

Article

Evaluation of a Novel Polymeric Flocculant for Enhanced Water Recovery of Mature Fine Tailings

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Abstract: The novel cationic flocculant, poly(lactic acid) choline iodide ester methacrylate (poly(PLA₄ChMA)), has been shown to provide improved flocculation of 5.0 wt.% mature fine tailings (MFT) diluted in deionized water compared to commercial anionic polymers, with continued dewatering of the sediment occurring as the polymer undergoes partial hydrolytic degradation. However, the elevated dosages (10,000 ppm) required would make the polymer costly to implement on an industrial scale. With this motivation, the impact of MFT loading and the use of process water is explored while comparing the settling performance of poly(PLA₄ChMA) to available commercial alternatives such as anionic FLOPAM A3338. Improved consolidation of 5.0 wt.% MFT diluted with process water could be achieved at reduced dosages (500 ppm) with poly(PLA₄ChMA). However, the final compaction levels after polymer degradation were similar to those achieved with the nondegradable commercial flocculants. Flocculation-filtration experiments with undiluted MFT are also conducted to compare the performance of the polymers. Significantly faster rates of water release were observed with the cationic flocculants compared to FLOPAM A3338, but no improvement in the overall tailings compaction was found either before or after poly(PLA₄ChMA) degradation. Thus, the improved dewatering observed with poly(PLA₄ChMA) in dilute MFT suspensions does not extend to conditions that would be encountered in the field.

Keywords: cationic polymers; flocculation; mature fine tailings; hydrolytic degradation; flocculation-filtration

1. Introduction

Oil extraction facilities recover bitumen from raw tailings but also generate tailings sludge. The finer particles from the sludge form a stable suspension composed of ~30% solids in water, known as mature fine tailings (MFT) [1,2]. The environmental impact of MFT is growing, as the water captured in the tailings cannot be effectively separated [1,3]. Improved technologies are required to manage the tailings volume, with the goal of reducing its environmental impact and to comply with Alberta's provincial mandate requiring that the water and tailings contained in MFT be reclaimable a decade after the end of mine life, as detailed in Directive 85 of the Oil Sands Conservation Act (OSCA) [4,5].

The stability of MFT is attributed to their ultrafine particle sizes (<44 µm), negative surface charge, and residual bitumen content [1,3,6,7]. In particular, the strong negative surface charge arising from the densely charged clays contained in the tailings causes the particles to repel each other to form a dispersed and stable colloidal suspension [1,8]. Over the past 20 years, various approaches have been proposed to recover the water and consolidate the MFT by increasing the particle sizes of the tailings to accelerate their settling velocity [9–13]. Flocculation has emerged as the preferred treatment strategy,

since polymers can be functionalized by adding charge or side units to the backbone to enhance settling through particle bridging [3].

Existing flocculants are primarily poly(acrylamide) (PAM)-based, as they can be synthesized to high molecular weights to enhance their performance [3,6]. However, anionic PAM has been found to be less effective in flocculating the finer particles contained in the tailing suspensions [3,13]. Modifications to the polymer structure or water chemistry of the suspended tailings result in significant improvements in MFT consolidation with PAM flocculants [9,14–17]. Hybrid inorganic-organic flocculants that bind an inorganic coagulant like $\text{Al}(\text{OH})_3$, CaCl_2 , or FeCl_2 to PAM have shown advantages in flocculating kaolinite suspensions compared to commercial PAM by reducing the electrostatic repulsion between the tailing particles through charge neutralization [3,14]. Similarly, improvements in compaction, as well as reduced capillary suction times and supernatant turbidities, were measured at varying sodium and calcium salt dosages combined with anionic PAM [9,15,18].

While these PAM-based flocculants are effective at inducing initial settling, the MFT aggregates formed are susceptible to higher levels of water retention, resulting in sediment that is less-closely packed [3,9,13–15,19]. To improve the densification of MFT over extended periods, partially hydrophobic polymers have been developed [12,16,20–22]. However, these generally require an external trigger such as heat or added chemicals, making them more energy intensive to implement on an industrial scale [12]. Our group has developed cationic partially degradable hydrophobic caprolactone and lactide-based polymers [12,13,19]. A controlled number of polyester units are added by a ring opening reaction with lactide [13,23,24] to form the cationically charged methacrylate macromonomer, poly(lactic acid) choline iodide ester methacrylate (PLA_4ChMA), that is then polymerized through micellar radical polymerization [13,19,25,26]. When applied as a flocculant, poly(PLA_4ChMA) undergoes partial hydrolytic degradation that results in additional dewatering over time after the initial settling and MFT aggregation [13,19,27].

