Stormwater Pond Sediment De-watering by Anionic PAM at Low Temperature

by

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Abstract

Storm water ponds have been widely constructed over the past four decades as part of municipal storm water drainage systems. These ponds are designed to collect neighborhood storm water run-off to reduce flooding, but can also improve the quality of water discharged to surface water bodies by allowing sediments to drop out of the water column. This sediment gradually accumulates at the bottom of the storm water pond, necessitating occasional dredging. Polyacrylamides (PAM) offer an option to decrease the water content, and therefore weight and volume, of this pond sediment before dredging. This study aimed to improve understanding of the performance of PAM-based sediment dewatering in different conditions, with a focus on the low northern temperatures of Canada. First, the characteristics of storm water pond sediments were reported. Then, dose and temperature effects of PAM were tested. The results indicated that the best dose of PAM (Clearflow Enviro Systems Inc. Soil Lynx 398) to be applied was 0.3g/L when treating pond sediment. The water content of sediment cake increased with increasing PAM concentration when PAM concentration was at 0.3-5 g/L. Meanwhile, in terms of temperature effects for a range of 4-30°C, the water content did not show any significant change ($p > 0.05$). Other parameters such as turbidity, initial settling rate, sediment volume were also measured in this study. The potential mechanisms involved were discussed as well.

Preface

This thesis is an original work by Zhenyuan Zhang. No part of this thesis has been previously published.

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1. Introduction

1.1 Drainage systems and storm water ponds

Municipal sewer systems consist of sanitary and storm sewers. The sanitary sewer system is designed to collect and convey household and industrial wastewater from urban areas to a wastewater treatment plant; whereas the storm sewer system is designed to collect, store and convey runoff from urban areas to a receiving waterbody (City of Edmonton, 2014). This waterbody could be a river, a natural lake or a storm water management pond.

Storm water ponds were initially designed to control the increased quantity of storm water runoff that results from increasing the area of impervious surfaces in urban landscapes. In recent years, the ponds have been increasingly used to reduce the concentration of contaminants in the runoff (Weiss et al. 2006). Storm water ponds have the following functions and benefits: 1) collect neighborhood storm water run-off; 2) improve water quality by allowing sediments to drop out of the water; 3) drain to a storm outfall, and 4) service land economically by storing peak flows and allowing small outlet pipes to be used instead of very large pipes (City of Edmonton, 2014). A pond usually consists of the following components: 1) vegetation for safety and aesthetics, 2) wetland plantings, 3) inlet and outlet structures, 4) submerged plantings, 5) sediment fore-bay, and 6) maintenance access (City of Hamilton, 2009) – see also Figure 1, below. Note in particular that the sediment fore-bay in storm water ponds is intended to diminish the speed of water currents from the pond inlet. Once the speed of water flow decreases, suspended particles settle more rapidly to the bottom of the pond. In addition, this storm water pond has an elongated shape with an inlet and outlet on opposite sides. This design increases the pond detention time and allows more suspended particles to settle.

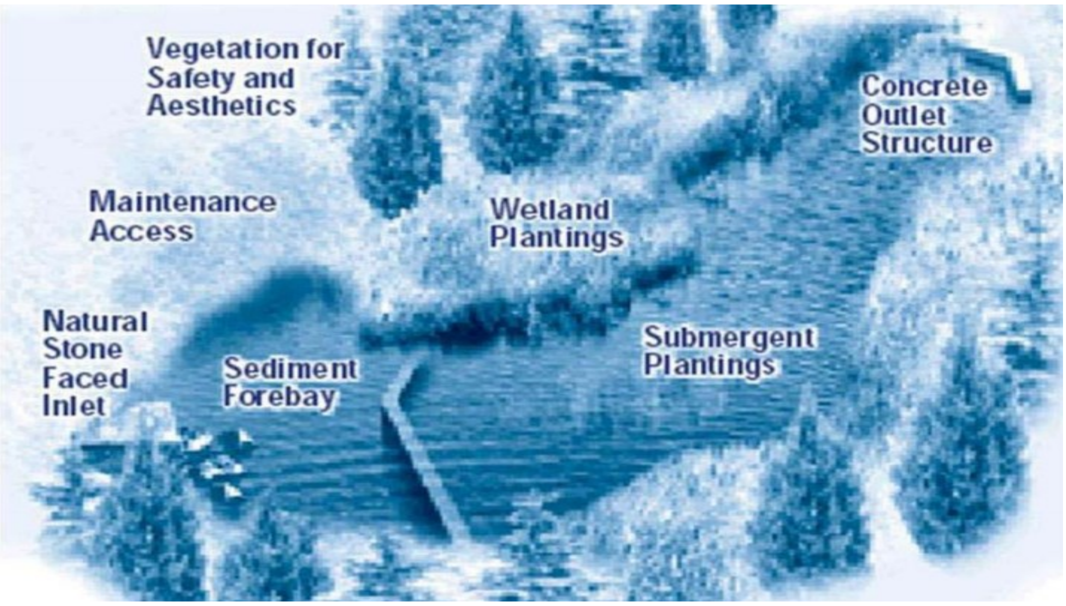


Figure 1. The typical components of a storm water pond (City of Hamilton, 2009)

However, despite the many benefits of storm water ponds, there are disadvantages as well. Since storm water ponds collect storm water run-off and serve, in a sense, as the retention tank of a wastewater treatment plant by allowing sediments to settle in the pond, the water quality and the potential decreased volume of the pond has to be considered in practice. Storm water can contain all sorts of salts, oil and particles, including 1) soil erosion from bare land, 2) lawn chemicals (fertilizers and pesticides), 3) road salt and other de-icing substances, 4) household products (paints, solvents, cleaning agents etc.), 5) oil leaks and illicit disposal, and 6) dust from the atmosphere (Pazwash, 2011). Fertilizers, as one of the pollutants in storm water, could cause serious algal blooms, a phenomenon that is very common in storm water ponds

(Siegel et al., 2011). Specifically, the long retention time of storm water ponds can cause large amounts of nutrients in fertilizers either to settle to the bottom the lake, if they are attached to large particles, or to be taken up by various types of hydrophytes. If these hydrophytes are not ‘harvested’ from the pond, the nutrients will be re-released to the pond when the hydrophytes die and will accumulate there (Hudnell, 2010). Moreover, since storm water ponds work like retention tanks that collect sediment from the water, sediments accumulate at the bottom of the storm water pond over time. Eventually, this accumulation will decrease the retention function of the pond by decreasing the pond volume. If the average permanent pool depth is less than 90 percent of the design depth, dredging is recommended. However, such operations are typically expensive and labor intensive (City of Hamilton, 2009).

1.2 Polyacrylamide (PAM) application

A polyacrylamide (PAM) is a polymer formed from acrylamide monomers ($-CH_2CHCONH_2-$). Different types of PAMs have different functional groups, net charge, shape and molecular weight. These differences allow PAMs to be applied under different conditions as a soil conditioner, a flocculent, a paper-making additive, and so on (Ahluwalia and Mishra, 2008).

As a flocculent, PAM has been used for many years. When applied to water, it can dramatically decrease the turbidity of the water by coagulating colloidal particles into relatively larger aggregates. As these aggregates, or ‘flocs’, grow, gravitational forces begin to dominate and their suspension stability is lost, which causes the aggregates to settle out of solution. Because some metal ions and nutrients are attached to the suspended particles, their concentration in the water column decreases in the short term. However, in the long term, as the polymer breaks down, they have the potential to be released again into the water. In addition, PAMs are also used in sediment sludge dewatering. PAMs with sediment particles can form agglomerations, which attach to each other through polymer bridging. This bridging causes the sediment water content to decrease as the sediment structure tightens (Besra et al., 2002). Importantly for pond dredging, the reduction of sediment water content means a reduction of sediment weight as well, which reduces the cost of the dredging operation. In dewatering with anionic PAMs, divalent ions (e.g. Ca^{2+} and Mg^{2+}) or surfactants (e.g. polyoxyethylenic ether) are usually used to enhance the performance (Besra et al., 2002; Zhu, et al., 2013).

Environmental impacts of PAMs are relevant concerns. For example, PAMs can damage fish gill tissue because the polymers can bind to the gill tissue. PAMs can also exhibit toxicity, with cationic PAMs expected to be more toxic than anionic PAMs (Kerr et al. 2014). Finally, studies have found that the PAM monomer, acrylamide, may be toxic as well (Hall and Mirenda, 1991; Weston et al., 2009).

1.3 Objectives

The current study focused on the Woodbridge Farms storm water pond, located in Sherwood Park to the east of Edmonton. This pond required dredging in the autumn of 2012, and Clearflow Enviro Systems Inc., Strathcona County, and the University of Alberta partnered to investigate the efficacy of polyacrylamides (PAM) in the dredging and sediment dewatering processes in the pond.

To minimize the weight of dredged pond sediments, and potentially to increase the water quality of the pond water through flocculation of suspended particles, anionic PAMs were tested in this study. Specifically, an anionic PAM with trade name Soil Lynx 398, provided by ClearFlow Enviro Systems Inc., was used – it is an acrylamide-acrylate-co-polymer. The acrylamide content of Soil Lynx 398 is less than 5% by weight. Soil Lynx is usually applied to areas requiring re-vegetation or to prevent soil erosion. In addition, when dredging storm water ponds, Soil Lynx powder can be added to the pond sediment to dewater and bind its particles together for easy removal with an excavator and standard dump truck (Clearflow, 2014).

In practice, one of the most important parameters in polymer application is the concentration. Hence, the optimal dosage of polymer when treating storm water pond sediment was examined first. Moreover, temperature is known to greatly affect PAM performance. However, while many studies on PAM dewatering applications have been conducted at or above room temperatures (Besra, et al., 2001; Zhu, et al., 2013; Mopfu, et al., 2004), very few studies have investigated PAM performance at low temperatures. For their application in the Edmonton area, it was necessary to investigate the anionic PAM performance on settling and dewatering at different temperatures, and particularly at low temperatures. Further, it is known that temperature affects many water and sediment particle parameters, such as zeta-potential, viscosity, pH and so on. It was therefore necessary to understand the effects of changes in these parameters on polymer performance, as well as the potential mechanisms involved. Accordingly, the objectives of this project were to,

(1) Identify the optimal polymer concentrations at room temperature in terms of settling and dewatering,

(2) Examine the polymer performance at different temperatures, especially at low temperatures, and,

(3) Investigate the potential mechanisms involved in polymer binding at low temperatures.

1.4 Chapter Overview

The thesis is organized as follows: Chapter 2 reviews the intended function of storm water ponds and potential problems associated with their use. It also focuses on polymers and their characteristics, and especially on polyacrylamide (PAM). Chapter 3 describes both the sampling and experimental methods adopted in this study. Chapter 4 provides the results and analysis of polymer dose and temperature effect experiments. This chapter also discusses the potential mechanisms based on the results from viscosity, zeta potential and Quartz crystal microbalance with dissipation (QCM-D) test. Finally, conclusions and recommendations for future research are presented in Chapter 5.

2. Literature Review

2.1 Storm water ponds and the storm water drainage system in the City of Edmonton

Storm water runoff has been identified as a significant contributor to the degradation of surface water quality in ponds, streams, wetlands, and lakes (Weiss et al. 2006). The most common pollutants found in storm water runoff originate from (1) soil erosion from bare land, (2) lawn chemicals (fertilizers and pesticides), (3) road salt and other de-icing substance, (4) household products (paints, solvents, cleaning agents etc.), (5) oil leaks and illicit disposal and (6) dust from atmosphere (Pazwash, 2011). Storm water ponds are one option for removing pollutants such as suspended solids, heavy metals, nutrients and hydrocarbons, and these ponds function like the retention tank of water treatment plant. By increasing the retention time, the suspended particles settle more easily to the bottom of the pond. Further, since contaminants are often attached to particles, they will be removed by the process of sedimentation as well. It also should be noted that there will be suspended solids stable in suspension in pond water, with the stability of the suspension dependent on pH, viscosity, zeta potential of the particle, particle size and temperature (Larsson et al. 2012).

The City of Edmonton has two types of sewer systems that collect and then discharge storm water: storm sewers and combined sewers. Combined sewers collect both sanitary sewage and storm water runoff in a single pipe system. Construction of combined sewers in Edmonton was an acceptable practice before the 1960s because it was more economical than building two separate sewer systems.(City of Edmonton, 2014). However, combined sewers may discharge wastewater and storm water from a combined sewer system directly into a river, stream, or lake, or the ocean without treatment, particularly after heavy rainfall, which may cause serious water pollution. Therefore, after the 1960s, the construction of combined systems was discontinued due to environmental concerns (City of Edmonton, 2014). Nowadays, most water from rainfall, snowmelt or excessive lawn watering enters the storm sewer system, which collects surface water into underground pipes and conveys it ultimately to a surface watercourse, lake, ravine or the river via 225 outfalls located throughout the city (City of Edmonton, 2014). To manage storm water runoff and reduce suspended particles that enter to the water course, City of Edmonton has built storm water management lakes, or “storm water ponds”, since the 1970s to collect neighborhood storm water run-off. These lakes serve as reservoirs or retention tanks to store storm water temporarily and can improve water quality by allowing sediments to drop out of the water (City of Edmonton, 2014). However, as time goes on, the sediments accumulate at the bottom of the storm water pond. Eventually, this accumulation will cause decreased retention function of the pond by decreasing the volume of the pond. It is suggested that the monitoring be carried out every five years and dredging be undertaken when the average permanent pool depth is less than 90 percent of the design depth (Ministry of Environment Ontario, 2003). The frequency of dredging depends on the amount of exposed soil in the drainage area, the rate of shoreline erosion, the amount of aquatic plant growth and the amount of debris released into the drainage system from roads and by residents. When dredging is required, it is usually expensive and labor intensive (City of Hamilton, 2009). Also, it is known that a large part of the weight and volume of dredged lake sediments will consist of water. If part of the sediment water content can be eliminated before dredging, the cost of the operation could be reduced. One option is application of polyacrylamides (PAM) into the lake to reduce the sediment volume – PAM function in this regard is investigated in this study.

