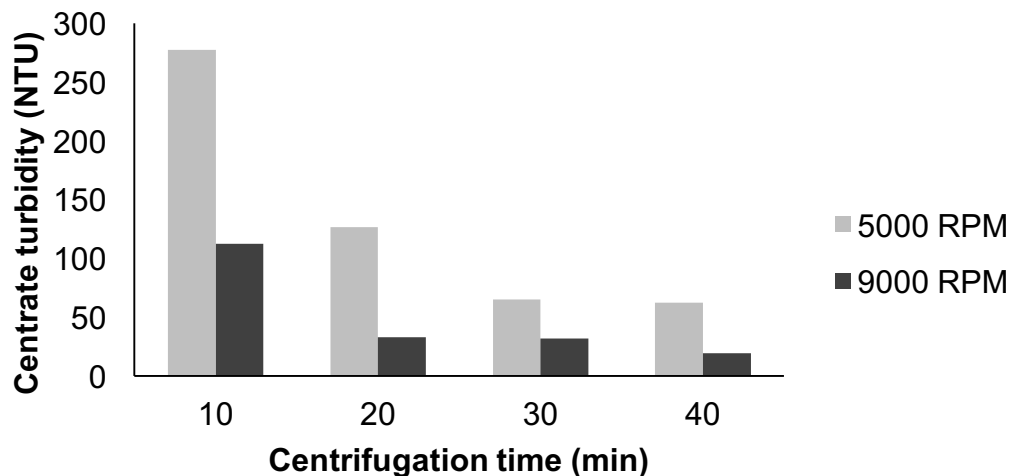


Figure 31: Centrate turbidity (NTU) obtained for a wastewater sample under different centrifugation conditions

Based on Figure 31 above, the optimum centrifugation conditions chosen for the experiments were 9000 RPM and 40 minutes of centrifugation.

After determining the above conditions, 4 different wastewater samples were centrifuged and their centrates were taken for UV absorbance measurements.

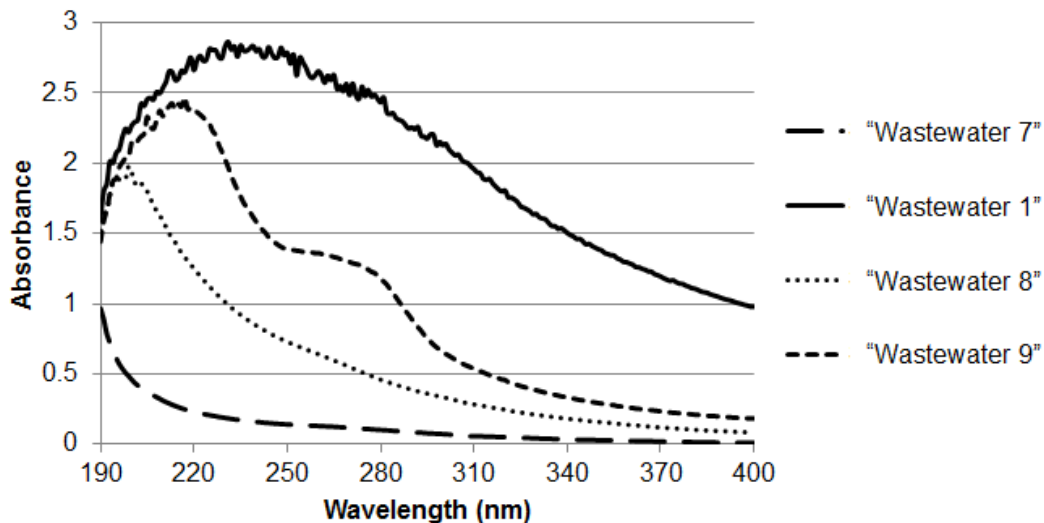


Figure 32: UV absorbance curves obtained for the centrates of 4 different wastewater samples.

The curves for the samples were clearly not identical, proving that UV absorbance can indeed recognize the different compositions of industrial wastewater samples and can thus be used to explore its potential as an in-line water quality measurement and polymer flocculant overdose detection.

To test the capability of UV absorbance in detecting polymer flocculant overdose, a wastewater sample ("wastewater 8") was treated using the high-throughput method with different polymer flocculant dosages. The supernatant phases were then taken and the UV absorbance and turbidity were measured.

The absorbance curve for the full wavelength range can be found in Appendix C. Since 197 nm was the wavelength at which the maximum absorbance was achieved for

most of the dosages, it was used to prepare a plot of absorbance at 197 nm versus polymer flocculant dosage. The results are displayed in Figure 33 below

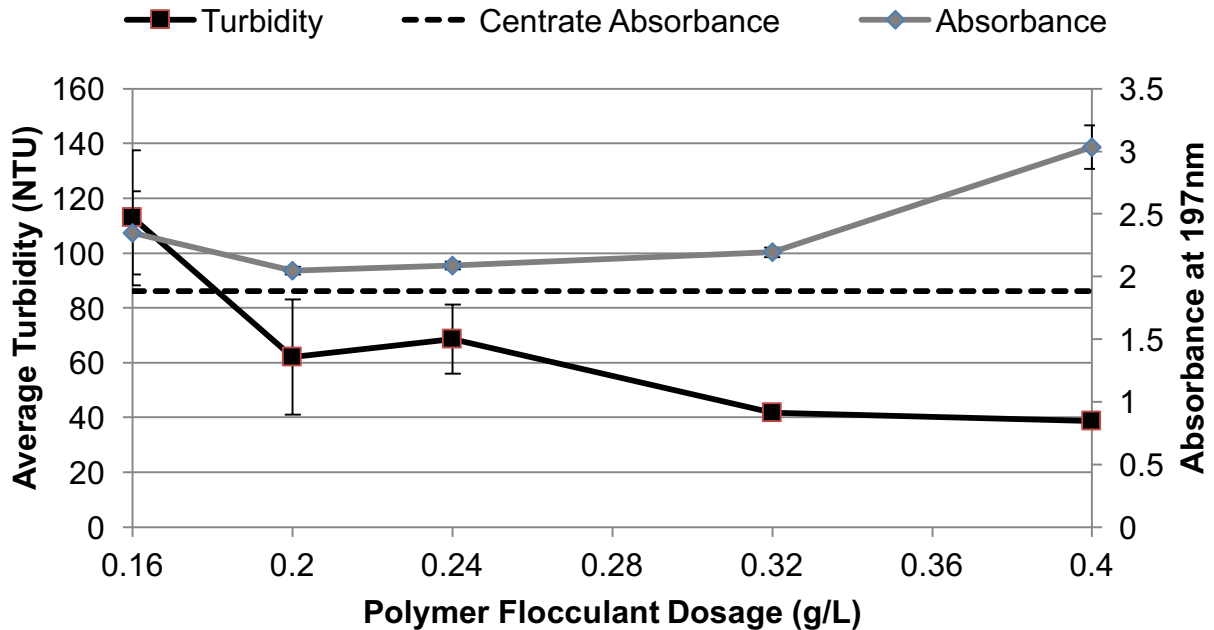


Figure 33: Absorbance at 197nm and average turbidity (NTU) obtained for the supernatant phase of a wastewater sample treated at different polymer flocculant dosages.

Turbidity usually tends to decrease as the dosage is increased. This is due to the fact that more suspended solids are removed with more polymer flocculant addition, resulting in a decrease in turbidity. However, as seen in the figure, the turbidity value eventually tends to plateau as the polymer flocculant dosage increases. This is due to the fact that the polymer flocculant already removed the maximum amount of particles and any additional quantities of it are not helping in lowering the turbidity any further. Instead, the additional flocculant just tends to float and remain in the supernatant phase. As for absorbance at 197 nm, for the first 3 polymer flocculant dosages, the pattern is exactly the same as the pattern observed in turbidity. At 0.16 g/L, the turbidity is high

and there are more suspended solids in the supernatant phase, thus the absorbance was high as well. However, at 0.2 g/L, the turbidity decreased, meaning the amount of particles in the supernatant phase decreased. Thus, the absorbance decreased as well. At 0.24 g/L dosage, the turbidity and absorbance did not undergo any significant changes and remained identical. For the 0.32 g/L and 0.4 g/L polymer flocculant dosages, the turbidity and absorbance curves began to vary in pattern. While the turbidity values at these dosages are lower than those at the other dosages and are identical, the absorbance values at these dosages are neither lower than at other dosages nor are they identical to each other. This is clear proof of how UV absorbance can be used to detect polymer flocculant overdose. When the 0.32 g/L dosage was added, there seemed to be a slight overdose that resulted in a slight increase in absorbance while the turbidity decreased. Thus, there could be a slightly lower dose that could give the same turbidity result without an increase in absorbance (i.e. without an overdose of polymer flocculant). When the 0.4 g/L was added, the turbidity value remained constant; however, there was a clear significant increase in absorbance. This is a clear case of overdose. There was some residual polymer flocculant in the supernatant phase of the sample after the maximum number of particles was already flocculated. This residual polymer flocculant that remained in the supernatant phase was detected by the UV absorbance, explaining the sudden increase in absorbance at that dose compared to the 0.32 g/L dose, despite the turbidity value being identical at both dosages.

Thus, in this experiment, implementing UV absorbance along with turbidity measurements helped in identifying that the optimum polymer flocculant dose to treat

this sample is a dose between 0.24 g/L and 0.32 g/L. A polymer flocculant dose within this range should result in low turbidity and UV absorbance, which would mean that the sample was treated without any overdose.

3.9. FBRM Studies

Since the FBRM has previously been proven to work as an in-line monitoring tool in some wastewater (other than industrial wastewater) treatment studies, it was also tested in this work for industrial wastewater treatment on various samples obtained from Aevitas.

The first set of experiments done in this section was on different wastewater samples to examine how particle size changes throughout the flocculation process at different polymer flocculant dosages and concentrations. One of the samples was treated using undiluted polymer flocculant and 0.3 wt% polymer flocculant, and the FBRM measurements were done using the exact same procedure mentioned earlier in Section 2.9. The polymer flocculant was usually added at around 60 seconds, mixing speed was reduced at around 70 seconds, and the mixing was stopped at around 240 seconds. The results in Figure 34 below show the FBRM output for the 100 - 300 micron particle size range while using the 0.3 wt% polymer flocculant for the treatment.