While this advance is promising, a high flocculation dosage (10,000 parts-per-million polymer added on a mass basis relative to the solids content in the slurry) of poly(PLA_4ChMA) was required to flocculate 5 wt.% MFT suspensions, while the target dosage for commercial flocculants is an order of magnitude lower. In addition, the previous work only considered flocculations in MFT diluted with deionized water rather than process water. This difference is expected to have a significant impact on flocculant performance, as the ions contained in process water have been shown to enhance settling and improve supernatant clarity using both nonionic and anionic PAM flocculants [11,18,28]. Thus, this study will examine the use of poly(PLA_4ChMA) as a potential flocculant for MFT diluted in process water, as well as for undiluted MFT suspensions.

Cylinder testing is first used to compare the flocculation performance of the degradable cationic polymer to that of commercial materials when applied to tailing suspensions diluted to 5.0 wt.% MFT; initial settling rates, MFT compactions, and supernatant solids achieved both after 24 h and after accelerated degradation were measured. While the results provide a useful indication of flocculant settling characteristics, they do not necessarily represent the performance that might be achieved during flocculations of more concentrated MFT (~30 wt.%) under field conditions. The filtration of high-solid MFTs following flocculation has been demonstrated to accelerate dewatering compared to filtration alone [29], and researchers are exploring methods of improving the process by using flocculants to first bridge the particles [30–32]. Pressure filtration has been successfully employed to characterize the filterability of various flocculants by examining the net water release (NWR) or specific resistance to filtration (SRF) of flocculated MFT [33] and, when modified with an airtight piston, is a method for estimating the long-term settling performance of flocculants in a compressed time frame [34]. The information from these testing methodologies can be combined to provide a more complete assessment of the expected field performance of poly(PLA_4ChMA).

2. Materials and Methods

2.1. Materials

The following chemicals were purchased from Sigma-Aldrich, Canada and used as received: (3*S*,6*S*)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione (L-Lactide, 98%), stannous octoate ($\text{Sn}(\text{oct})_2$), 2-(dimethylamino) ethanol initiator (De, >98%), triethylamine (TEA, >99%), tetrahydrofuran (THF, >99%), methacryloyl chloride (MACl, 97%), basic alumina, ethyl ether (anhydrous), iodomethane (ICH_3 , 99%), 2,2-azobis(2-methylpropionamidine) dihydrochloride initiator (V-50, 97%), trimethylaminoethyl methacrylate chloride (TMAEMC, 75 wt.% in water), and non-ionic poly(acrylamide) (PAM, 5–6 million Da). FLOPAM A3338, a commercial powdered anionic flocculant, and SNF C3276, a commercial powdered cationic flocculant, were provided by SNF (Edmonton, AB, Canada). Deuterated water (D_2O , 99.9%) and chloroform- d_1 (CDCl_3 , 99.8% D) were purchased from Cambridge Isotope Laboratories (Montreal, QC, Canada), and mature fine tailings (MFT, characterized in Tables S1 and S2) were used as received.

2.2. Synthesis of Poly(PLA_4ChMA)

Previously developed experimental methodologies [19] were implemented to synthesize poly(PLA_4ChMA) in a multistep process shown in Figure 1. Samples from each step of the synthesis were dissolved in deuterated chloroform to verify their structures using ^1H -NMR, detailed in Figures S1–S3.