2.2 Storm water pond/lake sediments

Sediments in natural lakes usually consist of three primary components: (1) organic matter in various stages of decomposition, (2) particulate mineral matter, including clays, carbonates, and non-clay silicates, and (3) inorganic components of biogenic origin (Wetzel, 2001). In storm water ponds, the water source means that nutrients and salts washed from lawns and roads are also present.

Rivers and streams carry significant amounts of the suspended sediment with them from local drainage and finally drain into lakes. This is one of the main sources of lake basin sediments. Current and wave action along the shoreline is responsible for additional erosion and sediment deposition, and some material may be introduced due to wind action. Rivers and streams (or storm sewers in this case) transport many different sized materials. When storm water enters a lake, its speed diminishes rapidly, and bed-load transport ceases. Meanwhile, the suspended load begins to settle to the bottom of the lake, with the largest sizes settling first. Only the really fine materials that are too small to have settled out from the inflows or those that have been introduced adjacent to the outflow will be carry out from the outlet of the lake. Because dynamic processes that keep materials suspended are generally more active near the shore, lake sediments are usually sorted by size. The rocks, pebbles, and coarse sands settle near shore, whereas the finer sands, silts, and muds are expected to be found offshore. Most of a lake basin consists of silts and clays, especially away from shores and the lake inlet clays exist in a variety of colors. Black clays contain large concentrations of organic matter or sulfides and whiter clays usually contain high concentrations of calcium carbonate. Other colors, including reds and greens, are known to reflect particular chemical and biological influences (Wetzel, 2001).

In terms of grain size, lake sediment contains clay, silt and sand. Clays are particles with diameters smaller than 0.002 mm. With a fixed volume, small particle size means that they have relatively large surface areas, giving them the capacity to adsorb water and other substances. Silts are particles smaller than 0.05 mm but larger than 0.002 mm in diameter. Sands are particles smaller than 2 mm but larger than 0.05 mm (Brady and Weil, 2008). Particle size is important because it is directly related to the water capacity of the sediment. As mentioned above, in a fixed volume, large numbers of small particles will hold more water than fewer large particles. In this case, knowledge of the proportions of different-sized particles in sediment (i.e., sediment texture) is critical to understand their capacity to hold water (Brady and Weil, 2008).

The surface charge of natural fine particles is negative. Beckett and Le (1990) measured electrophoretic mobility of natural suspended particles in river water and electrophoretic mobility of an organics-coated goethite colloid. Their study showed that the surface charge of particles was relatively similar (-25~-35mV) for all particles even though the particles were very different. The zeta-potential is used to measure the surface charge of particles, and is directly related to the electro-kinetic potential in colloidal dispersions (Andreja, 2009). In general if the magnitude of a particle's zeta-potential is larger than 30, the particles do not tend to stick together (Andreja, 2009). It is concluded that the adsorbed layer of natural organic matter (particularly the humic substance component) is the most important factor for the surface charge of particles in water. This charge could be furthermore modified mostly by the concentration of divalent ions in water. After addition of divalent ions like Ca^{2+} and Mg^{2+}, the surface charge will become less negative due to charge neutralization. In addition, pH will affect the surface charge as well, with increases in pH increasing the net charge of the particle and making particles more repulsive to each other.

2.3 Polymers and their definition

According to Ahluwalia and Mishra (2008), a polymer is a large molecule that comprises repeating structural units joined by covalent bonds – in other words, a polymer is a group formed by repeated small molecules. There are many types of polymers, organic and inorganic, natural and synthetic. For example, bricks, cement and glass are inorganic natural polymers, whereas adhesives, fibers and plastics are organic synthetic polymers (Akelah and Moet, 1990).

The small molecule, “repeating unit”, or “building block” of a polymer is called a “monomer”, and on the basis of its characteristics, a polymer can be classified into one of two groups, a homopolymer or a copolymer. Homopolymers contain only a single type of monomer. However, if a polymer is composed of two or more different monomers, it is called a copolymer (Ahluwalia and Mishra, 2008). Polymers that contain two or more different types of monomers have altered crystallinity, flexibility, melting temperatures and glass transition temperatures. For example, Poly(Nisopropylacrylamide) (PNIPAM), a thermosensitive polymer, exhibits thermo-reversible phase separation in the aqueous solution in the temperature range of 31–35℃ (Gawel, et al, 2013). Jin et al. (2010) found that the copolymer P(NIPAM-co-SA), which is synthesized by inverse suspension polymerization by adding sodium acrylate, has a maximal swelling ratio that increased from 6.5 to 13.75, while the lower critical solution temperature of the polymer increased from 32℃ to 40℃. Such changes can be beneficial in terms of their different applications under certain circumstances.

2.4 Bonding in polymers

Various types of bonding may exist in polymeric materials. They are (1) primary covalent, (2) hydrogen bonding, (3) dipole interaction, (4) van der Waals force and (5) ionic. Hydrogen bonding, dipole interaction, van der Waals, and ionic bonding are known as secondary forces in terms of their bond strength, and van der Waals bonds are the weakest while primary covalent bonds are the strongest (Ahluwalia and Mishra, 2008). In chemistry, the inter-atomic linkage that results from the sharing of an electron pair between two atoms is called a covalent bond. The binding arises from the electrostatic attraction of their nuclei for the same electrons. A covalent bond forms when the bonded atoms have lower total energy than that of widely separated atoms. A hydrogen bond, in contrast, is a non-covalent, attractive interaction between a proton donor X-H and a proton acceptor Y in the same or in a different molecule. In addition, when two polar molecules are near each other, there will be a dipole-dipole interaction between them that is analogous to that between two magnets (Israelachvili, 2011). Bonds dissociate when the available thermal energy exceeds their dissociation energy. The bond types and their dissociation energy are showed in Table 1.

Table 1. The bond types in polymers and their dissociation energy.

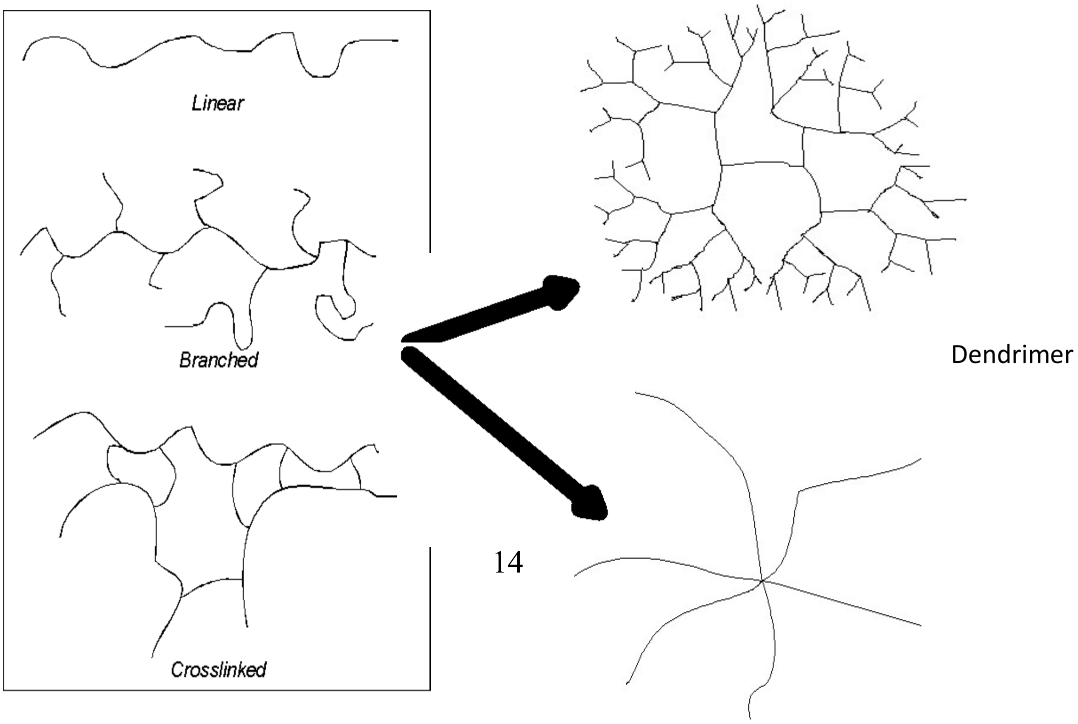
Bond type	**Dissociation energy (kcal/mol)**
Primary covalent	50-200
Hydrogen bond	3-7
Dipole interaction	1.5-3
Van der Waals	0.5-2
Ionic	10-20

Note: The data is reported by Akelah and Moet (1990). Grabowski (2006) reported that the dissociation energy of a conventional hydrogen bond and weak hydrogen bond are 4-15 kcal/mol and 1-3 kcal/mol respectively.

2.5 Polymer shapes

Polymer may take the shape of a linear chain, or may be branched or cross-linked. In a linear polymer, the units are connected to each other in a chain arrangement, with molecules that are not generally straight but are instead a tangled mass. When dissolved in water, they can be imagined as a mass of intertwined worms randomly thrown into a pail (Ahluwalia and Mishra, 2008).

Branched polymers contain a main chain of polymer molecules and also have small side-chains, or branches, of the same or different molecules of significant length, which are bonded to the main chain at branch points, and are characterized in terms of the number and size of the branches (Ahluwalia and Mishra, 2008). Sometimes the ends of several polymer chains are joined together at a common center. Such polymer shapes are called star polymers. Also, another type of branched polymer is called a dendrimer, and has no backbone chain; instead, the polymer branches grow out of the branches (Figure 2)(Akelah and Moet, 1990).



Star polymer

Figure 2. Different shapes of polymers.
From http://chem.chem.rochester.edu/~chem421/intro1.htm

Cross-linked polymers have two linear chains that are joined together by covalent bonds. Compare to linear and branched polymers, cross-linked polymers do not dissolve in solvents, because all the polymer chains are covalently tied together. However, they can absorb solvent – in fact, a piece of a cross-linked material that has absorbed a large quantity of solvent is called a gel (Ahluwalia and Mishra, 2008).

2.6 Polymer solution and solubility

The action of solvents on polymers is similar to the effects of heat. Appropriate solvents can penetrate the solid phase polymer, replace the inter-chain secondary bonds, and thereby pull apart and dissolve linear and branched polymers. The dissolution of a polymer is generally a slow process, and can take several weeks, depending on the structure and molecular weight of a given polymer (Hu, 2013).

Ahluwalia and Mishra (2008, page 78) summarized four general rules of polymer solubility:

(i) *Like dissolves like, i.e., polar solvents will tend to dissolve polar molecules and non-polar solvents to dissolve non-polar molecules.*
(ii) *In a given solvent, at a particular temperature, the solubility of a polymer will decrease with increasing molecular weight.*
(iii) *Cross-linking eliminates solubility.*
(iv) *The rate of solubility (a) increases with short branches, which loosen up the main chain structure, allowing the solvent molecules to*

> *penetrate more easily; (b) decrease with longer branches, because the entanglement of these branches makes it harder for the individual molecules to separate; and (c) decreases with the increasing molecular weight.*

It should be noted that rule (i), (ii) and (iii) are equilibrium, therefore could be describable thermodynamically. Whereas rule (iv) is governed by rates of diffusion of the polymer.

2.7 Polyacrylamides (PAMs)

A synthetic organic polymer called a “polyacrylamide” (PAM) is widely used in the areas of water treatment and soil erosion control. Polyacrylamides ($-CH_2CHCONH_2-$) are usually produced by polymerizing an acrylamide monomer (acrylamide) alone to form a nonionic polymer, or with acrylic acid or acrylic acid salts to form an anionic polymer, or with a cationic monomer to form a cationic polymer. The polymerization involved in this process is a chemical reaction in which two or more melecules of one or more substances combine together to form a molecule of high molecular weight. Anionic polymers may also be produced by alkaline hydrolysis of nonionic PAM (AWWA, 2001).

In water treatment, PAMs are mainly used as flocculants. The flocculation process coagulates colloidal particles into relatively larger aggregates (flocs) for which gravitational forces dominate and suspension stability is lost – the flocs then settle at the bottom of a treatment tank. The chemical agent that enhances the process is termed a flocculating agent or flocculant. Flocculants enhance aggregation either by modifying the energy of interaction between a pair of particles or by introducing new interaction terms, thereby destabilizing the suspension and affecting solid-liquid suspension.