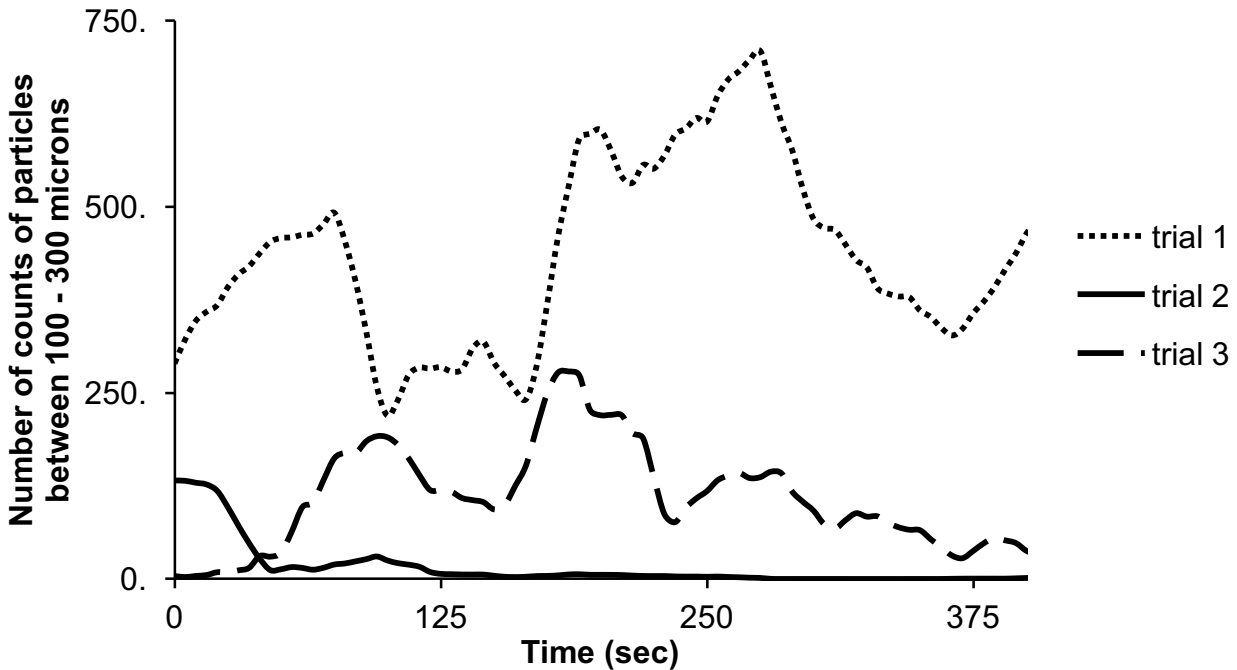


Figure 34: The FBRM output obtained while treating an industrial wastewater sample (“wastewater 10”) with 0.3 wt% polymer flocculant. For all the three trials, the polymer flocculant was added at 60 seconds and the mixing was stopped at 240 seconds.

As seen in the figure above, there was a problem with the reproducibility of the results.

This was evident in all of the experiments done using the FBRM. There was clearly a problem with the samples used in this project since the FBRM worked just fine with other samples treated using a similar procedure and the exact same apparatus [42].

Thus, further experiments were done in an attempt to optimize the system.

3.9.1. FBRM Optimization

Since the results were not reproducible, several aspects in the FBRM system and the samples were varied in an attempt to find optimal conditions to make the system work better. These involved varying the magnetic stirrer size, the stirring speed before the polymer flocculant addition, the FBRM probe orientation (i.e. its angle while it is in the wastewater sample), the FBRM probe depth into the sample, and pre-filtering

the samples using a filter cloth before using the FBRM to reduce the amount of solids in the wastewater sample. One of the main problems faced while using the FBRM on such samples was that the graphs were never steady enough before the polymer flocculant addition. It is more likely to work well if the graphs were steady before the flocculant addition. This way, the changes that occur after the addition can be better monitored. Thus, in all of the experiments done here, there was no polymer flocculant addition. The main focus was to find the best conditions that will give steady graphs while the sample is just being stirred in the beaker.

3.9.1.1. Magnetic stirrer size

The first factor tested was the magnetic stirrer size. Three different magnetic stirrer sizes from VWR were tested at different mixing speeds: a small stirrer (3/16" x 1/2"), a medium stirrer (1/4" x 3/4"), and a large stirrer (1/4" x 1"). The FBRM output results can be found in Appendix C. From the results, it was obvious that the graphs were most steady when using the medium stirrer. Thus, it was used for further optimization experiments.

3.9.1.2. Stirring speed (RPM)

Next, using the medium stirrer, the mixing speed was then varied. The output curves for the different speeds are presented in Figure 35 below. As seen in the figure, as long as the RPM was 400 and above, the graphs were steady. Thus, 400 RPM was chosen as the optimum RPM for further optimization.

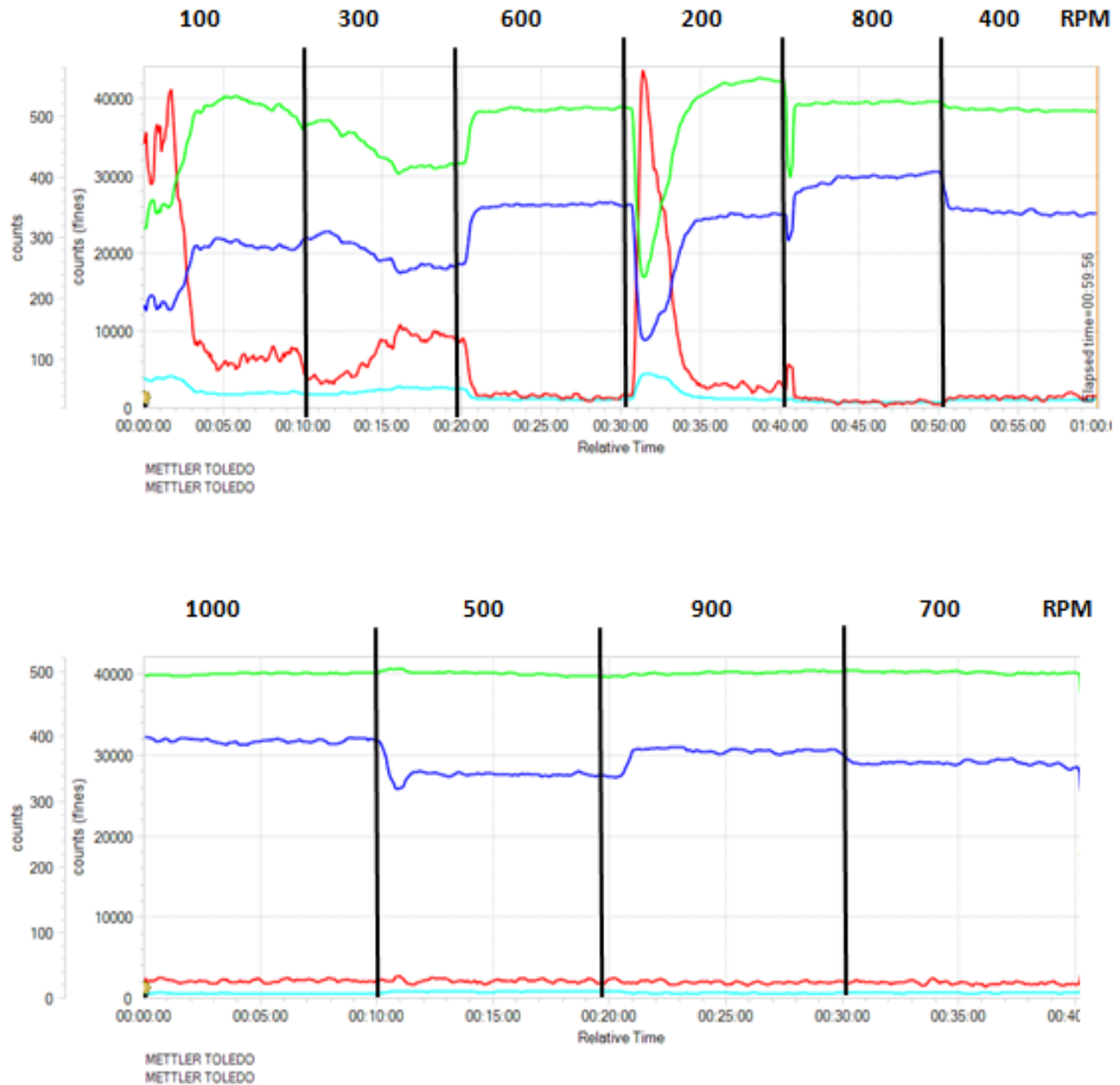


Figure 35: FBRM output curves for the different stirring speeds tested while using the medium stirrer. This was done using “wastewater 10”.

3.9.1.3. FBRM Probe Orientation

For testing the optimum probe orientation, a medium stirrer and 400 RPM mixing speed were used since they were chosen as the optimum conditions based on previous results. The placement of the FBRM probe angle into the sample was then varied. After

obtaining the graphs and data, the Total Sum of Squares was calculated. This is simply a representation of the deviation of the points from the mean. The lower this value is, the better are the results. The results for each of the trials can be seen in Table 9 below.

Table 9: Total Sum of Squares obtained for each trial while varying the FBRM probe orientation in the sample.

Angle (Degrees)	Trial 1	Trial 2	Trial 3
0	12557.3	2846.9	10118.2
10	322733.7	582.5	642.3
20	558222.3	564.2	1337.2
30	778	408.4	1334.687

As seen in the figure, based on the Total Sum of Squares, in the first two trials, the 30° probe orientation was the best. However, in trial 3, the 10° orientation was the better option. There is also a clear variation in the Total Sum of Squares obtained for each orientation in the three trials.

3.9.1.4. Probe Depth

The next factor that was varied was probe depth into the sample. This was done using a medium stirrer, 400 RPM mixing speed, and 10° probe orientation. Again, three trials were done and the Total Sum of Squares was obtained. The results can be seen in Table 10 below.

Table 10: Total Sum of Squares obtained for each trial while varying the FBRM probe depth into the sample.

Depth (cm)	Trial 1	Trial 2	Trial 3
1	995.17	5188	1330.9
2	15499.75	1466.95	10495.16
3	487060.1	26965.75	1271.54

Again, as was observed with the probe orientation results, the optimum probe depth was not similar in any of the trials done.