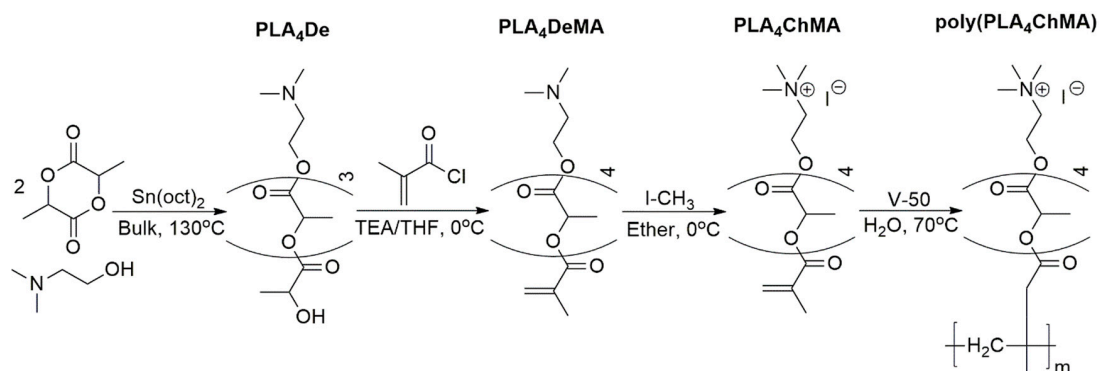


Figure 1. Mechanism to synthesize poly(PLA_4ChMA) [19].

In the first step of the synthesis, a ring opening reaction of the lactide (LA) monomer was performed with stannous octoate catalyst, $\text{Sn}(\text{oct})_2$, and 2-(dimethylamino)ethanol initiator. A catalyst to monomer molar ratio of 1:1000 and an initiator to monomer molar ratio of 1:2 was used for the reaction. $\text{Sn}(\text{oct})_2$ (45.4 mg) was measured in a clean 20-mL vial and mixed with 2-(dimethylamino)ethanol (5.00 g). LA (16.14 g) was measured and placed in a clean 100-mL round-bottom flask with a stir bar. The flask was purged with nitrogen gas for 10 min before placing it in an oil bath heated to 130°C . A syringe was used to transfer the well-mixed catalyst-initiator mixture from the vial to the reaction flask. After 7.5 min, the flask was removed from the oil bath and quenched in an ice bath.

The PLA_4De product was transferred to a 500-mL three-necked round-bottom flask and dissolved in tetrahydrofuran (THF) (200 mL), such that the concentration of the initiating OH groups in solution was approximately 0.2 mol/L. Triethylamine (TEA) (20 mL) was added to the reaction flask as a proton scavenger. The dissolved PLA_4De was purged under nitrogen for 15 min and submersed in an ice bath. An excess of distilled MACl (7.11 mL) was added dropwise over the course of 1 h at 0°C . The reaction was allowed to proceed for an additional 3 h. The product solution was poured into a 500-mL Erlenmeyer flask, diluted with approximately 200 mL of THF, and placed in a freezer to separate the liquid product from the solid phase. The solids were separated after 12 h using a Fritz filter, and the filtrate was passed through an alumina column to remove any excess MACl. After passing the product through the column, the THF was evaporated from the product using a rotovap at 40°C .

Diethyl ether was added to the product such that the concentration of amine groups was 0.1 mol/L. The product flask was purged with nitrogen for 5 min and added to an ice bath. Iodomethane was added to the agitated product flask and allowed to react for 48 h. The solvent was then evaporated from the macromonomer by rotovap with a bath temperature of 40 °C. The resulting PLA₄ChMA macromonomer was kept refrigerated until use.

A 10 wt.% PLA₄ChMA macromonomer solution with 0.22 wt.% V-50 initiator in deionized water was prepared in a single-neck round-bottom flask that was capped and purged with nitrogen for 1 h. The flask was then submersed in an oil bath maintained at 70 °C for the polymerization, with complete conversion reached in 120 min. TMAEMC, a commercially available nondegradable cationic monomer used for comparison purposes in this study, was polymerized using an aqueous 10 wt.% monomer solution with 0.40 wt.% V-50 at 50 °C for 120 min, following previously developed procedures [35]. Weight-average molecular weights of the cationic polymers produced under these synthesis conditions are in the range of 7–10 × 10⁵ Da [12,19,25,35,36].

2.3. Flocculation of 5.0 wt.% MFT

After preparing the 10 wt.% poly(PLA₄ChMA) by polymerization, the flocculant was diluted to 2 wt.% ($w_{\text{floc}} = 2\%$) in synthetic process water in order to roughly match the viscosity of a 5-wt.% MFT suspension ($w_{\text{MFT}} = 5\%$). Synthetic process water was prepared using a formulation containing 1000-ppm NaCl and 100-ppm CaSO₄ in deionized water. Similar compactions and supernatant solids were achieved in the flocculation of 5 wt.% MFT suspension prepared in synthetic water and in a sample of industrial process water [36]; thus, the synthetic process water used in this study provided a reasonable representation of conditions that would be encountered in the field.