Polymer-induced flocculation typically proceeds through one of two basic mechanisms: charge-patch interaction or particle bridging (Hogg, 2013). Addition of PAMs of the opposite electrical charge to suspended particles can cause flocculation with charge neutralization, as the polymer adsorbs onto the particle surface via electrostatic bonds. This charge neutralization results in a lowering of electrical repulsion between suspended particles, and thereby leads to their flocculation (Akelah and Moet, 1990). Cationic polymers, as the name suggests, have a positive net charge. Therefore, when a cationic polymer is adsorbed onto the surface of a particle, it neutralizes the negative charge and provides excess cationic charge to compensate for other negative charge sites on the surface. The mechanism involved in cationic polymer flocculation is an example of charge-patch interaction. In contrast to cationic polymer, particles and clays are bound to nonionic and anionic polymers mainly by a process called bridging. Bridging flocculation occurs when high molecular-weight polymer molecules adsorb simultaneously to more than one particle. When very long polymer molecules are adsorbed to the surface of particles, they tend to form loops that extend some distance from the surface into the aqueous phase. These loops and ends may attach to another particle to form a bridge between the two particles. Charge patch flocculation is usually effective and performs consistently, but results only in relatively small flocs, while bridging flocculation can produce very large flocs but the formation of these flocculants can be erratic.

In addition to their different flocculating mechanism and effects, it should be also noted that the two polymers have different environmental impacts. Generally, PAMs are safe for the environment if they remain in a polymer state; however, many studies have found that the monomer of PAM, acrylamide, may be toxic (Hall and Mirenda, 1991; Weston et al., 2009). Most direct releases of acrylamide to the environment are to underground sites or to air. Acrylamide dissolves when mixed with water, and breaks down to other chemicals in air. Microorganisms that live in water and in soil can also break down acrylamide. Because of its ability to mix with water and its inability to bind well to soil, acrylamide that makes its way into the ground can enter groundwater. Plants and animals are not likely to store acrylamide (USEPA, 1994), in such case, the acrylamide is not expected to have accumulation effect in the ecosystem. Effects of acrylamide on human health and the environment depend on how much acrylamide is present, the length and frequency of exposure, and the type of PAM – studies have shown that monomers from cationic polymers may be more toxic than monomer from anionic polymers. For example, Hall and Mirenda (1991) found that cationic polymers were clearly more toxic to *Pimephales promelas* (fathead minnow) than anionic polymers, with polymer toxicity to *P. promelas* generally increasing with increased positive charge density. Moreover, it is also should be noted that their results showed progressive reduction of the toxicity of a cationic polymer with addition of humic acid to the dilution water (Hall and Mirenda, 1991). Kerr et al.

(2014) investigated the anionic chronic exposure of PAMs (Clearflow Water lynx polymer) on juvenile rainbow trout and the induced gill pathology. They revealed that after 30 days exposure, sublethal exposure (≤38 mg/L) of juvenile rainbow trout to environmentally relevant doses of anionic polymer products resulted in either no damage or very low levels of damage to gill tissue. Mild to moderate levels of gill pathology were observed only when fish exposed to higher concentrations (100 mg/L) of anionic polymer products. In contrast, cationic polymer concentrations greater than 0.38 mg/L caused high levels of mortality. They believe that the toxicity of cationic polymer may be a result of buildup of cationic polymer on the negatively charged gill surface, leading to impairment of O2 uptake and subsequent death. (Kerr et al. 2014).

Since it has been proved that anionic PAMs are more environmentally safe than cationic PAMs, anionic PAMs are now preferred, especially when directly applied to the natural environment. For example, anionic PAMs have been widely used on irrigated croplands in the United States to minimize soil erosion (NRCS, 2011), with PAM dissolution and adsorption to soil particles increasing aggregate stability. In addition, the presence of PAMs in runoff increases sediment flocculation and decreases the runoff transport capacity – an effect that could further reduce soil loss (Abrol, 2013 and Yu 2011).

2.8 Degradation of PAMs

PAM degradation occurs slowly in the natural environment as a result of several processes including chemical, photo, biological, and even mechanical processes – tillage abrasion, freezing and thawing, and so on – because of large molecular sizes (Sojka et al., 2007). Azzam et al. (1983) estimated the degradation rates at around 10% per year; however, this degradation process is affected by both temperature and water salt content and so is variable. Further, although the degradation time of PAM can be long, the degradation of the acrylamide is fairly rapid, with decomposition to propionamide and propionic acid; propionamide then rapidly hydrolyzes to propionic acid as well (Sojka, et al., 2007). For example, acrylamide was completely degraded within 5 days after applying 1 kg PAM in 500kg garden soil (Shanker et al., 1990). *Pseudomonas strutzeri*, *Rhodococcus* spp. and *Xanthomonas* spp. have also demonstrated degrading abilities under aerobic conditions (Pemraj and Doble, 2004).

2.9 Functionalized PAMs

Functional polymers are macromolecules to which chemical functional groups are attached. They have the potential advantage of small molecules with the same functional groups. In principle, the functional groups may be part of the polymer backbone or linked to a side chain as a side group either directly or via a spacer group which is the flecxible part of the molecule that providing connection between two parts of the molecule (Janović et al., 2010). A required active functional group can be introduced onto a polymer side chain (a) by incorporation during the synthesis of the support itself through polymerization and copolymerization of a monomer containing the desired functional groups, (b) chemical modification of a suitable, non-functionalized, pre-formed support matrix and (c) by a combination of (a) and (b) (Akelah and Moet, 1990).

These functionalized PAMs usually have unique properties. For example, chitosan-graft-polyacrylamide is an efficient adsorbent for azo dyes, whereas acrylamide grafted cationic guar gum (CGG-g-PAM) and starch graft polyacrylamide (S-g-PAM) are found to be more efficient flocculants compared to ungrafted cationic PAMs (Singh, 2009; Wan, 2007; Song 2009). These functionalized PAMs usually have different physical and chemical characteristics compared to the original PAM as well.

2.10 'Smart' PAMs

Smart materials are materials that have one or more properties that could be significantly changed in a controlled fashion by external stimuli (Mascaraque and Palao-Suay, 2014). Shape-memory polymers (SMPs), a type of functionalized PAM, are a new family of "smart materials". As a kind of stimulus-responsive material, SMPs can deform their shape temporarily and recover an original shape under appropriate stimuli, such as temperature, pH, moisture, light, an electric field, a magnetic field, and so on. SMPs have the advantages of light weight, low cost, good manufacturability, high shape deformability, high shape recoverability, biodegradability, and tailorable switch temperatures (Zhang and Yang, 2010).

A thermo-sensitive polymer is one type of SMP that may be extremely helpful in sediment dewatering. As explained above, the flocculation of suspended solids using polymeric flocculants occurs by the bridging of the suspended solids through the polymer molecules. However, the flocs formed are usually bulky and contain a large amount of water, because the hydrophilicity of the polymer makes the polymer chains extend in the water. This hydrophilicity is not a fixed characteristic though, as SMPs are soluble in water at low temperature but are insoluble above the intrinsic temperature of the polymer, as the polymer transitions to hydrophobicity. This intrinsic temperature at which this transition occurs is referred to as the lower critical solution temperature (LCST) or the transition temperature. The LCST depends primarily on the side-chain structure of the polymer (Sakohara, et al. 2007). Based on this property of thermo-sensitive PAMs, when heat is applied and the temperature is above LCST, the hydrophilic PAMs will become hydrophobic.The hydrophilic-to-hydrophobic transition in a thermosensitive polymer is reversible. Importantly, if a sediment cake treated with thermo-sensitive polymers is heated above the transition temperature, the polymer will become hydrophobic. The hydrophobicity of the polymer will then repulse water from the sediment cake, and dewater the sludge.

Some SMPs are sensitive to other conditions. For example, H-bonded cholesteric polymer responds to both pH and temperature change. In addition, photo-sensitive polymers undergo a reversible or irreversible change in conformation, polarity, charge, optical chirality, conjugation, and so on, in response to a light stimulus (Chen, et al. 2012; Aguilar and Roman, 2014). These properties aid the applicability of SMPs to unique operating conditions.

2.11 Sediment Dewatering with PAMs

Conventional sediment dewatering techniques are usually accomplished by mechanical force. Examples of such a technique are vacuum filtration, pressure filtration and centrifugation. These techniques require significant energy input and are usually costly. Other methods include sludge lagoons, which spread out the sediment sludge onto an excavated area that allows the sludge to drain and dry over a period of months or even a year. Although it does not require a large energy input, the method is inefficient considering the time spent in this process (Kocurek, 1994).

PAMs as flocculants can bind particles on their side chains. For fine particles that can hold more water, PAMs are expected to tighten floc particles and squeeze out the water. Therefore, dewatering techniques using PAMs can be effective before applying alternative means, such as mechanical pressure, centrifugation or heating. As mentioned above, flocculation by ionic PAMs has different mechanisms – recall that particles bind to cationic PAMs mainly because of surface charge neutralization, whereas anionic PAMs bind particles through bridging. Ionic bonding is expected to be much stronger than bridging, and so cationic PAMs are more frequently used in dewatering (Zhu. et al., 2013 and Ren. et al., 2007). However, anionic PAMs can also be used in sludge dewatering. One of the case is that to apply surfactant with polymer (Besr et al. 2003). Surfactants have a hydrophilic head and a hydrophobic tail; therefore, if anionic PAMs in water solution are applied to cationic surfactants, their hydrophilic head will attach to the active component of anionic PAMs, and their hydrophobic tail will then squeeze the whole polymer chain into a coil – see Figure 3.

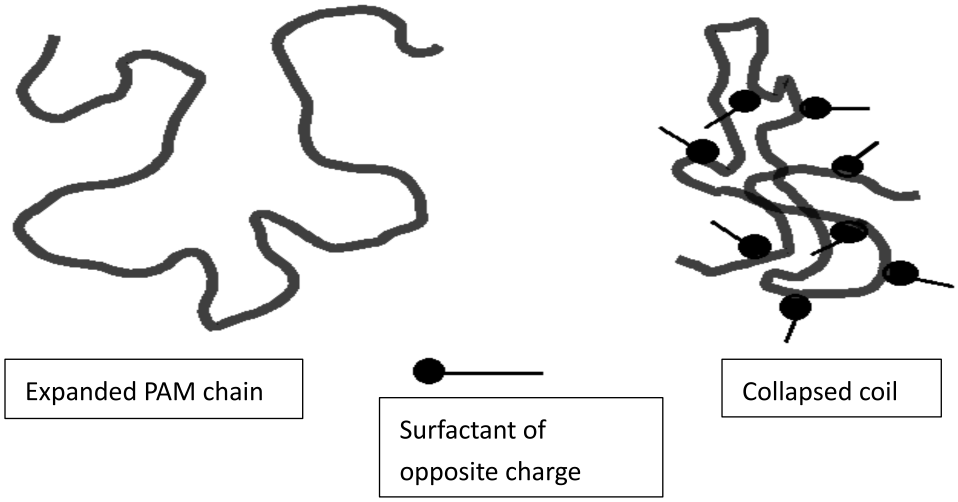


Figure 3. Polymer with an oppositely-charged surfactant (Zhu. et al., 2013).

Divalent particles can also be used in combination with anionic PAMs for dewatering. Since divalent cations, such as Mg^{2+} and Ca^{2+}, can bind together two active, negatively-charged sites on anionic PAM chains, the divalent cations pull together the polymer chains (Figure 4) and squeeze out the water content of the sediment cake. The black dots are suspended particles in the solution, and the red dots on polymer are the active points (where the functional group is) of the anionic PAM.

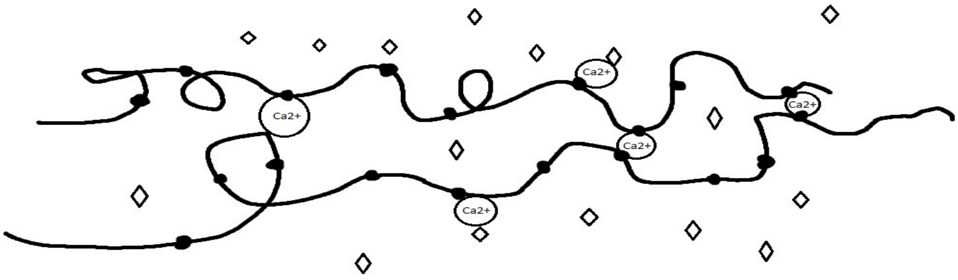


Figure 4. Demonstration of divalent particles with anionic PAMs.
Note: black dots are particles with negative charge; rhomboid dots are active points of anionic PAMs.

Smart polymers, such as thermo-sensitive PAMs, can be extremely efficient in sludge dewatering if heating is applied after flocculation. As mentioned in the previous section, thermo-sensitive PAMs change their morphology in different temperatures: at lower temperatures, polymer chains stretch out, while at high temperatures, they shrink and fold. These effects result from solubility in water of thermo-sensitive polymers at low temperatures and insolubility above the intrinsic temperature of the polymer (Schild, 1992 and Sakohara, 2007). The transition from hydrophilicity to hydrophobicity of thermo-sensitive polymers with heating can be exploited to make the dewatering process faster and more cost-effective.