3.9.1.5. Wastewater Sample Filtration

Before reaching a conclusion on whether the FBRM works with the industrial wastewater samples obtained from Aevitas or not, another experiment was done to reduce the amount of solids in the sample before placing the FBRM probe in it. After filtering the sample, it was added to the beaker and the FBRM was started. The conditions used for this experiment were using a medium stirrer, mixing at 400 RPM, and placing the FBRM probe at a 2 cm depth and 10° orientation. This was again without any polymer flocculant addition. The result obtained for the 100 - 300 micron particle size range can be seen in Figure 36 below

As seen in the figure, the results for the three trials were not similar. Thus, reducing the solids content in the wastewater samples did not help in getting reproducible and stable FBRM curves.

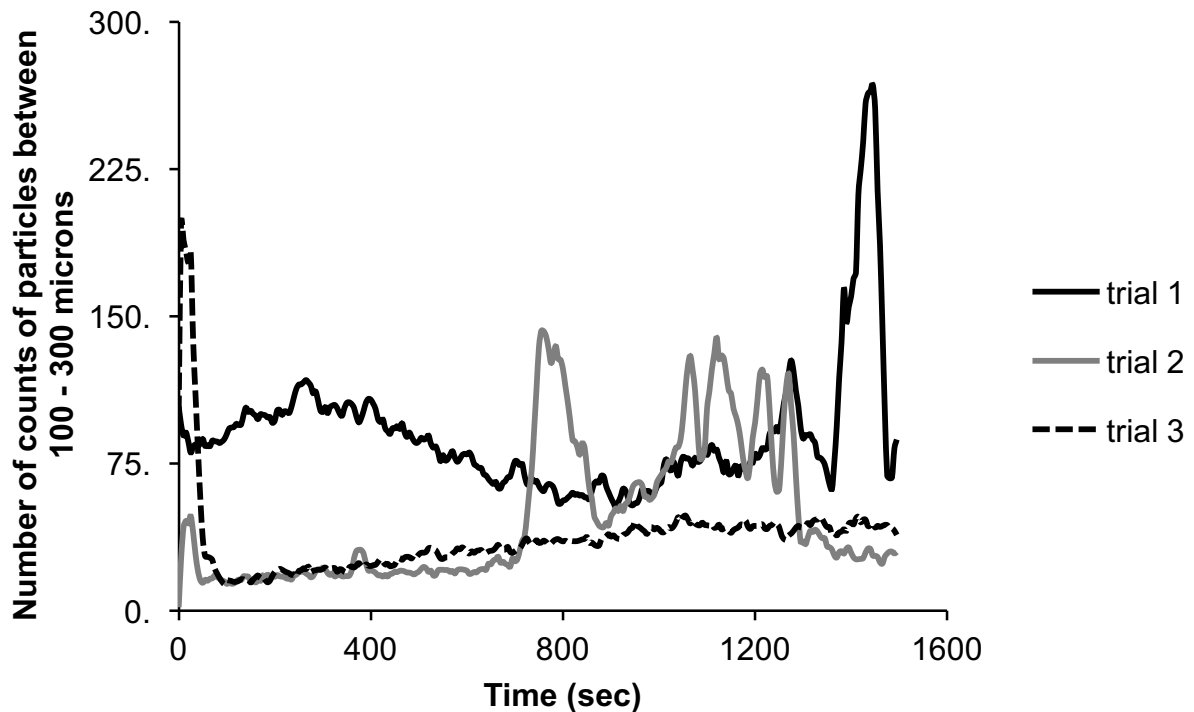


Figure 36: FBRM output for three different trials after filtering the wastewater sample to reduce the amount of solids in it.

3.10. Clay and Polymer Flocculation

The following section contains several concepts and aspects that were tested in this work in the area clays and their use during the polymer flocculation process as an aid to get a better treated water quality. All of the experiments done under this section were on “wastewater 1”, and done in duplicates.

3.10.1. Kaolin DOE Study

Table 11 below shows the design parameters and levels used to perform the kaolin DOE, as well as the final average COD (ppm) that was achieved for each duplicate.

Table 11: Kaolin DOE design table showing the factors tested, their levels, and the final obtained average COD (ppm) values for each of the runs

Standard order	Actual order	Kaolin dose (K)	Flocculant dose (F)	pH (P)	Average COD (ppm)
1	6	-	-	-	13300
2	2	+	-	-	9840
3	5	-	+	-	10720
4	3	+	+	-	10220
5	7	-	-	+	10780
6	1	+	-	+	12640
7	8	-	+	+	10760
8	4	+	+	+	10400

As seen in the table, the average COD value did not undergo any significant changes for the different conditions that were tested. Visually, the samples with the higher pH usually cleared out better than those at a lower pH, but clearly that did not have any effect on COD. A Pareto plot based on the above results was done using “R” software to examine the interactions between the three factors and their effect on COD. The plot is shown in Figure 37 below.

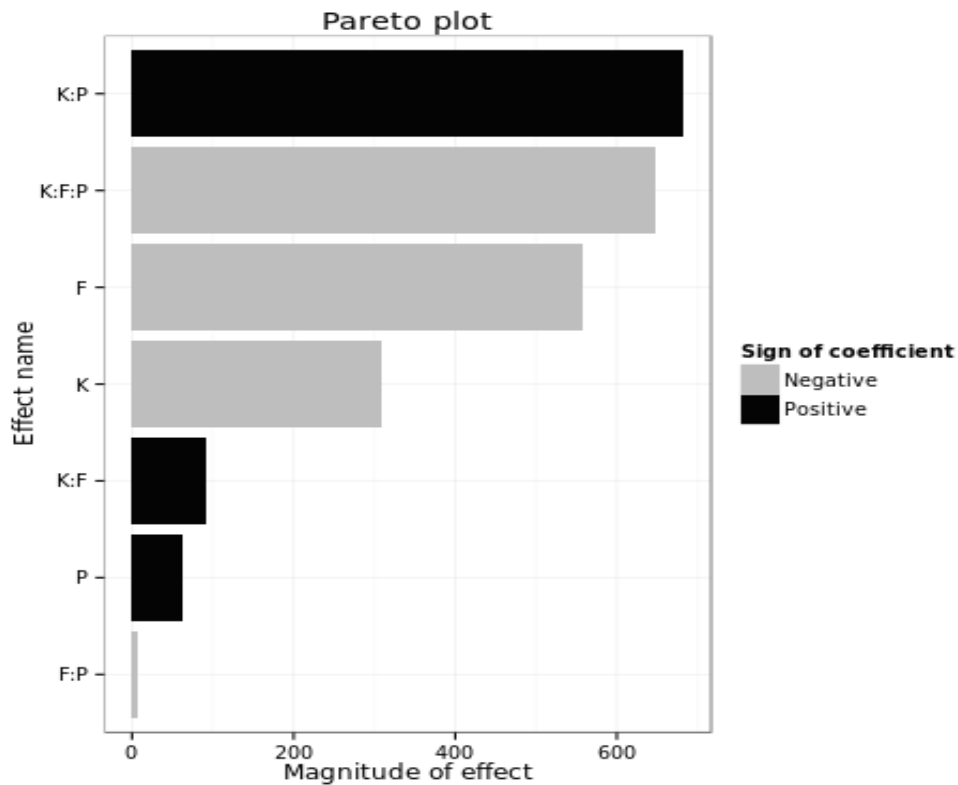


Figure 37: Pareto plot for the Kaolin DOE obtained using "R" software.

From the Pareto plot, it can be noticed that the kaolin (K) and pH (P) interaction is strong. However, since the COD values obtained in the DOE were very close to each other, the Pareto plot cannot really be used to make any sufficient conclusions about the effect of such interactions.

A theory that could be definitely established from this study is that the use of kaolin along with polymer flocculation for this wastewater sample does not enhance the final results of the treated water based on COD value. Samples treated with just the polymer flocculant could result in similar, or even lower, COD value.

3.10.2. Bentonite DOE Study

Table 12 below contains the design parameters and levels used to perform the bentonite DOE, as well as the final average COD (ppm) that was achieved for each duplicate.

Table 12: Kaolin DOE design table showing the factors tested, their levels, and the final obtained average COD (ppm) values for each of the runs

Standard order	Actual order	Bentonite dose (B)	Flocculant dose (F)	pH (P)	Average COD (ppm)
1	6	-	-	-	21880
2	2	+	-	-	8060
3	5	-	+	-	15660
4	3	+	+	-	4480
5	7	-	-	+	43280
6	1	+	-	+	34570
7	8	-	+	+	47490
8	4	+	+	+	40190

Unlike the kaolin DOE, the COD in the bentonite DOE changed significantly between the various conditions tested. Some of the COD values achieved in this DOE (bolded) were definitely lower than what is usually achieved via using the polymer flocculant only for the treatment. A Pareto plot based on the above results was done using “R” software to examine the interactions between the three factors and their effect on COD to better understand the results. The plot can be seen in Figure 38 below.

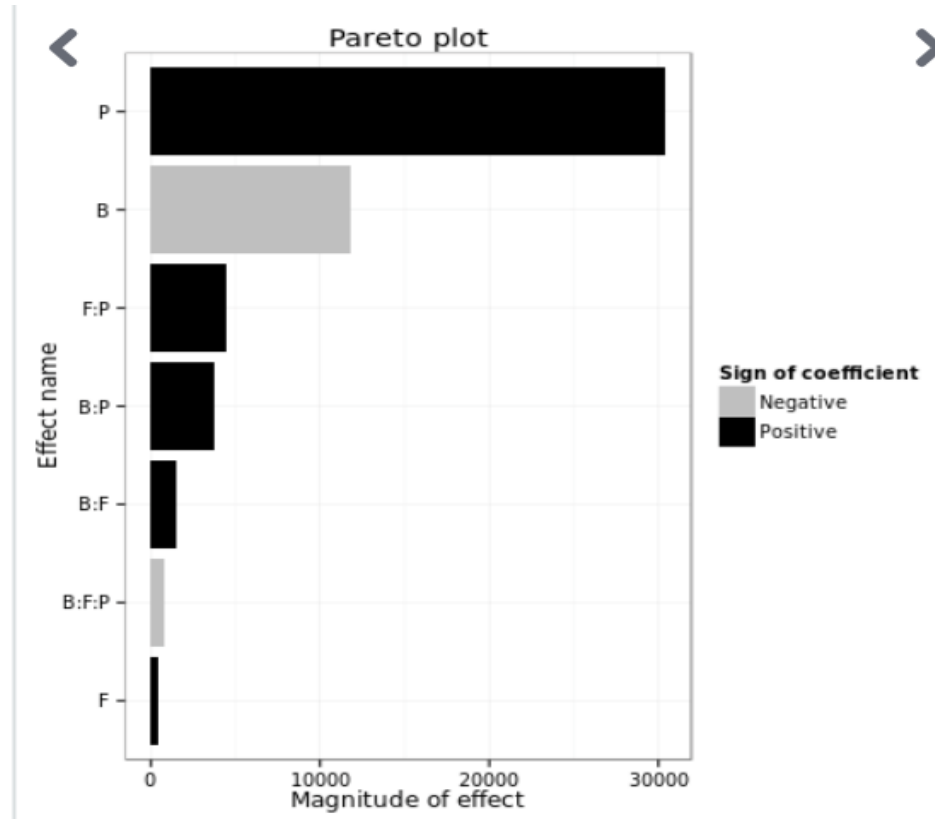


Figure 38: Pareto plot for the Bentonite DOE obtained using "R" software.