Flocculations were conducted in triplicate over a series of dosages to determine the optimal treatment dosage. Errors bars reported in compaction or supernatant clarity measurements represent standard deviations. The diluted MFT mixture was well-mixed before flocculations using an overhead agitator at 500 rpm for approximately 15 min. The mixed MFT suspension was transferred to a weighed graduated cylinder, and the mass of the cylinder with MFT was recorded. From the tailings mass (m_{MFT}), the required mass of flocculant (m_{floc}) to achieve the desired experimental dosage was calculated by rearranging Equation (1) to yield Equation (2).

$$\text{target dose (ppm)} = \frac{m_{\text{floc}}(\text{g}) \times w_{\text{floc}}(\%) \times 10^6}{m_{\text{MFT}}(\text{g}) \times w_{\text{MFT}}(\%)} \quad (1)$$

$$m_{\text{floc}}(\text{g}) = \frac{\text{target dose (ppm)} \times m_{\text{MFT}} \times w_{\text{MFT}}}{w_{\text{floc}}(\%) \times 10^6} \quad (2)$$

The calculated mass of flocculant solution was withdrawn from a storage container using a pre-weighed syringe. The flocculant was added in 2-mL aliquots immediately mixed into the suspension in the graduated cylinder with 3 vertical plunges using a stir rod, repeating the procedure until the total desired dosage was added to the MFT suspension. The exact mass of flocculation solution added was determined by reweighing the syringe after the last addition. A timer was started, and the rate of MFT settling was tracked over 30 min by recording the position of the line that separated the solids-rich region from the supernatant as flocculation and settling occurred; these data were used to calculate the initial settling rate (ISR) of the flocculated MFT suspension [36].

After 24 h, the solids compaction of the MFT in the cylinder was determined by weighing the test cylinder and documenting the supernatant liquid level and mudline level using Equation (3).

$$\text{wt.\% (solids)} = \frac{w_{\text{MFT}}(\%)m_{\text{MFT}}(\text{g})}{m_{\text{final}}(\text{g}) - v_{\text{water above mudline}}(\text{mL}) * \text{density of water (1 g/mL)}} \quad (3)$$

The assayed weight fraction was multiplied by the measured mass of MFT in the flocculation cylinder and divided by the final mass of the solids at the time of measurement, calculated by

subtracting from the total mass (m_{final}) the supernatant liquid mass above the mudline, calculated using the known volume (supernatant liquid level—mudline level) and assuming a density of 1 g/mL. Error bars correspond to the standard deviation of triplicate compaction measurements.

After measuring the solids compaction, the supernatant clarity was determined by removing the supernatant liquid from the cylinder, leaving approximately an inch of liquid above the mudline. The supernatant liquid was mixed in a beaker, and three 5-mL samples were weighed and placed in a vacuum oven until dry. The solids contents determined from the three measurements were used to calculate the average supernatant solids content reported for each experiment.

The effect of polymer degradation on MFT compaction was studied under accelerated degradation conditions. After collecting the initial solids compaction of the tailings and supernatant solids content measurements, the test cylinders were covered with aluminum foil to prevent evaporative losses and fully submersed in an oil bath maintained at 75 °C. Thermal degradation of the polymer was allowed to occur over 5 days. After this time, the solids content and supernatant clarity were determined using the same procedures detailed above. It has been shown that similar MFT compactions are achieved at room temperature over a period of 12 weeks compared to the accelerated degradation conditions used here [13].

2.4. Flocculation of Undiluted MFT

Three-hundred grams of mixed undiluted MFT (approximately 25 wt.%, with characterizations detailed in Tables S2 and S3 and Figure S4) was added to a 10.16-cm baffled metal cup device equipped with a flat blade gang mixer, as described by Sadighian et al. [37]. Flocculant was added in 5-mL increments with high mixing (320 rpm) until the desired dosage was attained. Mixing was reduced to 50 rpm after addition of the final flocculant increment for approximately 30 s.