In a PAM-based dewatering process, agitation and flocculant dosage are two of the key determinants of floc structure, with increasing intensity of agitation usually decreasing the size of flocs by physically breaking polymer chains. The water content of sediment cake likely decreases with floc size as well. Proper polymer dosage and agitation intensity may enhance the PAM dewatering efficiency by 35%. In addition, application of shear by a mixer to pre-sedimented flocs could result in significant additional sediment consolidation (5-15%) (McFarlane et al., 2005; Ofori et al., 2011). Finally, temperature also plays a very important role, since it affects not only the morphology of thermo-sensitive PAMs, but also the zeta-potential of particles, pH, viscosity, conductivity of supernatant etc. All of these parameters are critical to flocculation and dewatering processes (Mpofu etc., 2003).

3. Methodology.

In order to further identify the effect of Soil Lynx 398 on lake sediment and especially to investigate its performance at low temperature, a set of settling experiments was conducted. All lake sediment samples were taken from the Woodbridge Farms storm water pond in Sherwood Park, Alberta. A series of analyses was also performed after the experiment to investigate the potential mechanisms responsible for the experimental results.

3.1 Sampling.

The lake sediment samples were taken from Woodbridge Farms storm water pond on November 6th 2012. There were eight samples in total taken from both inlet and outlet through cross-section, and 1 core sample was taken near the bridge (Figure 5).

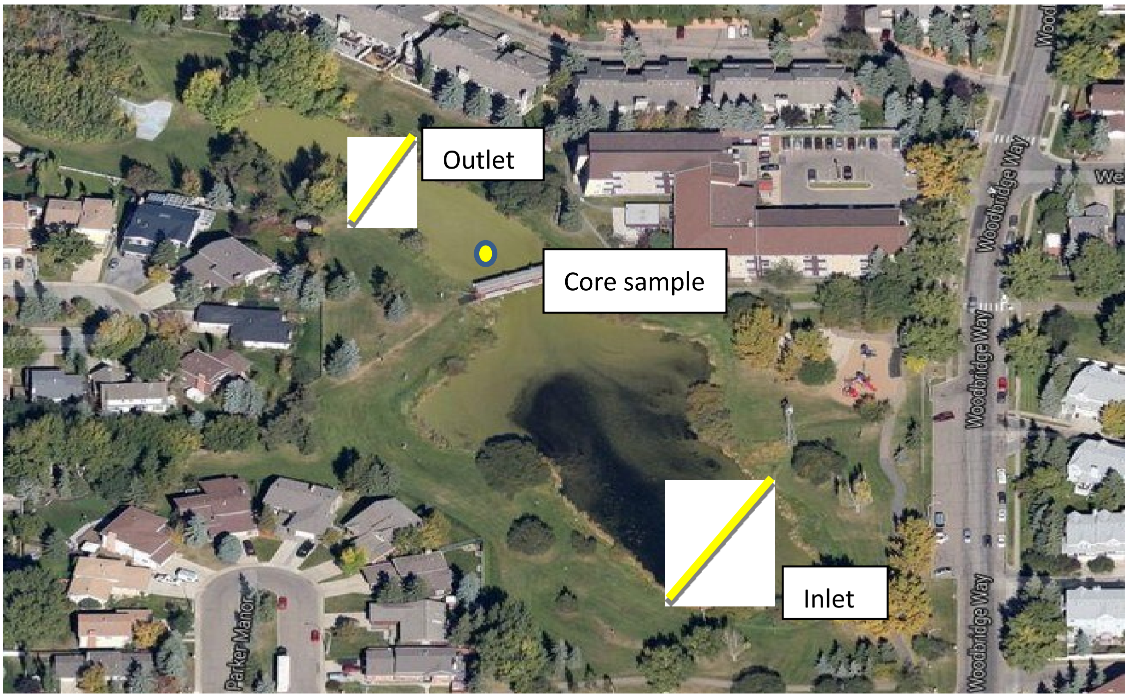


Figure 5. The sampling site of the storm water pond (Google map, 2010).

During the sampling, lake sediment samples were taken by a sediment grabber (15.2×15.2×15.2 cm^3). The samples were then filled in eight barrels (6 L each). Each barrel was filled with 4 L of lake sediment and 2 L of lake water. The purpose of filling water was to isolate the sample with air and keep it anaerobic. One sediment core sample was taken from the central area of the lake by a sediment core sampler and preserved in a core tube (Figure 5). Meanwhile, lake water was collected from both the center of the lake (2 L) and the outlet of the lake (1 L), and then preserved in 3 bottles. Finally, all sediment samples were preserved in 4℃ cold room.

3.2 Characterization of samples and preliminary experiment

In order to characterize the lake sediment sample, ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS) test of pore water, water content of sediment, zeta potential test and particle size distribution test was performed. IC tests the non-metal ions of the pore water, whereas the ICP-MS tests the major metal ions of the pore water. Zeta-potential of sediment particles can indicate the stability of the supernatant.

In the ICP-MS test, the porewater samples was filtered through 0.45 μm filters and then tested using a Perkin Elmer Sciex Elan 9000. Samples were diluted 50 times by 1% nitric acid (prepared with concentrated nitric acid of trace metal grade). After preparation, all the samples were transferred to test tubes. A multi-element standard and an internal standard for calibration and a stock solution for sampler rinsing were also used during the ICP-MS test.

In the IC test, the sample was diluted 100 times with ultrapure water. Then, diluted samples were filtered by using a 0.2 μm filter. During the test, seven anion solutions (fluoride, chloride, nitrite, sulfate, bromide, nitrate, and phosphate) at different dilution rates (1×, 2×, 5×, 10×, 20×) were used for system calibration.

In the zeta potential test, the sample was tested in a cell with electrodes on both ends. A potential was applied to the sample in the cell and particles then moved towards the electrode of the opposite charge. Then by using the Malvern Nano Zetasizer, the velocity of particles with Laser Doppler Velocimetry was measured. Zeta potential of sediment samples were then calculated by the software. There were 3 temperature condition been tested (4, 22 and 30 ℃). The zeta potential of both sediment supernatant and polymer solution were examined. It should be noted that the instrument could only test the suspended particles. In this case, only particles in the supernatant were measured.

The sediment particle size was directly counted under light microscope. For each sampling site, 10 glass slides were prepared. On each slide, 10 different locations were chosen to count out the particles. Particle sizes within the range of 10μm to 200μm were recorded. A distribution curve was produced after analysis in Excel.

To determine the best product to be applied in the lake sediment, Clear Flow conducted a settling experiment. Three products, Soil Lynx 395, Soil Lynx 398 and Soil Lynx 360, were tested and compared. The turbidity of supernatants was 26.05, 19.94 and 82.5 NTU, respectively. Based on the best result of turbidity, Soil Lynx 398 was chosen as the product, as described later in Chapter4..

3.3 Dose effect of Soil Lynx 398

To determine the dose effect of Soil Lynx 398, Soil Lynx dose at 0.05, 0.1, 0.3, 2, and 5 g/L were tested. In total, 8 sets of settling tests were performed (4 from inlet samples and another 4 from outlet samples); each set of experiments was triplicated. In each settling test, the lake sediment was diluted to 5% wt. and mixed with water by a mixer at 200 rpm for 2 minutes. De-ionized water was used in the experiment to eliminate any possible cation interruption of the polymer. Then Soil Lynx 398 was added in the cylinder and the mixing speed was reduced to 100 rpm. The mixing stopped after 1 minute. After 1 hour settling time, the settled sediment (sediment cake) and supernatant were taken out and preserved in centrifuge tubes. Next, the sediment cake was heated at 105 ℃ for 24 hours. The original weight of the sediment cake was compared with its dry weight to measure the water content. Based on the result of turbidity and initial settling rate tests and the water content of sediment cake, the best dose was selected as 0.3 g/L. The conductivity, pH, viscosity of supernatant were tested as well.

3.4 Temperature effect on Soil Lynx 398

Once the best dosage was selected (0.3 g/L), the temperature effect experiment was performed. In total, 8 sets of settling tests were performed (4 from inlet samples and another 4 from outlet samples), and each set of experiments was triplicated as well. The experimental set up was the same as in the Soil Lynx 398 dose effect. However, the experiments were performed for 5 different temperature conditions (4, 10, 15, 22 and 30 ℃) and used only one dose (0.3 g/L).

3.5 Scanning electron microscopy (SEM) and viscosity test

In order to understand the mechanisms involved in polymer binding at low temperature, SEM test was performed. The specimens were taken from both the original sediment and the sediment treated with polymer in the previous temperature effect experiments. The original sediment at 22 ℃ and sediment cake produced at 4 and 22 ℃ were used in this experiment. They were dehydrated and affixed to a small metal disk. The sample surface was then sputter-coated with gold. After that, all the samples were tested under the scanning electron microscope.

3.6 Quartz crystal microbalance with dissipation (QCM-D) test

To understand the particle and polymer binding mechanisms better, a QCM-D test was performed. The polymer concentration was 0.3g/L, and the sensor surface used in the experiment was SiO_2. There were three temperature conditions used in the experiment (10, 22 and 30 °C). Water was injected to the system first until the frequency curve was stable (about 10 minutes). After that, polymer was injected into the system. When the frequency curve stabilized again, water was injected into the system again to wash out any polymer that loosely attached on the sensor surface. For all temperature conditions, the frequency was monitored for 1 hour.

3.7 Viscosity test

At first, the viscosity of the polymer solution at different concentration (0.05, 0.1,0.3,0.5, 2 and 5g/L) and at different temperature (4, 22 and 30 ℃) was tested using a DV2T viscometer. During the test, the rotation rate (rpm) of the viscometer was adjusted in order to ensure the torque was larger than 80 N*m. The temperature was controlled by a water bath system connects to the viscometer. Secondly, the viscosity of water at different temperatures (4, 22 and 30 ℃) was tested as well by using the same method.

3.8 **Humic acid test**

In the humic acid test, 1 g of sample and 50mL of 0.1 N NaOH were placed into a 50 mL centrifuge tube. The tube was capped and shaken on a rotating shaker for 1.5 h. The cap was then rinsed with 5mL of 1% (0.25 N) NaOH, the rinse was added to the tube, and the cap was replaced. The tube was then centrifuged at 1000 g for 20 min. The supernatant was decanted into a second, pre-weighed, 50 mL centrifuge tube. An additional 5mL of 1% (2.5 M) NaOH was added to the first tube; the tube was vortexed to resuspend the residue and then centrifuged as before. The supernatant was then added to the second tube. The pH of the combined extracts in the second tube was adjusted to pH ≤ 1 with 6 N HCl, followed by shaking for 20 min. The tube was then centrifuged at 1000 g for 20 min, and the supernatant was decanted and discarded. The precipitate (i.e., the humic acid) was then washed by the addition of 25mL of distilled water previously adjusted to pH ≤ 1 with concentrated HCl, vortexed to resuspend the precipitate, and centrifuged at 1000 g for 20 min. The washing process was repeated again. After washing, the humic acid was dried in the pre-weighed tube at 100 ℃ overnight. Prior to weighing, the tubes were allowed to cool in a desiccator (Lamar and Talbot, 2009).

4. Results and analysis

4.1 Pore water chemistry

Lake sediment is a complex of many substances. To better characterize the sample, pore water IC and ICP-MS tests were conducted to identify ion species present. Table 2 shows the concentration of major ion species in lake sediment pore water sample. All metal ion species were more concentrated in inlet samples than in outlet samples. This is because most of the particles are likely to settle near the entrance of the pond due to gravity and some of the free ions and metallic salts are attached to them.

Table 2. Water chemistry of pore water from both inlet and outlet samples (mg/L).

	Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	NO_3^-	NH_4^+	SO_4^{2-}	CO_3^{2-}	PO_4^{3-}
Inlet	23.5	12.6	5.6	25.2	23.8	0.9	3.2	29.3	48.7	2.6
Outlet	6.9	10.9	4.9	24.1	6.9	0.7	2.2	24.4	48.5	3.2

In Table 2, Na^+, Mg^{2+}, K^+, and Ca^{2+} are the major cations and Cl^-, SO_4^{2-}, and CO_3^{2-} are the major anions that constitute the total ionic salinity of the pond water. These ions could be results of precipitation, weathering release, aerosol input, or salts from road and lawn. The atmosphere is a significant source of ions. Table 3 lists the major ions and their concentrations in continental rain. Because the major input of the storm water pond is from a storm water sewer, weathering would not have a great impact. However, there may be oxidation processes in the water-rock (or sediment) interface. For example, iron sulfides are common constituents of rock and water saturated soils. Oxidation of sulfides can be a major source of sulfate in natural waters (Wetzel, 2001). The aerosol input refers to the particles that enter the water from the surrounding air. The input from air depends on the magnitude of air pollution in the local area.

Water in a storm water pond could contain: (1) soil erosion from bare land, (2) lawn chemicals (fertilizers, pesticides), (3) road salt and other de-icing substances, (4) household products (paints, solvents, cleaning agents, etc.), (5) oil leaks and illicit disposal, and (6) dust from the atmosphere (Pazwash, 2011).