As seen in the plot and the design table, pH had the greatest effect on COD value. Increasing the pH increased the COD, and decreasing it reduced the COD. Bentonite dose also had a significant effect on COD, compared to flocculant dose and the interactions between the factors. From the plot, increasing the bentonite dose reduced the COD value. This is because when more bentonite is added, more surface area is provided for the oils and organic content to adsorb onto the surface of bentonite and settle down, resulting in a well-treated supernatant phase with a lower COD.

This DOE proved that bentonite, unlike kaolin, could be promising in treating these wastewater samples to a low COD level (at least 50% less than what Aevitas usually obtains with just polymer flocculation), and was thus focused on. Since the

results showed that a lower pH (i.e. pH of 4) results in a lower COD, this pH was used as the optimum pH to run the experiments. Thus, in all the experiments, the pH was first lowered to 4 before the treatment, without adding any base at the end.

3.10.3. Effect of Bentonite Dose on COD

Figure 39 below contains the COD results obtained at various bentonite dosages. The procedure for the experiment has already been explained in section 2.4.2.3. The polymer flocculant dosage used was 0.3 g/L.

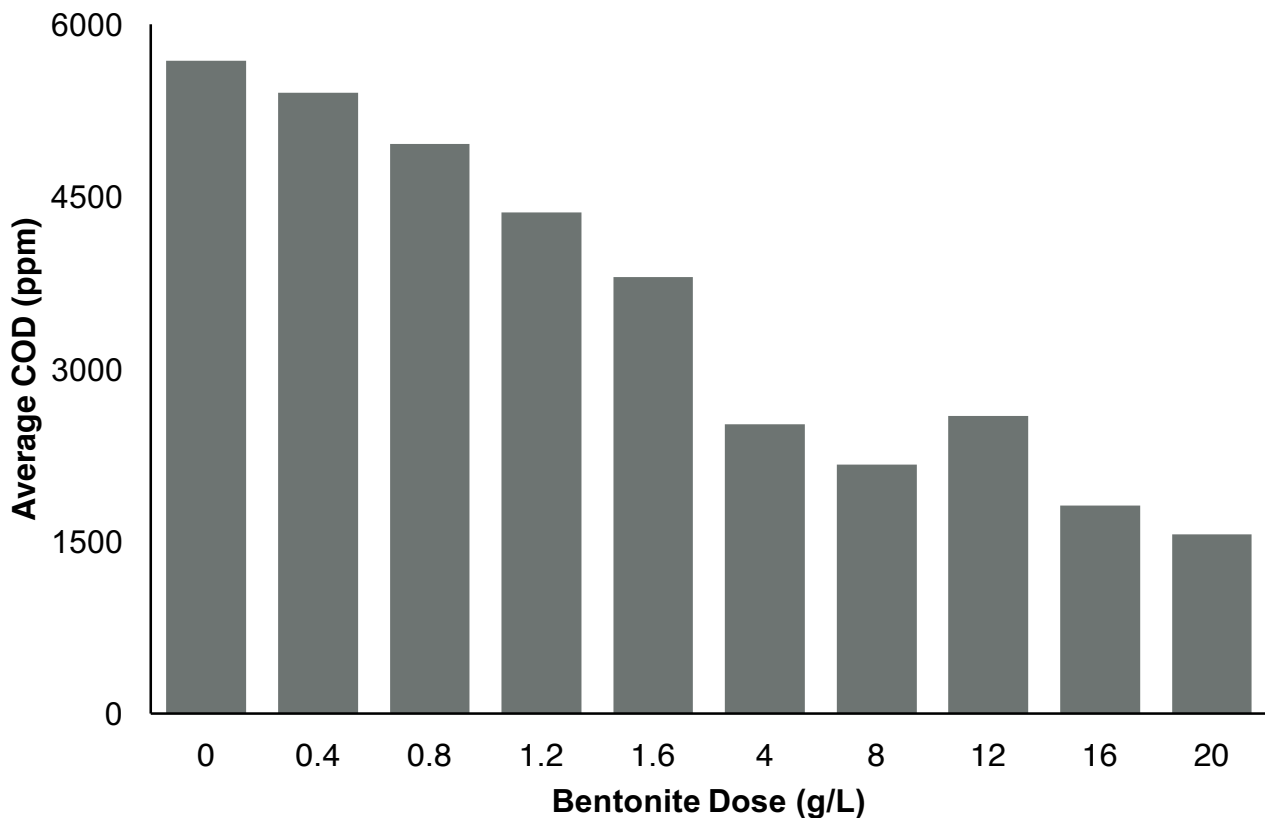


Figure 39: The effect of bentonite dose (g/L) on the final treated water COD (ppm) while using a constant 0.3 g/L polymer flocculant and a pH of 4

As can be clearly seen, the more bentonite is added, the lower the supernatant phase COD of the treated wastewater. The addition of the 20 g/L bentonite dose helped in reducing the average COD value by 72.5% when compared to the addition of none (i.e. treatment with just polymer flocculant). On the other hand, the 1.6 g/L bentonite dose resulted in a 33% reduction only. Clearly, the higher bentonite dosages definitely provided a better treated wastewater quality with a lower COD.

When the bentonite dose is increased, more surface area is provided for soluble oil and organic content in a wastewater sample to adsorb on. When the polymer flocculant is added after bentonite, the bentonite particles along with the adsorbed content all come together to form flocs and settle down (or float in some cases; this will be discussed later), leaving a clear treated supernatant phase with a lower COD value.

While higher bentonite dosages proved to work well in reducing COD in wastewater, there could be some disadvantages when applied at a large scale. At a larger scale, the amount of bentonite needed to achieve COD values as low as those obtained at a lab scale is large and the associated costs might be high. In addition to that, large volumes of sludge are likely to form at a higher bentonite dose, which might require dewatering.

3.10.4. Effect of Polymer Flocculant Characteristics along with Bentonite on COD

3.10.4.1. Varying Polymer Flocculant Dose

The first set of experiments done under this section was varying the polymer flocculant dose. The usual procedure was implemented and a constant 12 g/L bentonite dose was used. The results obtained are in the figure below.

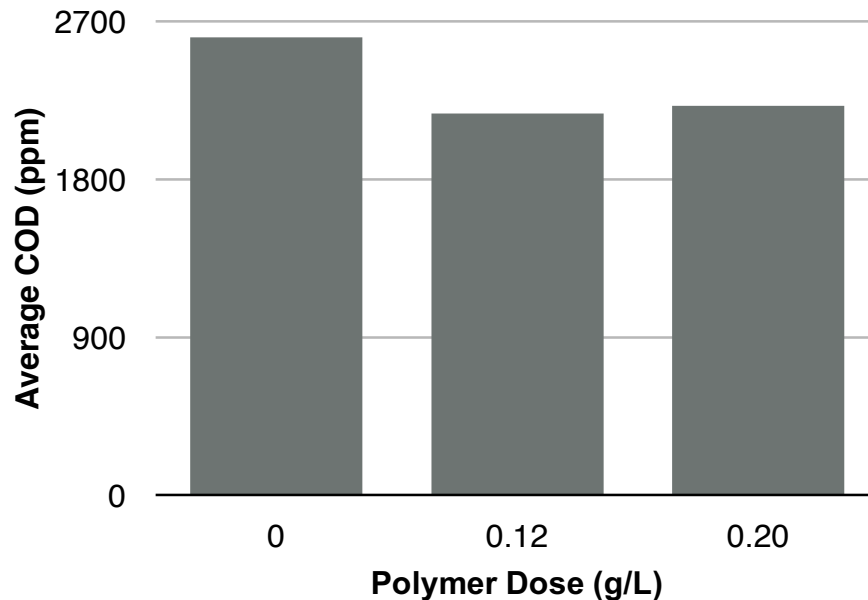


Figure 40: Effect of polymer flocculant dose (g/L) while using bentonite on the final treated water COD (ppm)

As can be seen, the COD values obtained at a 0.12 g/L and 0.20 g/L polymer flocculant were almost similar (2% difference), with 0.12 g/L even performing slightly better. The figure below (Figure 41) shows a picture of the actual samples for one of the runs obtained after settling for the 0.12 and 0.20 g/L polymer flocculant dosages.

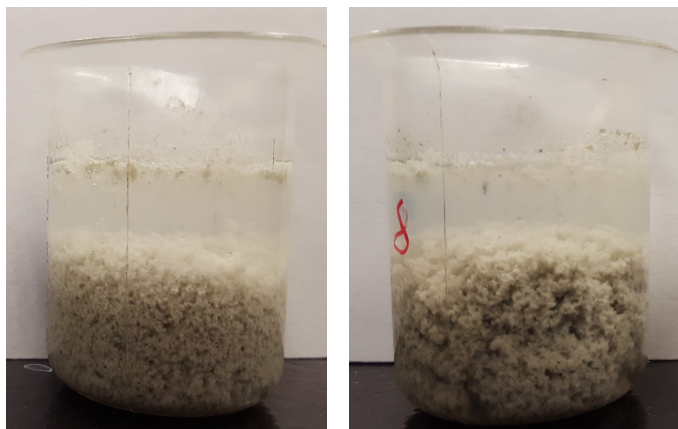


Figure 41: The picture on the left is for the sample that was treated with a 0.12 g/L flocculant dosage. The picture on the right is for that treated using the 0.20 g/L polymer flocculant dosage. The pictures were taken after the samples were allowed to settle for 15 minutes

While a lower polymer flocculant dose could result in a similar, or lower in some cases, COD value compared to the higher polymer flocculant dose, there is a significant difference between the two in terms of the structure of formed flocs. This is evident in the picture shown above. When the polymer flocculant dose was low, the flocs that formed appeared small and smooth. On the other hand, at a higher dose, the flocs that formed were clearly bigger in size. The latter is what wastewater companies usually prefer to have as it makes it easier for the flocs to be “sludged” out of the treatment tank. Thus, a higher polymer flocculant dose is more ideal for such treatments, as long as it is not being added in excess. Accordingly, for the rest of the experiments, the polymer flocculant dose used was either 0.28 g/L or 0.30 g/L in order to form larger flocs and get a larger treated water quantity.