Capillary suction time (CST) tests evaluate the dewaterability of the flocculated tailings (either immediately after flocculation or after 24 h) by measuring the time required for the water released to pass through a capillary [12,13]. As a homogeneous floc structure was observed, the analysis was performed immediately after mixing in the flocculant by scooping the tailings into a Triton Electronics 319 CST apparatus. The CST measurements were done in triplicate to generate dosage response curves used to determine an optimum dosage. Error bars correspond to the standard deviation of the CST measurements.

Two-hundred and fifty grams of the flocculated sample was transferred to a test cell containing a 90-mm-diameter Whatman 50 filter paper diameter (2.7 µm pore). The test cell, including the airtight piston described in Li et al. [34], was assembled and fixed to an OFITE Multi-Unit filter press. A 500-mL baffled beaker was placed on a balance below the test cell and tared. The pressure valves to the filter press were closed, and the nitrogen pressure was adjusted to 42 psig. The mass of water released from the test cell was tracked until water release ceased. The filter cake was weighed and dried to determine the solids content of the filtered tailings. Each test was conducted in triplicate, using the average net water release to generate a water release curve.

The filterability of the MFT samples flocculated with poly(PLA₄ChMA) and poly(TMAEMC) was also assessed after degradation at high temperatures. First, 300-g MFT samples were flocculated with 4.00 wt.% poly(TMAEMC) and 2.00 wt.% poly(PLA₄ChMA) at their respective optimum dosages. After flocculation, the tailing samples were covered with aluminum foil and placed in an oven at 75 °C for 5 days, followed by removal of the supernatant and weighing of the settled solids. The sample size of the subsequent SRF test was the difference between the 250-g test basis (previously used) and the measured mass of the supernatant. For example, if 50 g of water was removed as the supernatant from a flocculated tailing sample after degradation, 200 g of the flocculated tailings sludge would be filtered under pressure. To standardize the presentation of results, the initial starting point of the net water release curves plotted in this section represents the difference between the weighed supernatant following degradation and the added volume of flocculant during dosing (relative to the 250-g filtration loading).

3. Results and Discussion

3.1. Flocculation of Dilute MFT

The flocculation performances of poly(TMAEMC) and poly(PLA₄ChMA) with 5.0 wt.% MFT were first studied in deionized water using high dosages (10,000 ppm) in order to compare to the previous results that demonstrated their superior flocculation performances to anionic and non-ionic PAM [18,26]. Both the flocculant and diluted MFT mixtures were prepared using deionized water. In agreement with the previous studies, poly(PLA₄ChMA) offers a better initial compaction after 24 h compared to poly(TMAEMC); as shown in Figure 2, the mudline in the 100-mL graduated cylinder is 38 mL compared to the 62-mL position with poly(TMAEMC). In addition, the mudline decreases to 22 mL (i.e., almost 50% further sediment compaction) as the poly(PLA₄ChMA) partially degrades when the slurry is held at 75 °C for 5 days, making the sediment nearly twice as compact as that obtained with poly(TMAEMC). There is a little additional compaction of the nondegradable analog poly(TMAEMC)—the mudline decreases from 62 to 50 mL when held under accelerated degradation conditions—also in agreement with the earlier work.