Table 3. Common concentration (mg/L) of major ions in continental rainfall

Ion	**continental rain (mg/L)**
Ca^{2+}	0.2-4
Mg^{2+}	0.05-0.5
Na^{+}	0.2-1
K^{+}	0.1-0.5
NH_4^{+}	0.1-0.5
SO_4^{2-}	1-3
Cl^{-}	0.2-2
NO_3^{-}	0.4-1.3
H^{+}	pH=4-6

(Berner and Berner,1987).

The result from IC and ICP tests (Table 2) showed some hydrolyzed monovalent ions such as Na^{+} and K^{+} in the lake sediment. Although they will not have a significant impact on solid settlement, these monovalent ions could bind to the active site of the anionic polymer and obstruct the binding of charged particles or divalent ions to anionic PAM. However, their effect on flocculation was apparently limited because anionic polymer was used in this study and the major mechanism was not an electrostatic effect. The molecular weight of the anionic polymer was the main impact factor (Akelah and Moet, 1990).

Divalent ions such as Mg^{2+} and Ca^{2+} had a great impact on both the surface charge of particles and the anionic PAMs. Hence, flocculation and the dewatering performance will be impacted as well. As mentioned in the literature review section, the surface charge of natural particles is usually negative. Binding of positive divalent ions to the particles will lead to a systematic reduction in zeta potential due to specific adsorption of positively charged metal ion-based hydrolysis products at the particle–water interface. The particles are more likely to stick together when their surface charges are neutralized. Moreover, positive divalent ions could bind to active sites of the anionic PAM strains due to electrostatic force (Besra et al., 2002; Zhu, et al., 2013). In this circumstance, positive divalent ions will tend either to bend the PAM strains or pull two PAM strains together (Figure 4).

The storm water was also tested for various forms of nitrogen. Nitrogen occurs in natural lakes in numerous forms: dissolved molecular N_2; organic compounds such as amino acids, amines, and proteins; and recalcitrant humic compounds of low nitrogen content—ammonia (NH_4^+), nitrite (NO_3^-), and nitrate (NO_2^-). The source of nitrogen in the lake comes from: (a) precipitation falling directly into the lake, (b) nitrogen fixation in lake water and lake sediment, and (c) input from surface and groundwater drainage (Wetzel, 2001). In the lake, much of the ammonia arises as a primary product of the decomposition of organic matter by heterotrophic bacteria from the deamination of proteins, amino acids, urea, and other nitrogenous organic compounds. A large percentage of this ammonia is adsorbed on the sediment particles (Wetzel, 2001). However, with the loss of the microzone at the sediment-water interface under anoxic conditions, the adsorptive capacity of the sediments was greatly reduced (Verdouw et al., 1985). In this case, the ammonia concentration increased with the depth of the lake. Since the data are derived from sediment pore water, it was expected that the concentration of ammonia would be lower in the pond water. NH_4^+ was present; however, NO_2^- was absent in the pore water and NO_3^- was at a low concentration. NO_2^- is an unstable nitrogen form that can be oxidized to produce NO_3^-. The concentration of NO_2^- in natural lake water was expected to be very low, in the range of 0–0.01 mg/L (Wetzel, 2001). NO_3^- was present in the pore water test, but this anion is not expected to be stable after sampling. Although the sediment samples were kept in anaerobic condition at 4 °C at all times, denitrification by bacteria can still occur. In this case, NO_3^- will be reduced to N_2.

This storm water pond had serious algae growth problems, which were mostly related to the high nutrient concentrations in the water, especially phosphorus (Wetzel, 2001). The phosphorus content of precipitation and of ground water is generally low (Gibson et al. 1995). In this study, the regional chemical characteristics, phosphorus in particular, of surface water were closely related to the soil characteristics of their drainage basin. As described in the literature review section, the main water source was the storm water drainage sewer, the main drainage basin of the residential area of the city. Although precipitation contains limited phosphorus, precipitated water can mobilize a considerable amount of phosphorus from lawns, especially when many people apply fertilizer to their lawn every year. In this case, the fertilizer from lawns was expected to account for most of the phosphorus in the storm water pond.

An algal bloom can be seen in the picture of the storm water pond (Figure 5). Studies have shown that with phosphorus concentrations exceeding 60 μg/L, the frequency or risk of a 40 μg/L algal bloom averages 19% in an open lake (William and Karl, 1995). The pond water test indicated that the phosphorus concentrations of the pond water near the inlet and outlet were 0.453 mg/L and 0.468 mg/L, respectively. Therefore, the high concentration of phosphorus in the lake water is likely to cause an algal bloom again during the summer. However, because the sampling was done during the winter, the concentration of algae in the pond water could not be tested. Although it was expected that a higher concentration of phosphorus would be found near the inlet of the pond, the concentration of phosphorus in the pore water was actually slightly higher near the outlet of the pond, although the difference in phosphorus concentrations was not significant. A possible reason for the difference in phosphorous concentrations in pore water and pond water might be the specific shape of the pond (Figure 5). Due to the inlet and outlet locations, the water current flows from the southeast to the northwest of the pond. However, the width of the pond near inlet is nearly three times larger than the width of the outlet. The water current would stagnate at the narrow end of the channel, allowing the phosphorus to settle down with the fine particles in the water. In addition, due to the water flow direction and the change of water flow rate throughout the lake, algae could be carried to the northeast part of the lake and multiply there by consuming phosphorus and other nutrients. Dead algae would settle to the bottom of the pond and the phosphorus they consumed would go through the internal cycle across the sediment/water interface (Wetzel, 2001). This process could explain why the concentration of phosphorus was higher in pore water near the lake outlet than in the pore water near the lake inlet.

The concentration of humic acid in sediment pore water was 31.35±2.1 g/L and 37.70±3.5 g/L from inlet and outlet, respectively. The concentration range of humic acid in typical lake water is reported from 20 to 150 mg/L (Klavins et al., 2003). It is known that high molecular weight humic materials exhibit a colloidal structure, which may interact with PAM polymers (Akelah and Moet, 1990).

4.2 Characteristics of sediment

The physical properties of the lake sediment could impact the results of the experiment. The original water content of pond sediments was 44±6 % for the inlet sample and 41±5% for outlet sample. Sediment particle size was examined under a light microscope. Sediment is a mixture of clay, silt, sand and rock that is carried by the various sources that drain into the storm water pond, in this case mainly the storm water sewer. The shapes of sediment particles are irregular and they contain both organic and inorganic matter. The range of particle size was less than 10 μm to over 200 μm (Figure 6 and 7). The average particle size was 92.14 ± 38.8 μm near the lake inlet and 77.78± 35.50 μm near the lake outlet. Particle size distribution charts indicate that particle size near the inlet was significantly larger than particle size near the outlet ($P \leqslant 0.05$). Sediment particles had various shapes and sizes, as shown by an SEM image of sediment aggregates in Figure 8 (a). Figure 8 (b) shows a diatom (a type of algae) on the surface of the pond sediment. Bacteria and other microoganisms in the natural environment could attach to the sediment particle surfaces, acting as a natural polymer to stabilize the sediment on the bottom of the pond.

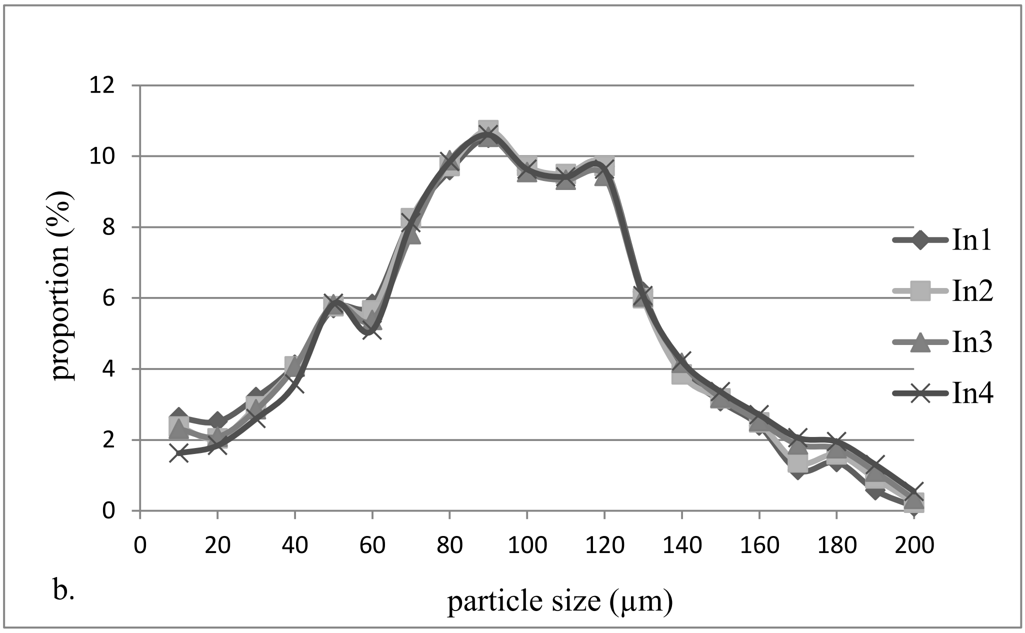


Figure 6. Particle size distribution of lake sediment samples from inlet.

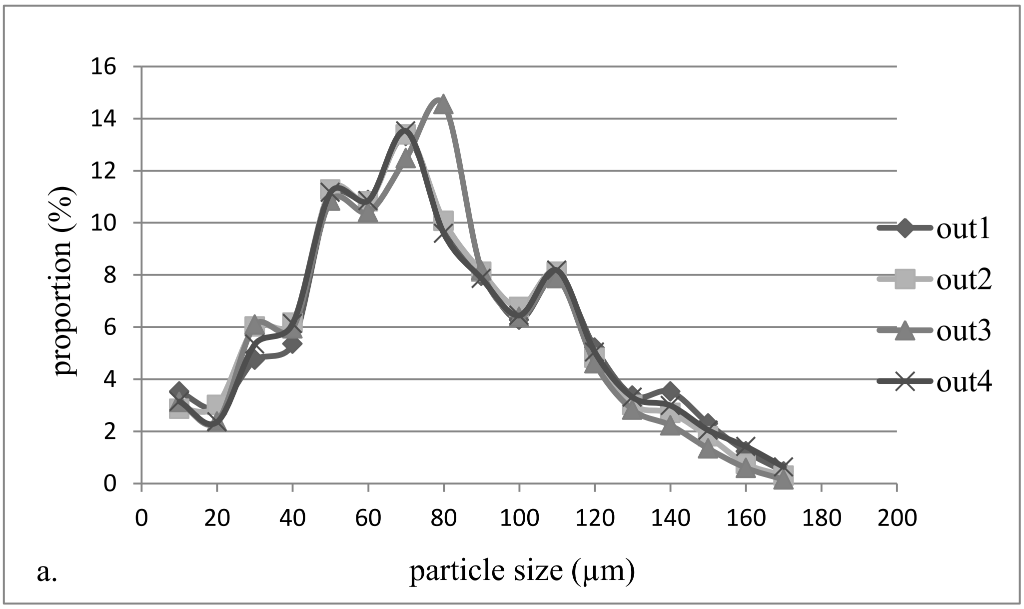


Figure 7. Particle size distribution of lake sediment samples from outlet.

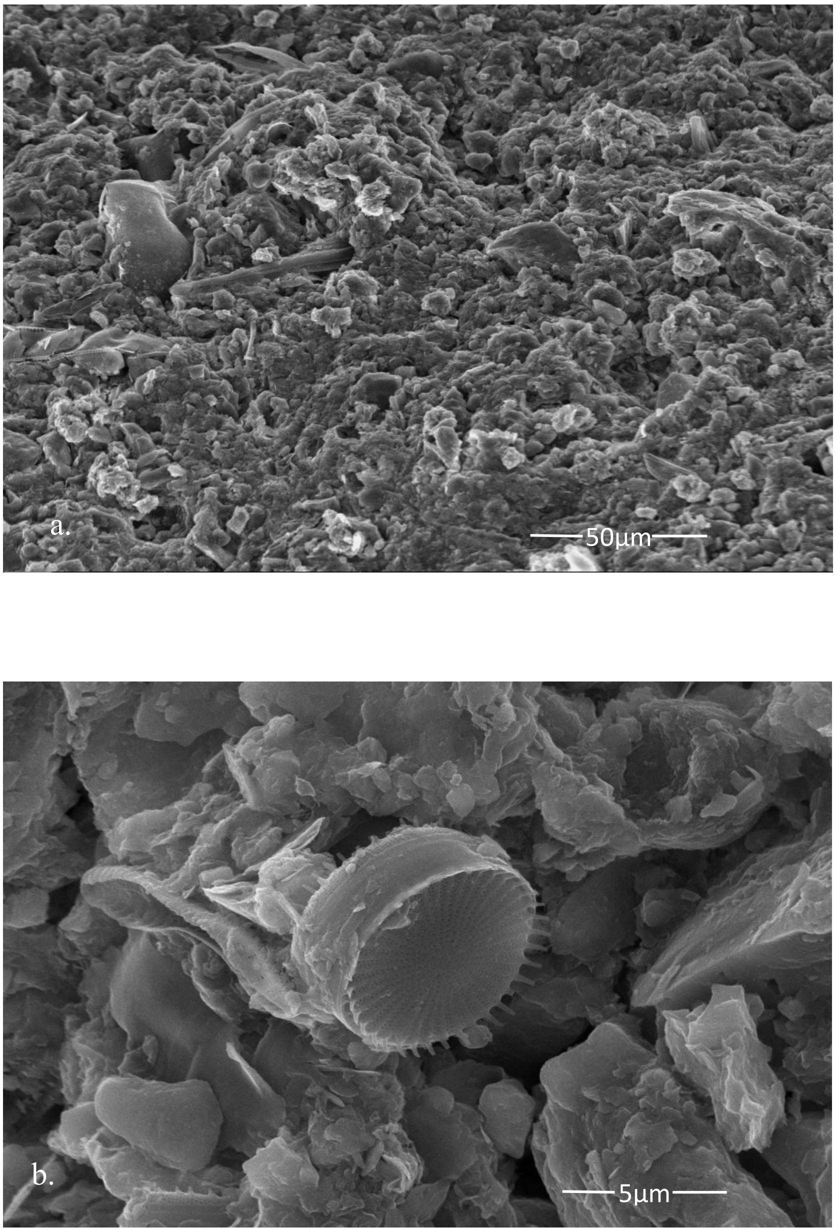


Figure 8. SEM images from inlet and outlet sediment samples at different temperatures. a. lake sediment at 22 °C. b. microorganism (diatom) at the surface of the sediment.