3.10.4.2. Varying Polymer Flocculant Charge

After varying the polymer flocculant dose, the polymer flocculant charge was varied by doing the treatment using an anionic polymer flocculant (P8 – refer to Table 5) as well as the usual cationic polymer flocculant for comparison. The cationic polymer flocculant was added at a 0.28 g/L. However, when the anionic polymer flocculant was added at the dose, the wastewater samples were not flocculating. Thus, for the anionic polymer flocculant, a 0.56 g/L dose was added instead. Figure 42 below shows pictures of the samples for one of the runs after the treatment was completed, and the COD results are displayed in Table 13.

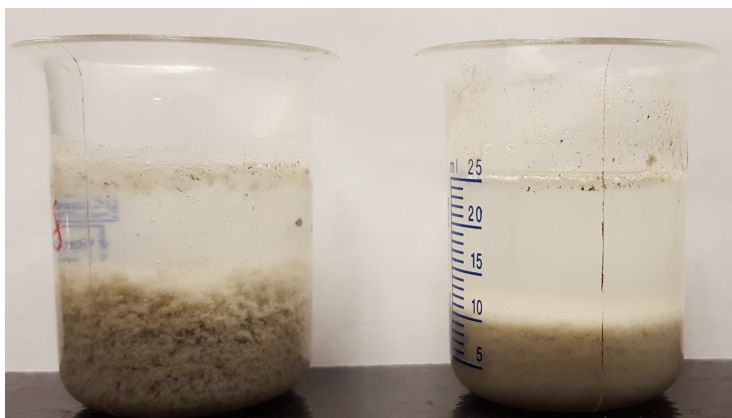


Figure 41: The beaker on the left shows the sample that was treated with the cationic polymer flocculant. The one on the right is for that treated with the anionic polymer flocculant.

Table 13: COD (ppm) values obtained after treating a wastewater sample with two different polymer flocculants of two different charges

Flocculant charge	Trial 1 COD (ppm)	Trial 2 COD (ppm)	Average COD (ppm)
Cationic	2380	2182	2281
Anionic	2200	2760	2480

Clearly, the supernatant phase of the sample treated with the anionic polymer flocculant, even though at a higher dose, did not result in a lower COD value than that treated with the cationic polymer flocculant. In addition to that, there is a clear difference in the structure of the flocs formed. Those formed by the anionic polymer looked small and smooth, and this is definitely not desired at a larger scale. Accordingly, a cationic polymer flocculant is a better option for such treatment.

3.10.5. Effect of Order of Bentonite and Polymer Flocculant Addition on COD

The order in which bentonite and the polymer flocculant are added could also potentially have an effect on the final treated water quality. Thus, a treatment was done by using simultaneous addition of the bentonite and polymer flocculant, and compared to the treatment via the regular addition (i.e. addition of bentonite first, following the procedure in section 2.4.2.3). The samples treated via simultaneous addition were done without waiting 2 minutes before the polymer flocculant addition. The COD results obtained are in the figure below.

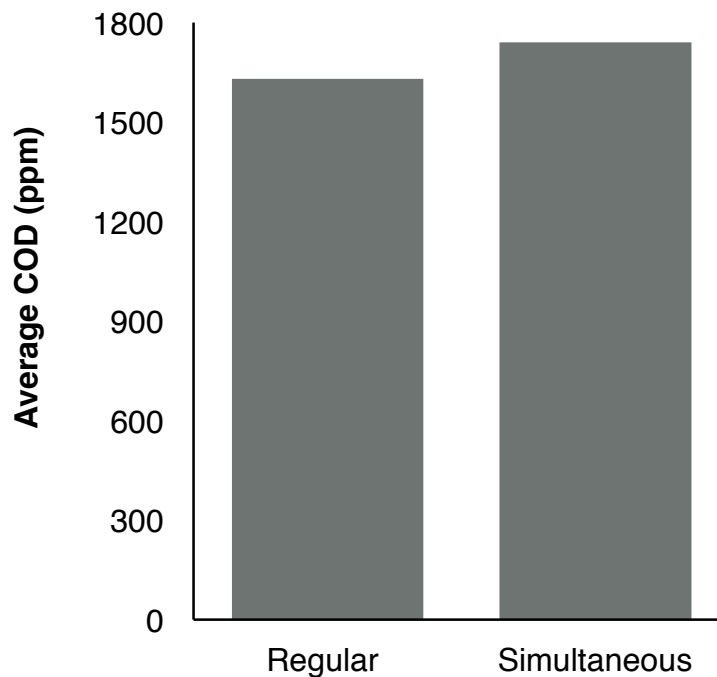


Figure 42: COD (ppm) results obtained while experimenting with the order of addition of bentonite and the polymer flocculant. Regular addition was done using the normal procedure, while the simultaneous was done without waiting 2 minutes between the bentonite and polymer flocculant addition.

In terms of the COD value of the supernatant phases, there was not a significant difference between the two and either of the methods could be used. However, the main difference was again the structure of the flocs formed. Samples treated by adding bentonite and the polymer flocculant simultaneously resulted in smooth and small flocs, which is not desirable.

3.10.6. Effect of Using a Combination of Bentonite and Kaolin along with Polymer Flocculant on COD

After the several experiments that proved bentonite to be working efficiently in reducing COD, and the DOE that showed kaolin not to be very effective, experiments were done to test what would happen if a mixture of kaolin and bentonite was used instead of either by itself. The results obtained in one of the experiments are shown below. Bentonite and kaolin were mixed to a 1:1 ratio and the general procedure for this section was used. The results were similar for all the experiments done in this section.

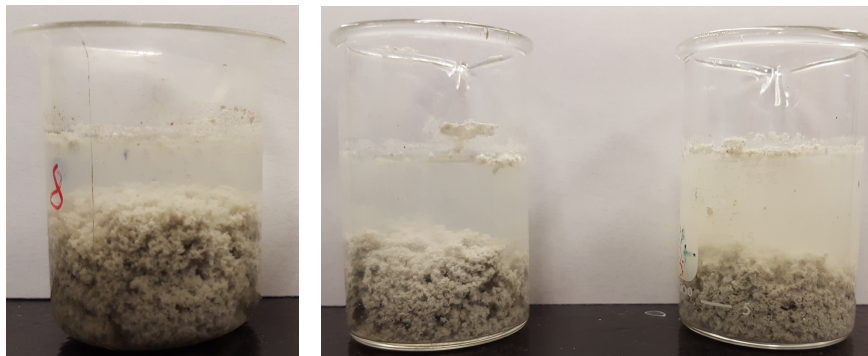


Figure 43: A picture of the samples after the treatment was completed. Starting from the left side, the first beaker contains the sample that was treated with just 16 g/L bentonite. The second beaker contains the sample that was treated with a mixture of bentonite and kaolin, 8 g/L of each. The last beaker shows the sample that was treated with just 16 g/L kaolin.

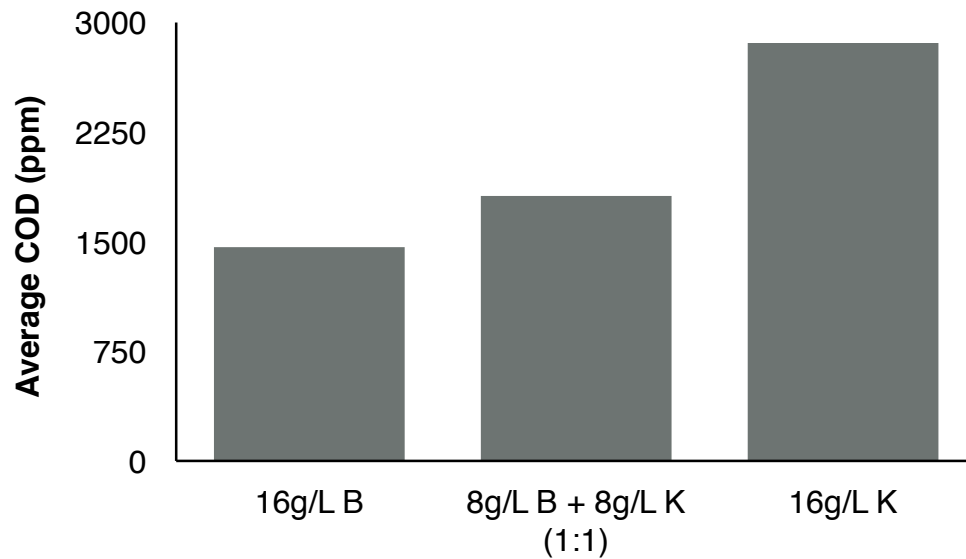


Figure 44: COD (ppm) results obtained for treating a wastewater sample with just bentonite (B), a 1:1 ration of kaolin (K) and bentonite (B), and then just kaolin (K).

As seen in the results, bentonite by itself was able to achieve the lowest COD, and the clearest supernatant phase. It was already proven by the DOE that kaolin does not work well in treating such wastewater samples to a low COD. The reason could be the general characteristics of kaolin itself and that of such a type of wastewater. This was also evident in the results; when kaolin was mixed with bentonite, the supernatant phase became less clear and its COD value increased, and when kaolin was added by itself the results got even worse. This further proves that kaolin should not be considered at all for this treatment. The reason for that is that when compared to kaolin, bentonite is known to expand and swell in water, and has a larger specific surface area (20 times that of kaolin), which increases its capability in removing contaminants.