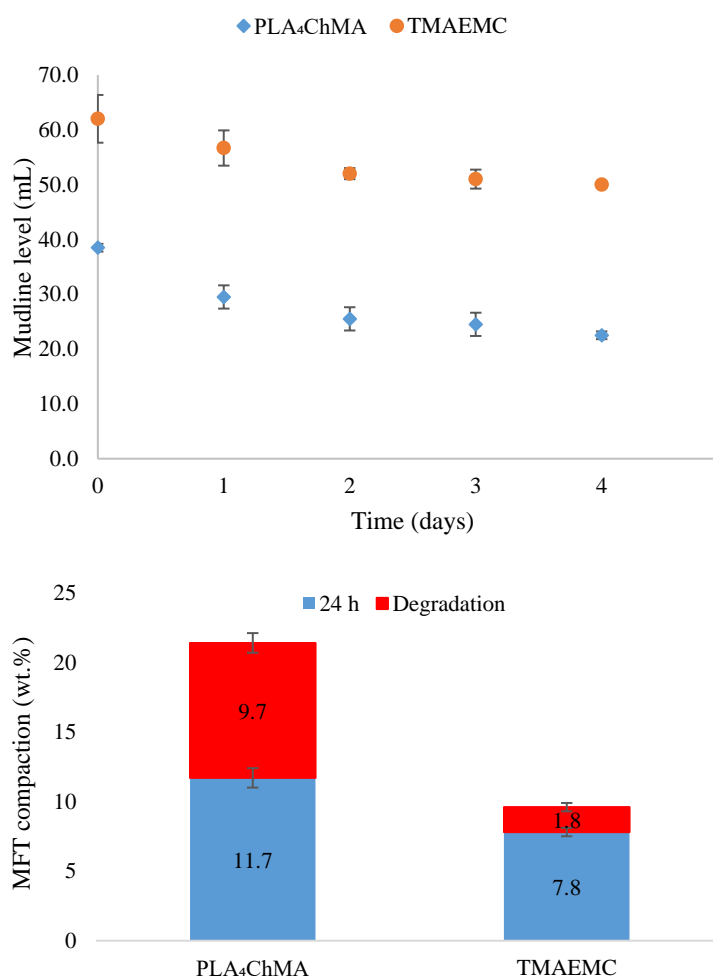


Figure 2. Comparison of continued settling during accelerated degradation after initial 24 h settling (**top**) and compactions before and after degradation (**bottom**) of 5.0 wt.% mature fine tailings (MFT) from flocculation in deionized water using 10,000 ppm of poly(PLA₄ChMA) and poly(TMAEMC) (trimethylaminoethyl methacrylate chloride).

Despite the improvement in performance observed with poly(PLA₄ChMA) compared to nondegradable poly(TMAEMC), the elevated dosages required for flocculation make poly(PLA₄ChMA)

less attractive for industrial applications. To better evaluate the performance of poly(PLA₄ChMA) under field conditions, experiments were conducted in process water synthesized to mimic the aqueous composition of MFT to determine if reduced polymer dosages could be used to flocculate MFT and to evaluate the compactions and supernatant solids of poly(PLA₄ChMA) relative to commercially available flocculants under these conditions. Experiments were first conducted with poly(PLA₄ChMA) with 500, 1000, and 3000 ppm to determine a suitable dosage before comparing its performance to other industrial flocculants, shown in Figure 3.

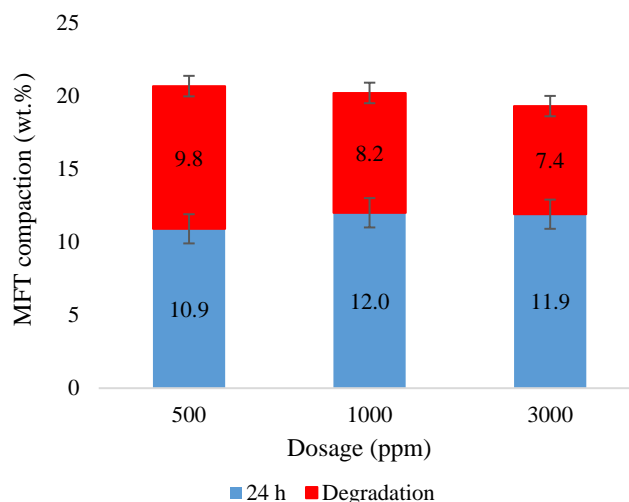


Figure 3. Comparison of compactions of 5.0 wt.% MFT in synthetic process water after treatments with poly(PLA₄ChMA) at various dosages.

The compactions and supernatant solids (<0.3 wt.%) achieved using 500 ppm of poly(PLA₄ChMA) to flocculate MFT diluted in process water (Figure 3) are comparable to those obtained with the much higher dosages (10,000 ppm) required for the MFT diluted in deionized water (Figure 2). No further improvement in overall compaction is observed at flocculant loadings of 1000 and 3000 ppm, as indicated by a *t*-test (Table S4). The improved settling properties at these lowered dosages in process water are likely because the ions act as salt linkages to facilitate bridging of the particles in the presence of the polymeric flocculant, thereby improving compaction of the tailings and clarity of the supernatant [18,28]. Similar flocculation methods, involving the injection of CaCl₂ to diluted MFT suspensions prior to addition of polymer, have been shown to improve the level of compactions at reduced dosages using low molecular weight flocculants [15]. The use of calcium salts at low dosages (50 ppm) also improved the performance of anionic polyacrylamides flocculants in MFT treatment processes, a result attributed to a decrease in particle-particle repulsive forces and the promoted adhesion of the flocculant onto the particles [18].