Table 4. Zeta potential (mV) of sediment samples at different temperatures

	4°C	**22°C**	**30°C**
Inlet1	-33	-31.733	-31.33
Inlet2	-32.56	-31	-29.7
Inlet3	-34.1	-28.7	-28.83
Inlet4	-35.13	-30.02	-29.04
Ave ± standard deviation	-33.22±0.65	-30.36±1.13	-29.23±0.98

Outlet1	-34.6	-29.9	-29.77
Outlet2	-32.67	-29.94	-29.65
Outlet3	-33.47	-30.03	-29.93
Outlet4	-34.01	-29.75	-28.44
Ave ± standard deviation	-33.69±0.71	-29.91±0.1	-29.45±0.59
Polymer	-14.4	-15.9	-15

The magnitude of the zeta potential increased as the temperature increased (Table 4). The zeta potential reflects the stability of particles in the water. A reduction in the negativity of the sediment particles reduces their stability (Petryshyn et al. 2010). Our results are consistent with a study that showed that the zeta potential of a kaolinite suspension decreased in magnitude with increasing temperature (Mpofu et al., 2003).

Factors that affect the zeta potential of particles are temperature, pH, viscosity, and the concentration of metal ions in aqueous solution. Permittivity and viscosity are temperature dependent and both can impact the zeta potential of particles. Permittivity is a measure of the resistance encountered when forming an electric field in a medium and has a positive correlation with temperature (Svorcik, 2001). Viscosity has a negative correlation with temperature and a positive relationship with the magnitude of the zeta potential. A decreasing temperature will lead to a lower value of permittivity and a higher viscosity, which will lead to a larger magnitude of zeta potential. This prediction is in agreement with the data in Table 4. Other parameters that can affect the zeta potential of sediment particles in water are pH and conductivity. However, the values of pH and conductivity in the lake samples did not change much from 4 to 30 ℃.

4.3 Polymer Dose Effect Experiment

To decide the best polymer dose at the temperature of the experiment, turbidity and initial settling rate were measured for the flocculation test, and the water content of the sediment cake and the sediment cake volume were measured for the sediment dewatering test. The integrated results were used to identify the optimal dose of Soil Lynx 398 when treating the real lake sediment.

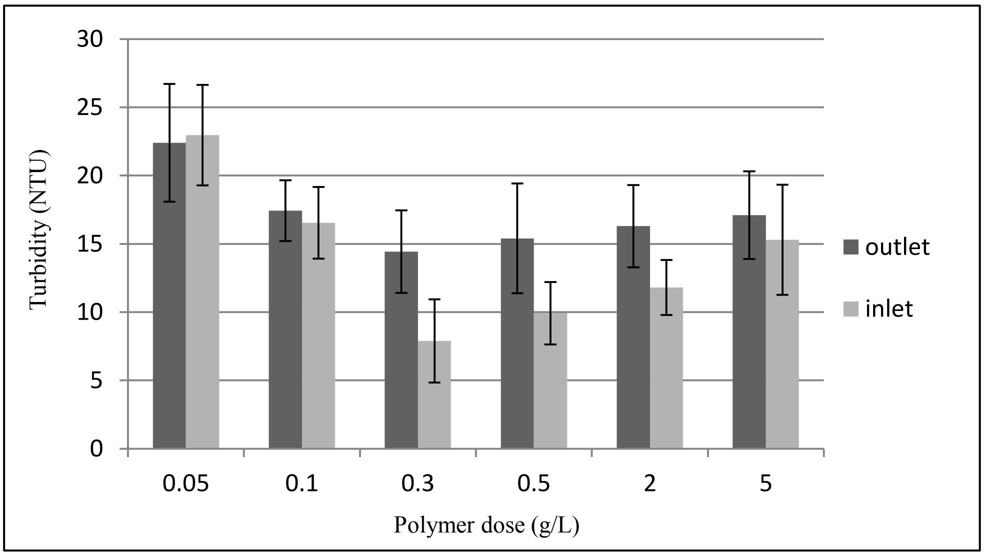


Figure 9. Turbidity of supernatant at different polymer dose applications at room temperature. The settling time was 1 hour.

The results indicated that the turbidity of supernatants was relatively high (22.4 ± 4.31 and 22.96 ± 3.69 NTU from outlet and inlet, respectively) when the polymer concentration was 0.05 g/L, and turbidity decreased with as the polymer dose increased up to 0.3 g/L. A polymer dose of 0.3 g/L generated the lowest turbidity (14.43 ± 3.03 and 7.89 ± 3.04 NTU from outlet and inlet, respectively). The difference was significant compared to the turbidity when the polymer dose was at 0.05 g/L ($p \leqslant 0.05$). Although the turbidity increased with polymer doses of 0.3 g/L to 5 g/L, the difference between turbidity increases was not statistically significant ($p > 0.05$)

(Figure 9). The reason the turbidity was relatively high at low polymer doses is that, at low polymer concentrations, not all sediment particles can attach to polymer chains, hence, some particles were left in the supernatant. Larger particles left in the supernatant could settle with gravity, however, very fine particles will tend to remain suspended in the supernatant. In contrast, when the polymer concentration is too high, anionic polymer species will start to repel each other based on their negative electronic charge. The repulsion might obstruct the ability of polymer chains to stretch out; if the coil of the polymer is relatively compact (Ofori, et al. 2011), fewer particles are likely bind to the polymer chains. Moreover, the high concentration of polymer in solution will dramatically increase the viscosity of the supernatant, leading more particles to be suspended in the supernatant. Because the standard errors in both inlet and outlet experiments were large, turbidity differences between inlet and outlet experiments are not comparable.

Figure 10 shows that the initial settling rate was optimized at polymer concentrations of 0.3 and 0.5 g/L. There is no significant difference between these two conditions ($p > 0.05$), therefore, it cannot be concluded which one was the optimized dose. Two reasons might explain this phenomenon. One, at higher polymer concentrations, polymer chain repulsion might interrupt the settling. Two, the higher polymer concentration greatly increased the viscosity of the supernatant (Figure 15). At 22 ℃, when the polymer dose increased from 0.05 mg/L to 5 mg/L, the viscosity of the polymer solution increased from 1.21×10^{-3} Ps*s to 1.37×10^{-2} Ps*s. A highly viscous supernatant will prevent the settling of fine particles due to the high resistance between particles and supernatant. At low polymer concentrations, there were not enough polymer chains to bind all the particles. Polymer particles that bind together form large flocs and settle quickly. Free particles take a longer time to settle. Because the turbidity result was better with a polymer concentration larger than 0.3 g/L and the initial settling result was better when polymer concentration was between 0.3 and 0.5 g/L, it demonstrated that the flocculation experiment performed best when the polymer dose was between 0.3 and 0.5 g/L.

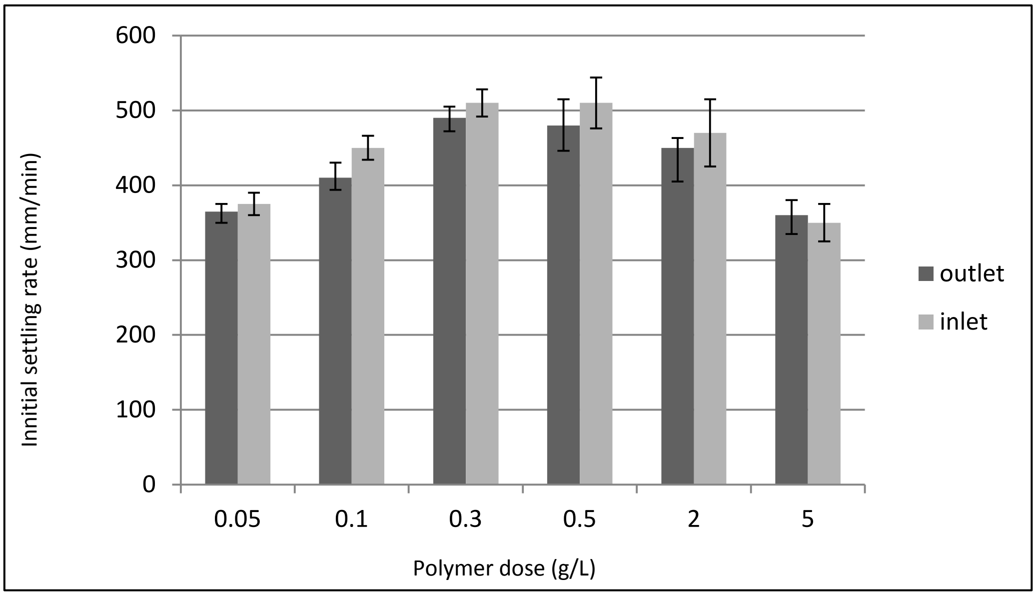


Figure 10. Initial settling rate of sediments at different polymer dose applications at room temperature. The settling time was 1 hour.

At low polymer concentrations (0.05, 0.1, 0.3 g/L), differences in the water content in the sediment cake were not significant ($p > 0.05$). However, compared to low polymer concentration conditions, the water content significantly increased when the polymer concentration was higher than 0.5 g/L ($p \leq 0.05$). A polymer concentration of 5 g/L yielded a water content nearly twice as high as when the polymer dose was at 0.05 g/L (Figure 11). Figure 11 shows that the polymer concentration reached a critical point at 0.5 g/L. When the polymer concentration is low, there are particles without attachment to the polymer and polymer chains are more likely to be stretched out, forming a looser structure in the sediment cake (Ofori et al. 2011). Unattached particles will fill out the hollow spaces in the sediment cake. Thus, the water content of the sediment cake was low at low polymer concentrations. When particles eventually settle down with the polymer, the loose structure of stacked polymer chains will act like a sponge, which allows more water to enter the sediment cake. At high polymer concentration, the anionic chains will be close together and repel each other due to the electrostatic force. The repulsion of anionic polymer chains will lead to a more loose sediment cake structure (Ofori et al. 2011).

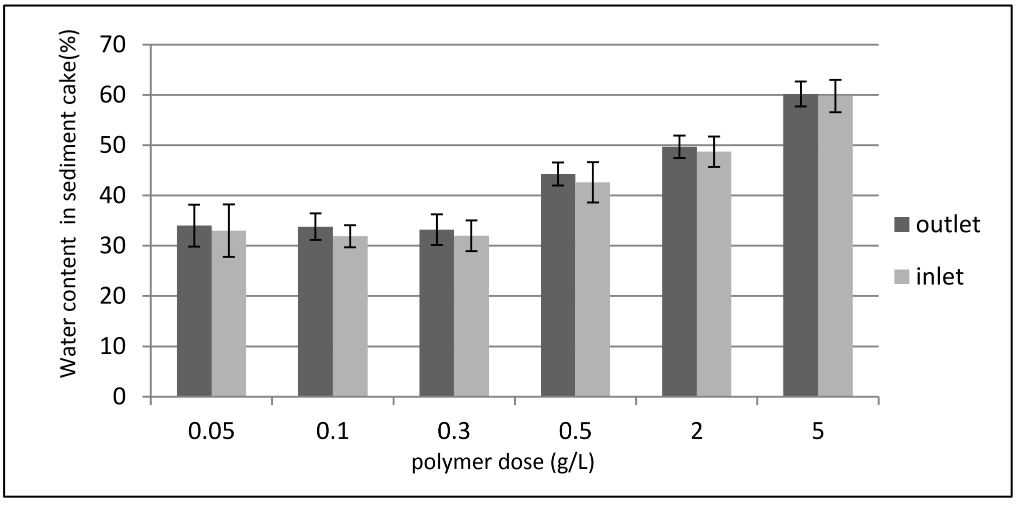


Figure 11. Water content of sediment cake at different polymer dose applications at room temperature. The settling time was 1 hour.