3.10.7. Effect of Bentonite Dose on Floc Behavior

Previously, in section 3.3, it was mentioned that the charge of the polymer flocculant and the dose at which it is added did not help in allowing the flocs to settle rather than float. In this set of experiments, it became more obvious why flocs were behaving in this manner.

Below are the results of the experiment that tested the effect of bentonite dose on floc behavior. No water quality measurements were taken as the main focus was to just observe whether flocs float or settle at low and high bentonite dosages.

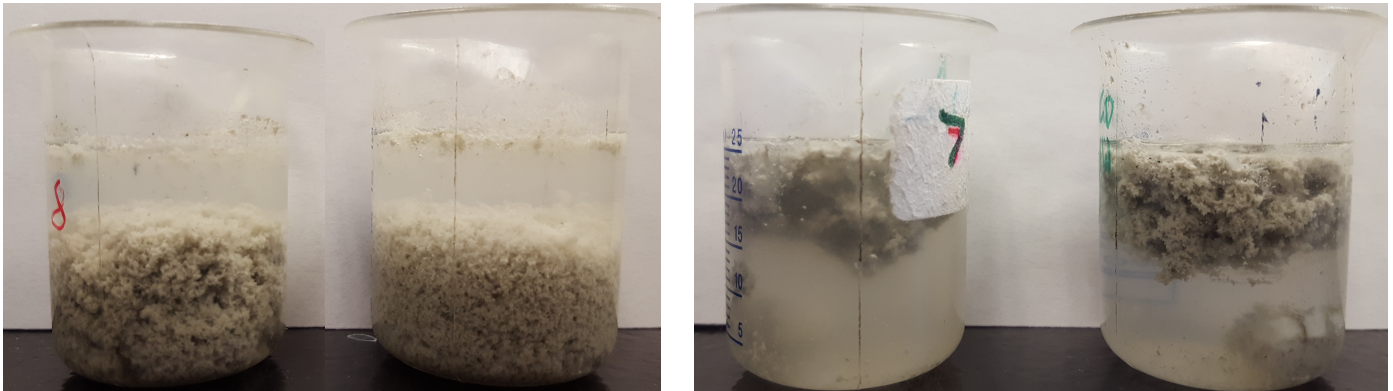


Figure 45: The two beakers on the left show samples that were treated using 16 g/L bentonite at a high and low flocculant dose respectively. The two beakers on the right show samples that were treated using 1.6 g/L bentonite at high and low flocculant dose respectively.

Again, the only difference that the polymer flocculant dose made is in the structure of the flocs; a higher dose gave larger flocs. However, it did not affect how the flocs behave. On the other hand, the bentonite dose had a great effect on the structure of the flocs. As can be seen in Figure 46, the flocs were able to settle when a high bentonite dose was added. When a lower dose of bentonite was added however, the flocs still floated to the top. Before coming to a solid conclusion, the results below are for the

second set of experiments done in this section, which was to measure the mass of the sludge formed after filtering and drying it for 24 hours.

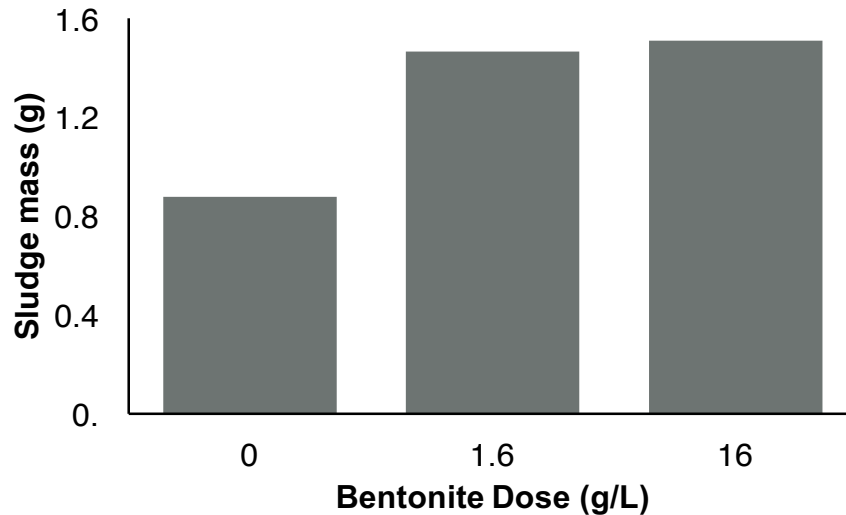


Figure 46: Sludge mass (g) obtained for a wastewater sample treated at different bentonite dosages and at a constant polymer flocculant dose (0.3 g/L).

As seen in the figure, the flocs formed when using 16 g/L bentonite had a higher mass than those formed using 1.6 g/L. While the mass of flocs was not significantly different, those with a higher mass (formed using 16 g/L bentonite) were able to settle, unlike the ones with a slightly lower mass. Thus, there could be a bentonite dose a bit lower than 16 g/L that could provide similar results and thus save the amount of bentonite used. However, this has not been tested.

After running these experiments and finding the results, it was concluded that the main reasons that flocs tend to float, both in the lab and treatment plant, is because the polymer flocculant itself is not “heavy” enough to allow the organic content and other

particles, which tend to float usually, to attach to its chains and settle down. Thus, the main problem is both in the wastewater type and in the polymer flocculant characteristics. However, most polymer flocculants will still give the same results, whether the charge or molecular weight of them was varied or not.

As seen above, the problem of the floating flocs could be solved by adding a coagulant or clay material at a certain dose before polymer flocculation. This will add more weight on the polymer chains when flocculation happens, and this will enable the flocs to settle to the bottom of the tank. It is important that flocs settle rather than float in the flocculation tank. Most flocculation tanks in plants transport the sludge from the bottom for discharge or further treatment. If flocs float to the top, a skimmer would be needed to remove the sludge from the top and this will just complicate the procedure since the top of the tank is usually used to transfer the treated water. If flocs floated to the top, it would not be easy to transport the supernatant phase by itself; flocs might get transported with it.

3.10.8. Sludge Recycling

The last set of experiments done under this section was on sludge recycling. This was done in an attempt to find scenarios that would reduce that treatment cost by using the sludge from a previous treatment to flocculate the wastewater in another treatment. The results of the 3 scenarios tested under this section of experiments can be seen in the figure below. The difference between each has been explained in the Section 2.4.3.

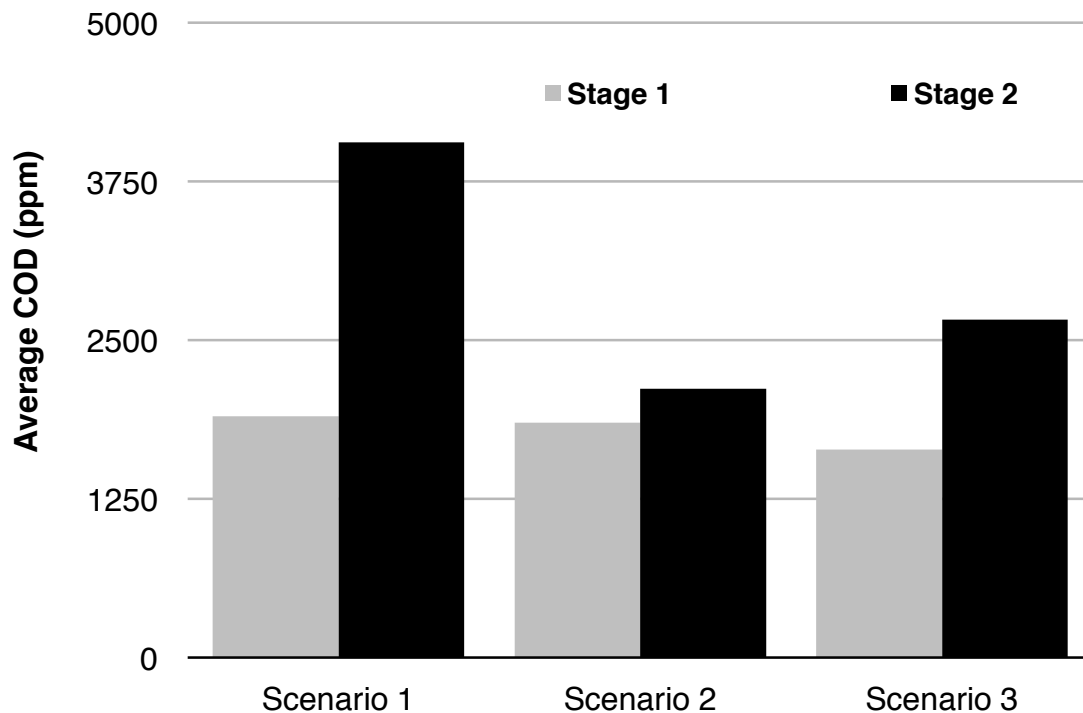


Figure 47: Average COD (ppm) obtained for the different scenarios that dealt with finding an option to reduce treatment costs by using the sludge from a previous treatment to treat a new sample

From the results, it is clear that scenario 2 gave average COD values for stages 1 and 2 that are quite close to each other, unlike the other scenarios. Accordingly, it is the best scenario to be used for sludge recycling, if necessary. This is when the regular bentonite and polymer flocculant dosages are added in stage 1, and just the regular polymer flocculant dosage in stage 2 (while using the sludge formed from stage 1).

On a small scale, this will not be really useful as there will not be a significant difference in expenses if the sludge of a previous treatment was used to treat a new sample rather than adding regular bentonite and flocculant dosages to it. However, at a larger scale, the bentonite costs could get expensive and thus using the sludge from a previous tank that was treated with bentonite and polymer flocculant to treat a new tank without having to use bentonite again could actually result in some savings.

Chapter 4: Conclusions and Recommendations

4.1. Conclusions

The work presented in this thesis was in collaboration with Aevitas, a specialized industrial wastewater treatment facility located in Brantford, ON. After the City of Brantford set new by-law discharge limits as a result of the WSER federal law, it was essential for Aevitas to optimize their process to meet the new limits. Like most specialized industrial wastewater treatment facilities, Aevitas receives tanker truck shipments of wastewater from various industrial generators. This makes it challenging to identify optimum treatment options for wastewater loads that vary in characteristics. Thus, it is crucial for facilities that receive varying wastewater loads on a daily basis, such as Aevitas, to have a method to run rapid tests to identify the best treatment conditions and options.