The settling properties of 500-ppm poly(PLA₄ChMA) were compared to anionic FLOPAM A3338 and cationic SNF C3276 using 5.0 wt.% MFT in synthetic process water. The compaction of the MFT was measured 24 h after flocculation, as well as after holding the sludge for five days at 75 °C; although the commercial materials are not expected to degrade, extra compaction may occur. Figure 4 compares the compaction and supernatant solids contents for the three flocculants. The supernatant solids measured with FLOPAM A3338 in process water were comparable to those obtained with cationic flocculants, ranging from 0.20 to 0.25 wt.% solids after 24 h and improving slightly over the five-day degradation period; this finding was in contrast to the elevated supernatant turbidities found when flocculating dilute MFT suspensions in deionized water with FLOPAM A3338 [19]. In addition, FLOPAM A3338 exhibited better compaction of the sediment after 24 h, as indicated by a *t*-test (Table S5). While a more extensive compaction was found with poly(PLA₄ChMA) after the degradation period, similar compaction profiles were also found for the cationic flocculant SNF C3276, even though the latter is not believed to degrade, a result that indicates that less hydrophobic cationic materials

can effectively dewater the tailings over time under these conditions. The final compaction levels achieved with all three flocculants in the synthetic process water were quite similar (within 2% solids compaction after degradation), despite the clear advantage of poly(PLA₄ChMA) for MFT dispersed in deionized water.

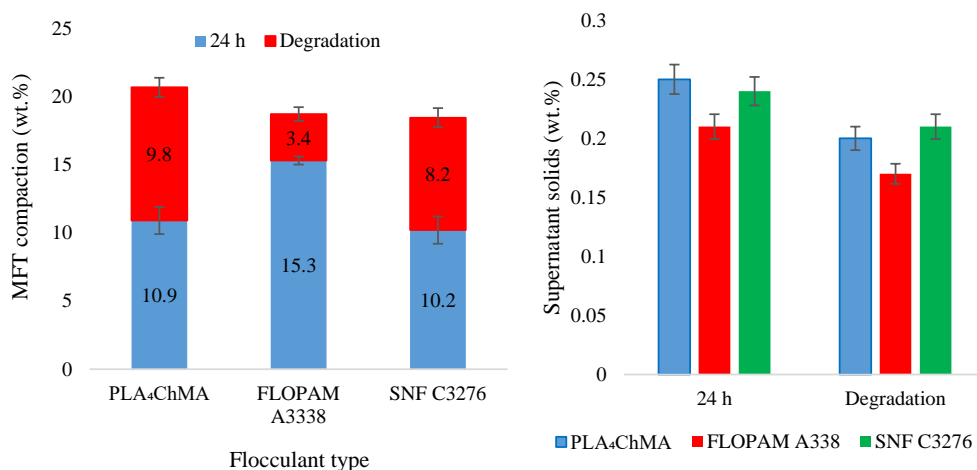


Figure 4. Comparison of compactions (**left**) and supernatant clarities (**right**) of 5.0 wt.% MFT in synthetic process water after treatments with various flocculants at 500 ppm.

The degradable and commercial cationic flocculants also offered slow initial settling rates (ISR < 0.4 m/h) under the range of dosages tested, with negligible settling observed in the first hour after treatment at 500 ppm. This behavior has been observed in previous studies, with similar ISRs reported in flocculations performed in deionized water with poly(PLA₄ChMA) at high dosages (10,000 ppm) [19], and earlier studies also found negligible settling rates with a degradable caprolactone analog at low dosages (1000–2000 ppm) [12]. In contrast, anionic FLOPAM A3338 offers considerably higher ISRs (4.8 m/h) at 500 ppm, while also achieving a higher compaction of the sediment over 24 h. Thus, low dosages of poly(PLA₄ChMA) do not induce the desired settling properties of MFT in process water, despite the clear advantage of poly(PLA₄ChMA) for MFT dispersed in deionized water. In addition, the overall compaction level following degradation of the poly(PLA₄ChMA) was only marginally better than those achieved with commercial flocculants in process water.