Changes in the sediment cake volume showed pattern similar to changes in the sediment water volume (Figures 11 and 12), confirming that water content contributed the most to sediment cake volume growth. This result suggested that the polymer concentration was lower than 0.3 g/L in the polymer dewatering test. In addition, since divalent ion concentrations were higher in inlet pore water samples than in lake samples, and they are expected to be helpful in sediment cake compaction, it was expected that the sediment cake volume of inlet sediments would be lower than that in outlet sediments. The results corresponded with our expectations.

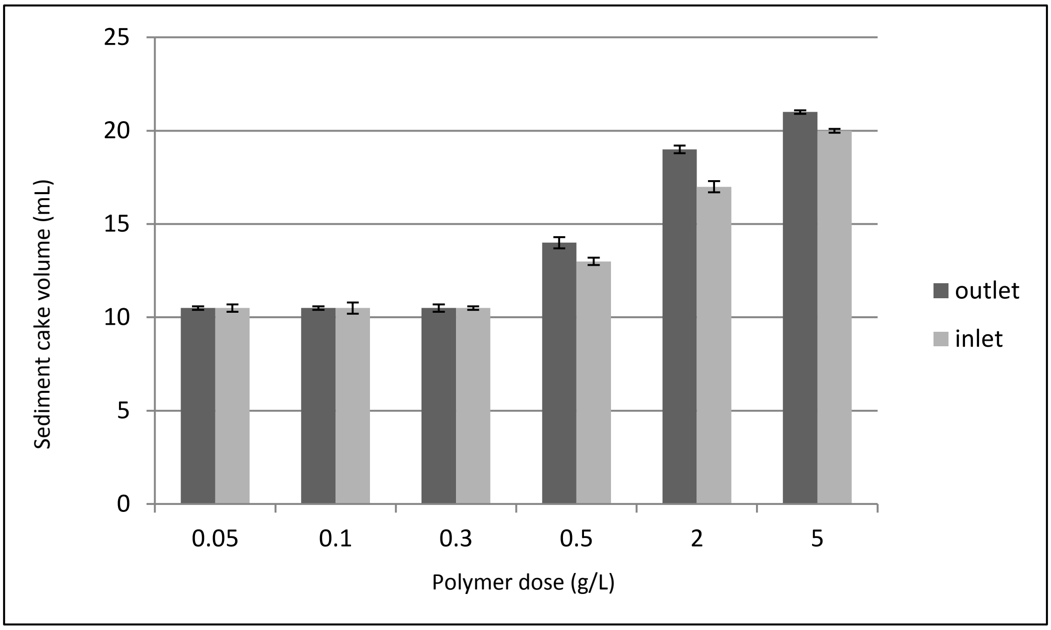


Figure 12. Sediment cake volume at different polymer dose applications at room temperature. The settling time was 1 hour.

To summarize the results from dose effect experiments, flocculation was greatest when the polymer dose was between 0.3 and 0.5 g/L, and dewatering was greatest when polymer was at lower concentrations (concentration <0.3 g/L). Therefore, it can be concluded that Soil Lynx 398 should be applied at 0.3 g/L when treating lake sediment. The polymer concentration used in temperature effect experiment (next section) was 0.3 g/L. The results imply that, if lowering the turbidity of the water is the primary goal, the polymer dose could be optimized between 0.3 to 0.5 g/L. If dewatering is the primary purpose, the polymer dose can be much lower than the dose needed to produce flocculation.

4.4 Temperature Effect Experiment

Temperature effects on turbidity, water content of the sediment cake, initial particle settling rate, and sediment cake volume were measured at a polymer concentration of 0.3 g/L.

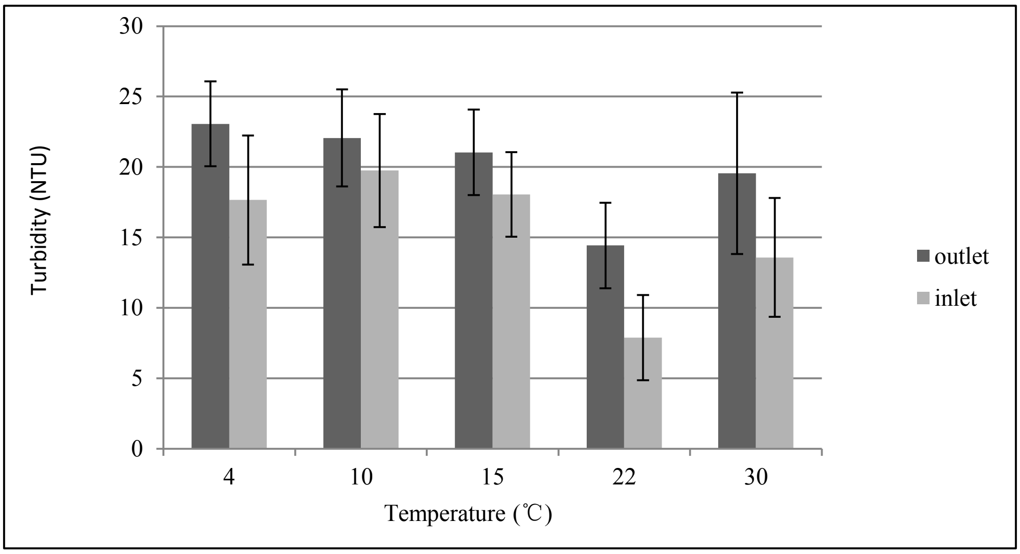


Figure 13. Turbidity of supernatant at different temperatures. The polymer dose was 0.3 g/L for all temperature conditions and the settling time was 1 hour.

Figure 13 shows that the change in supernatant turbidity was not significant when the temperature was increased from 4 to 15 °C ($P > 0.05$). However, when the temperature increased from 15 to 22 °C, there was a significant drop in supernatant turbidity in both outlet and inlet samples (14.43 ± 3.03 and 7.89 ± 3.04 NTU from outlet and inlet, respectively), indicating that higher temperature facilitates greater particle flocculation. Further increase in temperature to 30 °C did not significantly change the supernatant turbidity ($p > 0.05$).

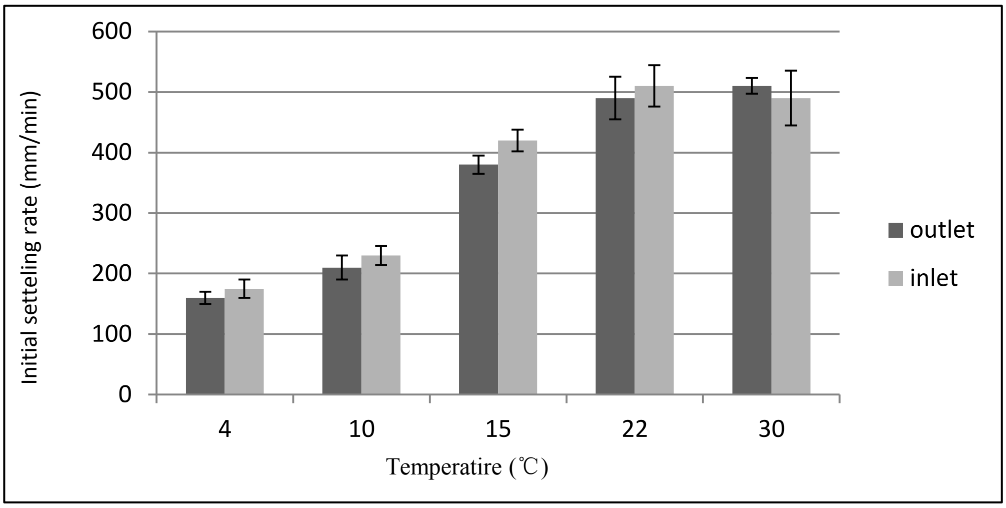


Figure 14. Initial settling rate of supernatant at different temperatures. The polymer dose was 0.3 g/L for all temperature conditions and the settling time was 1 hour.

In both inlet and outlet samples, higher initial settling rates were observed as the temperature increased from 4 to 22 °C (Figure 14). The settling rate increased from 160 ± 9.7 mm/min to 490 ± 20.2 mm/min in the outlet sample when the temperature increased from 4 to 22 °C. The initial settling rates were about the same at 22 and 30 °C.

A possible explanation for the above observations might be the solution viscosity differences at different temperatures (Hogg, 2007). Figure 15 shows that the viscosity increased when either the temperature decreased or the polymer concentration increased. In addition, although the viscosity of the polymer solution did not change significantly between 22 and 30 °C ($p > 0.05$), there was a significant decrease ($p \leqslant$

0.05) at low temperature (4 °C). The viscosities of a 0.3 g/L polymer solution at 4 and 30 °C were 2.87×10^{-3} Pa*s and 1.34×10^{-3}Pa*s.

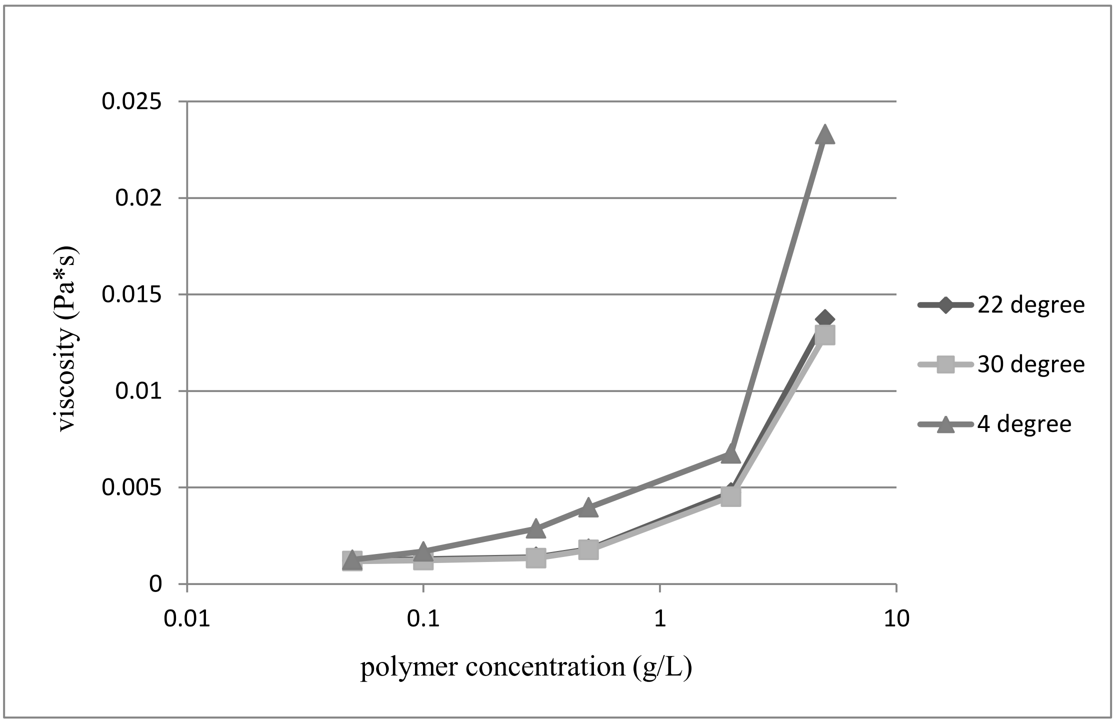


Figure 15. Viscosity of different dosages of Soil Lynx 398 at 4, 22, and 30 ℃.

Table 5. Viscosity (Pa*s) of pure water at different temperatures

	4 ℃	**22 ℃**	**30 ℃**
viscosity (Pa*s)	1.24×10^{-3}	1.05×10^{-3}	1.02×10^{-3}

An increase in temperature causes the following effects on the viscosity of a polymer solution. At low temperature, polymer chains are entangled and the solution viscosity is high. When the temperature is increased, the entanglement points on the polymer chains start to break due to the thermal motion of the polymer chains and the result is a lower solution viscosity (Ngai and Roland, 1997). In addition, as the kinetic energy increases with increasing temperature, the binding energy between molecules in the solution is reduced, therefore, the viscosity is reduced. Both of the effects are caused by Brownian motion.

Stokes' law states: $Fd = 6\pi\mu Vd$, where Fd is the drag force of the fluid on a sphere, μ is the fluid viscosity, V is the velocity of the particle relative to the fluid, and d is the diameter of the sphere. Therefore, when the solution viscosity was high at the lower testing temperature, the drag force of the fluid on the particle was high (Moigne, 1958). At high viscosity, polymer chains that have just a few particles attached on them and fine particles that are not attached to a polymer chain will be suspended in the supernatant, increasing the turbidity and decreasing the initial settling rate of the particles. Decreasing the temperature could increase the density and buoyancy of the water solution, which will contribute to a higher number of particles being suspended in the supernatant. Another theory suggests that a thin layer of water will adsorb on the particles and that this thin layer is thinner at higher temperatures. Since the polymer is also hydrophilic, there will be a thin water layer at the surface of the polymer as well. In this case if the water layer from both particle and polymer are too thick, it will obstruct the binding of particles with polymer. The particle will more easily attach to the polymer when the water layer is thinner. (Gao and Wu, 1997; Barker et al., 2003). As the viscosity decreases with a temperature increase and the Brownian motion of the molecules increases, the fine particles have more chances to bind with the polymer. That is also one of the reasons that the turbidity decreased at higher temperatures. It should be pointed out that Brownian motion is more effective with fine particles. This could explain why we observed that the initial settling rate decreased when the temperature decreased and the turbidity was much higher at lower temperatures (Figure 13 and Figure 14).