The main process used by Aevitas for their treatment is polymer flocculation. Thus, in this work, a high-throughput method (at a 25 mL scale) was used to investigate and test several aspects in the area of polymer flocculation for industrial wastewater treatment. While there have been many studies that focused on industrial wastewater treatment previously, most of them were on samples from a single source and done using a jar test, which requires larger volumes of wastewater samples for running experiments. However, the wastewater samples used for experiments in this project were from Aevitas, and thus, there was a significant variation in their characteristics.

The high-throughput technique was successfully used for screening various polymer flocculants at different concentrations and dosages to identify the optimum

ones for different wastewater samples. In addition to that, the aspect of multi-stage polymer flocculation was tested and proven to treat wastewater samples to a lower turbidity value when compared to adding the polymer flocculant dose all at once. It was also proven that multi-stage polymer flocculant addition could actually result in cost savings since half the regular polymer flocculant dose added in a multi-stage manner could perform flocculation just as well as the regular dose added directly. Moreover, scale-up experiments were done in the plant on 45000 L tanks to compare the performance of undiluted polymer flocculant and 1 wt% polymer flocculant. The 1 wt% polymer flocculant solution was able to treat wastewater tanks just as well as undiluted polymer flocculant and using only half the amount of “neat” polymer. More savings could be achieved if a better system was used to prepare the 1 wt% solution rather than doing it manually.

Moreover, methods previously used for in-line monitoring and polymer concentration detection were implemented in this work for industrial wastewater treatment as well. The FBRM was tested as a method to be applied for in-line monitoring to detect the size distribution of flocs after polymer flocculation in industrial wastewater. The main problem with using the FBRM on industrial wastewater samples obtained from Aevitas was that the results were never reproducible, and there was always some noise in the graphs even when the sample was just being mixed at a constant speed and all other conditions were kept constant. An attempt was done to vary and optimize several conditions that contribute to the performance of the FBRM. However, it was almost impossible to find any optimum conditions that allow the FBRM to characterize such wastewater samples. Thus, although the FBRM was a successful

tool for in-line monitoring in some previous studies in wastewater treatment and in other fields, it is not the ideal tool for industrial wastewater sources similar to the ones tested in this project. The concept of UV absorbance was also investigated as a method to detect residual polymer concentration in the supernatant phase of a treated wastewater sample and find the optimum polymer flocculant dose by relating the UV absorbance of the supernatant phases of samples treated at different dosages with turbidity. It was proven that UV absorbance can be a promising method in industrial wastewater polymer flocculation and could be used to optimize the process and avoid an overdose in the amount of flocculant added.

Finally, the high-throughput method was also used to study the application of bentonite along with polymer flocculation in an attempt to lower the COD value of one of the wastewater samples to 600 ppm, which is the new limit for COD set by the City of Brantford. When using bentonite, COD was reduced to a range of 1000 – 1500 ppm in most cases. However, it could be eventually possible to lower the COD further and reach 600 ppm by using a bentonite dose higher than what has been used in the lab. This might have some disadvantages though at a larger scale such as the associated costs and the larger amounts of sludge that would form. Several other aspects regarding using bentonite along with polymer flocculation were also tested such as the effect of the polymer flocculant dose and charge, sludge recycling and the effect of bentonite dose on the behavior of the flocs. Cationic polymer flocculant was a better option than an anionic one for the wastewater samples tested. In addition to that, after using bentonite with polymer flocculation, it was found that a high bentonite dose would enable the flocs to settle down rather than float (in some cases, flocs were floating to

the top rather than settling when the treatment was done using just a polymer flocculant) and this is essential in a treatment tank since sludge is removed from the bottom of the tank. Also, possible cost savings in bentonite could be achieved on a large-scale treatment by using the sludge from a previous treatment to treat wastewater in another tank (i.e. sludge recycling).

As mentioned earlier, the main challenge in this work was that unlike most of the previous studies in industrial wastewater treatment, there was a great variety in the characteristics and sources of the wastewater samples that were tested. The concepts and ideas that were implemented in this study could be beneficial for any specialized industrial wastewater treatment facility that receives various loads on a daily basis and is on the look for a simple and quick method to run rapid experiments to optimize their process, a method for detecting residual polymer concentration and monitoring their polymer flocculant consumption, or an alternative for reducing COD in wastewater samples without using complicated biological treatments or activated carbon.

4.2. Recommendations

When treating wastewater, knowing its characteristics and the main compounds and contaminants present in it can help in identifying the best treatment options and conditions. However, as was seen in Table 4, there was not sufficient information about the chemistry of the industrial wastewater samples that were used in this project, and this was a major drawback. “Wastewater 1” was the most commonly used sample in the experiments. This sample was never successfully treated in the lab to a COD level low enough to meet the new by-law limits. As mentioned earlier, the primary source of this wastewater load is automotive industry. Thus, it most likely contains oil and organic matter. It would have definitely been beneficial if the composition of these compounds was known, since COD is mainly as a result of organic matter. Thus, knowing what organic matter is available in the sample would enable one to identify the proper treatment to remove them and decrease the COD. However, since there was no available information at all as to what organic compounds may be present in the sample, it was not recommended to use gas chromatography (GC). To be able to detect some of the compounds present in the sample, there has to be a general idea as to what might be in it. Thus, all of the experiments were done without really knowing what organic compounds were present and which ones were the polymer flocculants and clay materials actually able to remove from the sample. Thus, an experiment focusing on characterizing this sample and screening some polymer flocculants and chemicals based on the characterization could be greatly beneficial for this work.

While there was a great variation in the characteristics of the wastewater samples that were used in the project, the variables that could affect the final treated

water quality in each could actually be related. Thus, after characterizing the wastewater samples used and identifying the main components in each and the variables that would affect the treatment, a statistical analysis could be beneficial as part of optimizing the treatment process, since there would be large sets of data by then. Principal Component Analysis (PCA) is a “technique used to emphasize variation and bring out strong patterns in a dataset” [69]. When having large data sets, PCA makes it easier to “explore and visualize it” [69]. Thus, with the variation of characteristics in wastewater loads which specialized industrial wastewater treatment facilities such as Aevitas treats, PCA could be helpful in finding patterns between them and be able to optimize their process. PCA has been previously implemented in some wastewater studies. For example, Mishra [70] collected several wastewater samples and identified and analyzed some variables present in them, and then used PCA to successfully find the parameters essential in assessing the variation in water quality.

As mentioned in Section 2.2.1, pH plays an important role in flocculation since it is a factor that controls the stability of the particles in a sample. Stable particles in a suspension are difficult to coagulate or flocculate. In the experiments done in this thesis, the pH used was usually based either on visual observations of the suspension at different pH values, or based on previous experiments and pH conditions used in the treatment plant or the lab. While the pH values the samples were set to were able to achieve good flocculation results, they might not necessarily be the optimum ones. Zeta potential is a measure of the electrostatic potential (or electric charge) on the surface of a particle [71]. It is usually measured in mV and each range of zeta potentials

characterizes the stability of the colloids or particles in a suspension, as shown in the table below.

Table 14: The stability behavior for the different zeta potential ranges [72]

Zeta potential (mV)	Stability behavior of the colloid
0 to ± 5	Rapid coagulation/flocculation
± 10 to ± 30	Incipient instability
± 30 to ± 40	Moderate stability
± 40 to ± 60	Good stability
$> \pm 61$	Excellent stability

An attempt was done to measure the zeta potential of some of the samples, however, there was a problem with the concentration of the samples and the capability of the zeta potential analyzer to detect the zeta potential at these concentrations. Thus, there is an opportunity to alter the samples, either via dilution or centrifugation, to get a better concentration, set them to different pH values and measure their zeta potential. This enables the formation of a graph of zeta potential vs. pH from which one can identify the optimum pH for flocculation (when zeta potential is closest to zero). Knowing that might enhance the flocculation performance of the samples tested in this thesis.

It was shown in this work that the FBRM did not work well with the samples tested. Being able to actually monitor floc formation and size can be a beneficial marker for the efficiency of a polymer flocculant in treating a sample. Thus, it would be

worthwhile to explore other alternatives for floc monitoring. For example, one study used photometric dispersion analyzer (PDA) to monitor and examine how floc size varies during flocculation in wastewater treatment [73]. A German company, Aquen, also developed a photo-optical sensor (FlocSens) that aims to assist in determining floc properties [74]. It was successfully used to determine dewatering properties and identifying the optimum out of two polymer flocculants for treating sewage sludge [75]. Thus, there are other on-line monitoring systems that could work with the industrial wastewater samples on which the FBRM was not successful. Being able to monitor floc formation can also be beneficial in grasping a better understanding of what happens when a polymer flocculant is added at different stages throughout the treatment (i.e. multi-stage addition).

Appendices

Appendix A: “R” Software Input Code

The code displayed below is the code the was used in “R” software for the bentonite

DOE:

```
B <- F <- P <- c(-1, +1)

design <- expand.grid(B=B, F=F, P=P)
B <- design$B
F <- design$F
P <- design$P
y <- c(43760, 8140, 31320, 4480, 86560, 69140, 94980, 80380)
water <- lm(y ~ B*F*P)
summary(water)

library(pid)
paretoPlot(water)
```

The output that was obtained, which is used to form the Pareto plots and relationship

between the factors, using the above code was as follows:

Coefficients:				
	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	52345	NA	NA	NA
B	-11810	NA	NA	NA
F	445	NA	NA	NA
P	30420	NA	NA	NA
B:F	1450	NA	NA	NA
B:P	3805	NA	NA	NA
F:P	4470	NA	NA	NA
B:F:P	-745	NA	NA	NA

Appendix B: T-test Analysis Results

According to the T-test, there is a significant difference when the absolute value of t Stat is greater than or equal to t Critical.

Table A-1: T-test analysis results for undiluted polymer flocculant for the data in Figure 8

	<i>Variable 1</i>	<i>Variable 2</i>
Mean	18.06667	49.83333
Variance	15.77333	544.4133
Observations	3	3
Hypothesized Mean Difference	0	
df	2	
t Stat	-2.32469	
P(T<=t) one-tail	0.072834	
t Critical one-tail	2.919986	
P(T<=t) two-tail	0.145668	
t Critical two-tail	4.302653	

Table A-2: T-test analysis results for the data in plot “wastewater 2” in Figure 9

	<i>Variable 1</i>	<i>Variable 2</i>
Mean	63.26667	75.43333
Variance	400.4933	700.6433
Observations	3	3
Pooled Variance	550.5683	
Hypothesized Mean Difference	0	
df	4	
t Stat	-0.63506	
P(T<=t) one-tail	0.279951	
t Critical one-tail	2.131847	
P(T<=t) two-tail	0.559903	
t Critical two-tail	2.776445	

Table A-3: T-test analysis results for the data in Figure 28

	<i>Variable 1</i>	<i>Variable 2</i>
Mean	46.53333	62.33333
Variance	593.2133	651.5733
Observations	3	3
Pooled Variance	622.3933	
Hypothesized Mean Difference	0	
df	4	
t Stat	-0.77566	
P(T<=t) one-tail	0.240628	
t Critical one-tail	2.131847	
P(T<=t) two-tail	0.481256	
t Critical two-tail	2.776445	

Table A-4: T-test analysis results for the 1.6 L scale-up experiment comparing undiluted polymer flocculant and 1 wt% polymer flocculant in Figure 16

	<i>Variable 1</i>	<i>Variable 2</i>
Mean	11.43667	12.33333
Variance	8.095033	2.573333
Observations	3	3
Pooled Variance	5.334183	
Hypothesized Mean Difference	0	
df	4	
t Stat	-0.47549	
P(T<=t) one-tail	0.32962	
t Critical one-tail	2.131847	
P(T<=t) two-tail	0.659239	
t Critical two-tail	2.776445	

Appendix C: Graphs for UV Absorbance and FBRM

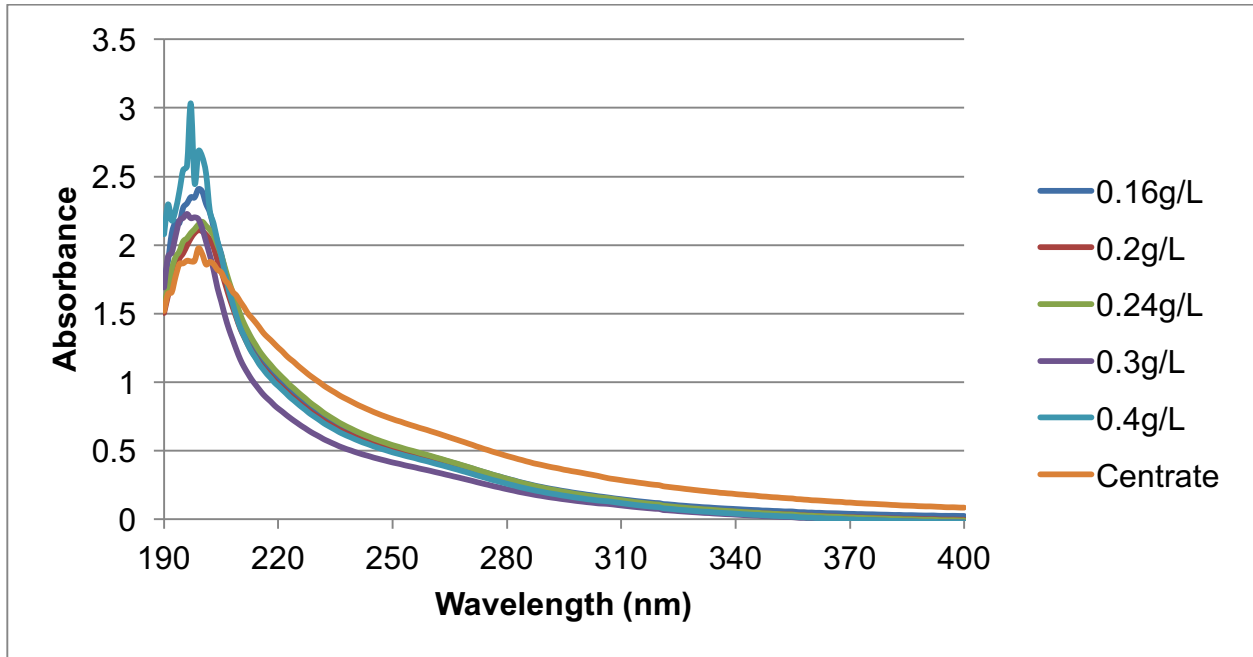
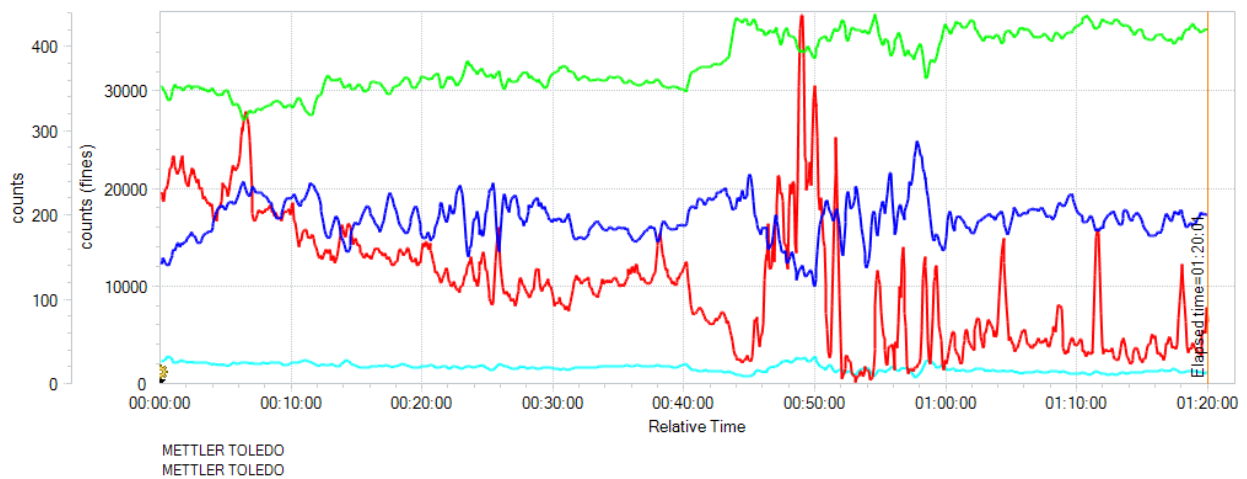
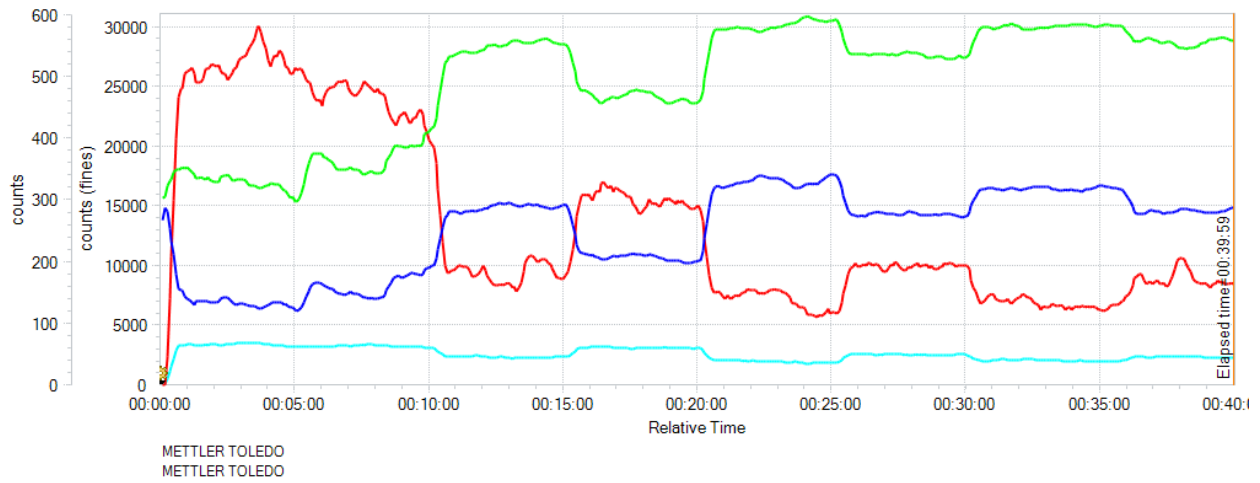


Figure A-1: Absorbance curves over 190 - 400 nm wavelength for the data in Figure 32

Large stirrer



Medium stirrer



Small stirrer

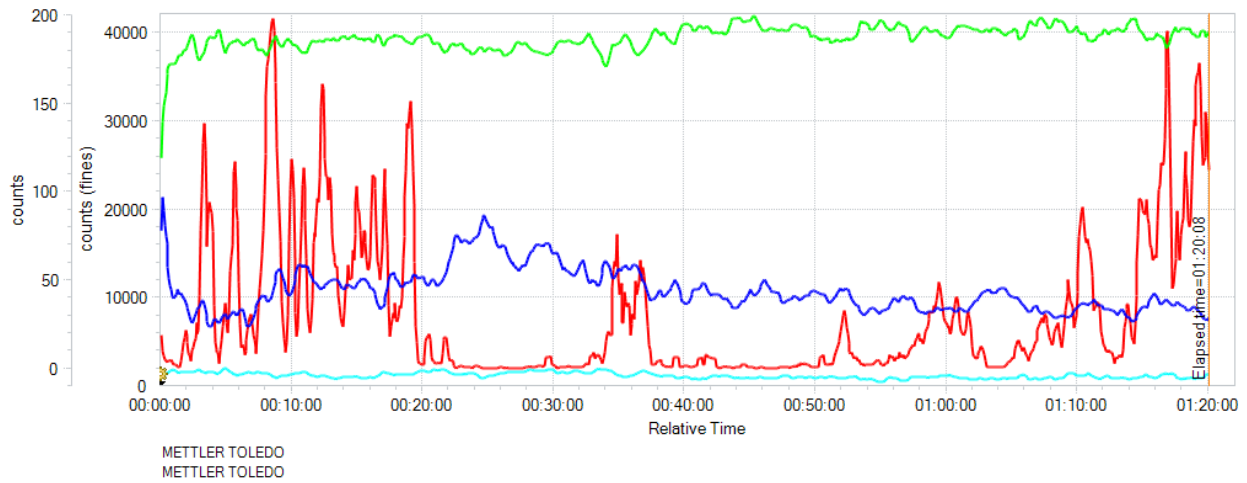


Figure A-2: FBRM output curves for testing different magnetic stirrer sizes

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