The zeta potential could have a significant effect on the stability of particles in the supernatant. Table 4 shows that the zeta potential of the lake sediment decreased in magnitude as the temperature increased. According to the data in Table 4, the zeta potential of the polymer itself (0.3g/L) did not change much with changes in temperature. The zeta potential of the sediment solution, however, decreased significantly when the temperature increased from 4 °C to 30 °C ($p \leqslant 0.05$). In this case, the sediment solution will be more unstable at higher temperatures. Hence the decreasing turbidity and increasing initial settling rate at higher temperatures is further explained.

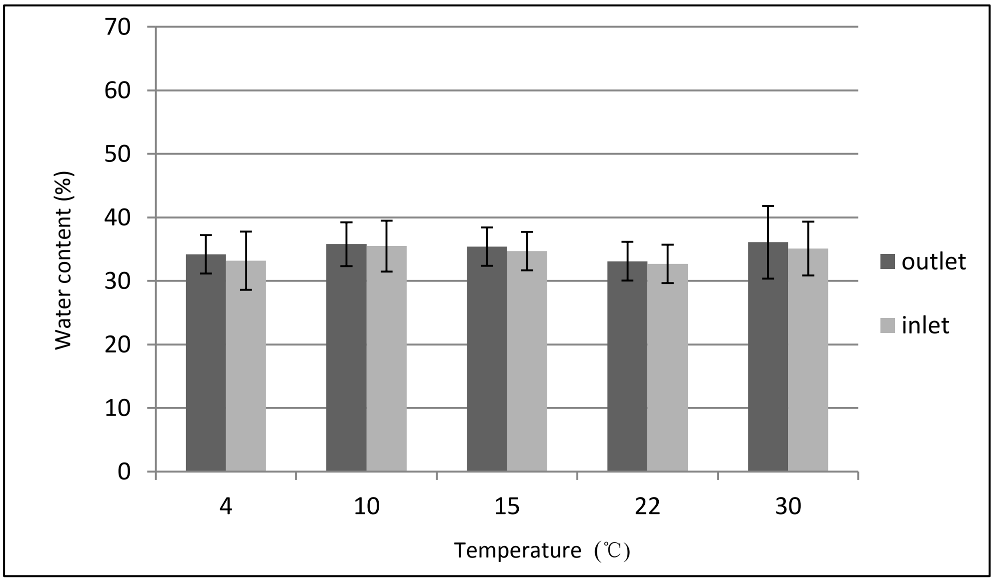


Figure 16. Water content of sediment cakes at different temperatures. The polymer dose was 0.3 g/L in all temperature conditions and the settling time was 1 hour.

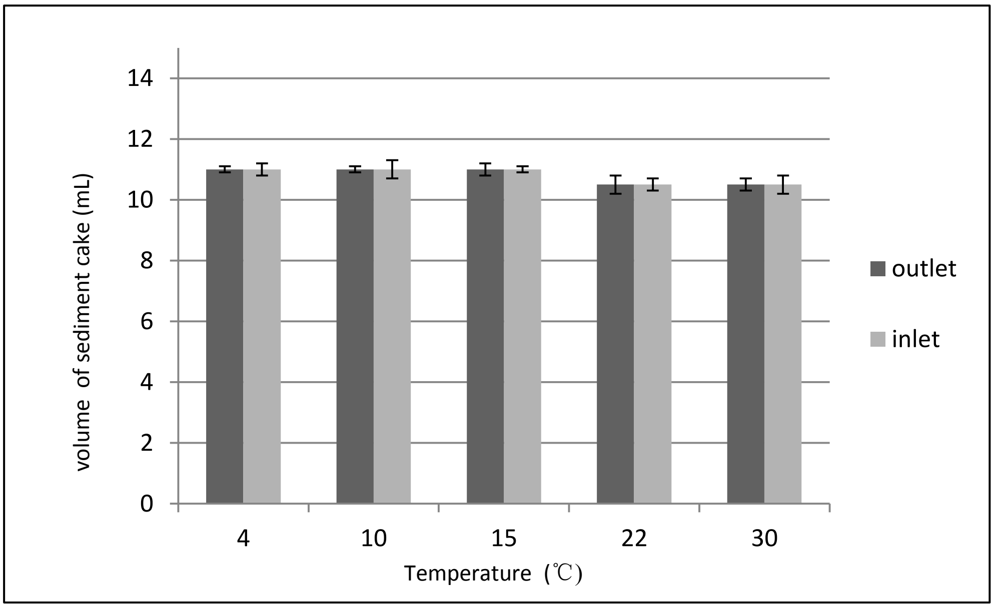


Figure 17. Volume of sediment cakes at different temperatures. The polymer dose was 0.3 g/L for all temperature conditions and the settling time was 1 hour.

The sediment properties in Figures 16 and 17 indicate that both water content and sediment cake volume did not change significantly at different temperatures ($p > 0.05$), mainly because the Soil Lynx 398 used in these experiments is not a thermally sensitive polymer. However, studies have shown that even non-thermally sensitive polymers can change conformation with changes in temperature. For example, the polymer chain could swell at higher temperatures in certain solutions. This is mainly due to the thermal dynamics of chain mobilization (Devotta, et al., 1994; Rubinstein, et al., 2003). The particle settling performance and the sediment water content should be impacted by such polymer conformational changes. However, our results indicate that the water content and sediment cake volume did not change significantly at all temperature conditions. We conclude that temperature effects on the conformational change of a non-thermally sensitive polymer are limited.

Table 6. Frequency measured by QCM-D in polymer solution at different temperatures

Temperature	ΔF (Hz)
10 °C	-5.94±2.62
22 °C	-12.76±3.01
30 °C	-16.93±2.27

Note: the polymer concentration was 0.3 g/L; the frequency was monitored for 1 hour.

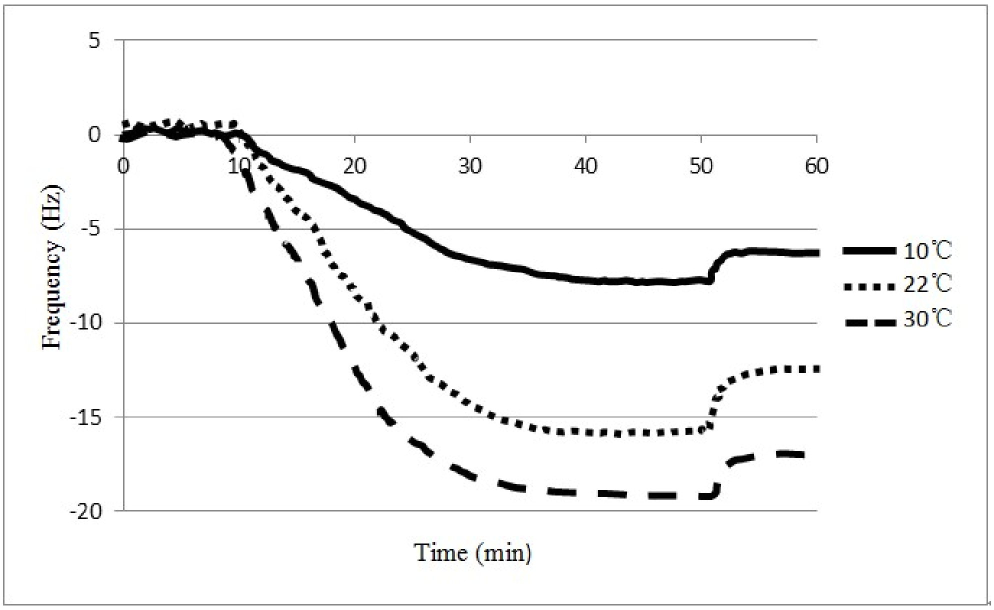


Figure 18. Frequency changes of the QCM-D sensor in polymer solution at different temperatures.

A quartz crystal microbalance with dissipation monitoring (QCM-D) measures changes in frequency (Δf) and energy dissipation (ΔD) in a polymer solution. When the crystal is excited to oscillate in the thickness shear mode at its fundamental resonant frequency f_0 by applying an radio frequency voltage across the electrodes near the resonant frequency, a small mass added to the electrodes induces a decrease in resonant frequency (Δ f) which is proportional to the mass (Δ m) (Zhang, 2004).

In the experiment, after equilibration (at 10 minutes), the polymer solution was introduced to the system, and then the frequency of the coated sensor decreased at all temperatures but at different rates. At 50 minutes, the injection of polymer solution was replaced by an injection of pure water to wash out polymer chains that were not firmly attached (Figure 18 and Table 6). Results showed that the frequency decreased with increasing temperature, which means with increasing temperature the polymer adsorbed more onto the sensor surface. In addition, at higher temperatures, the time was shorter to reach the stable point (35 minutes for 30 ℃ and 42 minutes for 10 ℃). It reveals that at higher temperatures, polymers adsorb more easily to the sensor. As discussed before, it is expected that there would be a thin layer of water adsorbed on the particles. The layer would be thinner at higher temperatures making it easier for the particles to attach to polymer surfaces. In the QCM-D experiment, it is expected that a thin layer of water also formed on the sensor surface. Since the polymer is also hydrophilic, there will be a thin water layer at the surface of the polymer as well. In this case, if the water layer is too thick, it will obstruct the binding of particles with polymer chains. Hence, the polymer adsorption of particles at different temperatures is different. Table 6 and Figure 18 indicate that particles are more easily attached to polymers at higher temperatures. Our results are consistent with the results of previous polymer binding studies (Gao and Wu, 1997; Barker et al., 2003).

Data from Figures 13, 14, and 15 indicate that turbidity, initial settling rate, and viscosity changes in the settling tests were not significant ($p > 0.05$) when the temperature increased from 22 °C to 30 °C. However, the QCM-D experiment showed a significant frequency change between 22 °C and 30 °C ($p \leqslant 0.05$). Two possible explanations for the dichotomy in the results follow: first, the sediment particles used in the settling test were from a storm water pond. Natural particles are complex in terms of particle shape, size, and composition. For example, various types of ions attached to these particles could affect polymer binding. In addition, the pore water from natural sediments could contain different types of acids that could change the pH of the supernatant which would impact particle settling. In QCM-D test, the frequency was tested with a SiO_2 sensor. The surface of the sensor is expected to be much more uniform than the surface of a natural particle. These factors could affect the results of the tests. As the QCM-D is considered to be a considerably more sensitive test than the settling test, the QCM-D results between 22 °C and 30 °C should be emphasized compared to the settling test results.

5. Conclusions and Recommendations

The sediments that flow into a storm water pond could bring nutrients and also decrease the volume of the pond as time goes on. By applying PAM, the suspended particles along with attached nutrients and the water content of sediment are expected to be decreased.

In the polymer dose effect experiment, the result indicated that flocculation was greatest when the polymer dose was between 0.3 and 0.5 g/L, and dewatering of storm water sediment was greatest when polymer was lower than 0.3 g/L.

In the temperature effect experiment, the overall flocculation performance was compromised at lower temperatures. The turbidity was the lowest (decreased by 45.2% with a temperature change from 4-15 ℃) and the initial settling rate was the highest (increased by 198.5% compared to 4 ℃) at22-30 ℃. It was found that the change of supernatant turbidity was not significant when the temperature was increased from 4 to 15 °C ($P > 0.05$). However, when the temperature increased from 15 to 22 °C, there was a significant drop in supernatant turbidity in both outlet and inlet samples. A further increase in temperature to 30 °C did not significantly change the supernatant turbidity. In addition, higher initial settling rates were observed as the temperature increased from 4 to 22 °C. Moreover, the water content did not show any significant change ($p>0.05$) through different temperatures (4-30 °C).

The result from viscosity, zeta potential and QCM-D tests further revealed the potential mechanisms involved. Viscosity variation at different temperature could greatly impact on the PAM dewatering performance. Further, zeta potential of the particles could affect the stability of suspension. The greater negativity of zeta potential is, the more stable of the supernatant will be. It should be noted that both of these factors are temperature-dependent. The viscosity of the supernatant increased and the negativity of sediment particles decreased with decreasing temperature. QCM-D test indicated that at higher temperatures, polymer chains are more easily adsorbed on the SiO_2 surfaces.

Based on the results, several recommendations can be drawn from this project regarding the practical application of PAMs. First, the impact of temperature on turbidity and settling rate was clear. However, the water content of sediment cake did not show any significant change at different temperature. In this case, the overall settling performance will be reduced at low temperatures as compared to the high temperature conditions. Second, in terms of flocculation, appropriate polymer dosage should be applied, since too much or too little polymer could lead to poor turbidity removal and low initial settling rate. Third, the water content of sediment cake increased with increasing polymer concentrations in this study. This phenomenon was more obvious at high polymer concentration condition (0.5-5g/L). Thus, if sludge dewatering is the primary objective of the study, the polymer dose should be controlled carefully.

In future studies, the potential conformational change of polymers under different temperature conditions should be studied. Also, the composition and functional groups of the polymers need to be investigated.

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