3.2. Flocculation-Filtration of Undiluted MFT

Since the majority of MFT treatment occurs in undiluted conditions, the poly(TMAEMC) and poly(PLA₄ChMA) were tested on undiluted MFT following the procedures outlined by Sadighian et al. [37]. Dosages of cationic flocculants were first optimized by measuring the capillary suction time (CST) of the MFT flocs immediately after flocculation. The dosage response curves for poly(TMAEMC) and poly(PLA₄ChMA) are shown in Figure 5, with the optimum dosages corresponding to the minimum CST value, approximately 10,000 and 20,000 ppm for poly(TMAEMC) and poly(PLA₄ChMA), respectively. As poly(PLA₄ChMA) exists as a suspension of relatively low viscosity compared to the MFT slurry, the CST measurements did not rise at dosages beyond 20,000 ppm. In contrast, poly(TMAEMC) exhibited a minimum, with dosages in excess of 10,000 ppm having a detrimental impact on the dewaterability of the flocs; the expected improvements in the water release from increased flocculant levels were offset by the reduction in dewaterability caused by the increased viscosity of the tailings mixture from the added flocculant. These optimum dosages measured for the cationic flocculants corresponded well with those used for flocculations with MFT diluted in deionized water [12,13]. However, they were considerably higher than those required for commercial flocculants, as an optimum FLOPAM A3338 dosage of approximately 1500 ppm was measured.

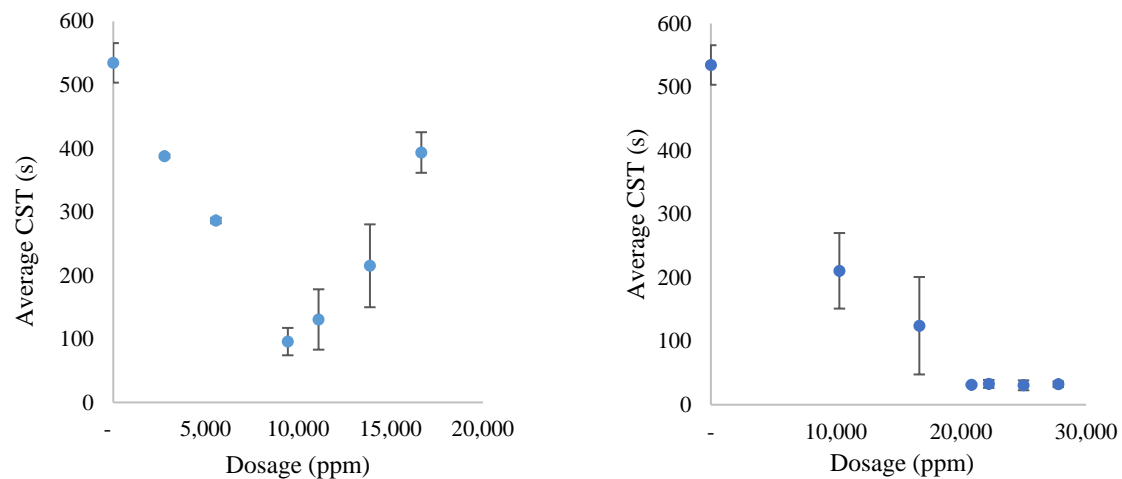


Figure 5. Capillary suction time measurement of MFT flocs after treatments with poly(TMAEMC) (**left**) and poly(PLA₄ChMA) (**right**) at varying dosages. CST: capillary suction time.

Net water release experiments were conducted by adding anionic FLOPAM A3338 and cationic poly(TMAEMC) and poly(PLA₄ChMA) to undiluted MFT at their respective optimum dosages; this test determines the effectiveness in dewatering undiluted tailings by determining the amount of water released from the tailings when placed in a sieve for 24 h following flocculation without added pressure. FLOPAM A3338 exhibited a significant net water release following flocculation, resulting in a compacted sediment of 39.0 wt.% after 24 h (relative to an initial MFT of approximately 25 wt.%). However, negligible net water releases were achieved from the samples flocculated with poly(TMAEMC) and poly(PLA₄ChMA) at their optimum dosages, showing that these cationic flocculants are less effective in single-step flocculations of undiluted tailings compared to commercial alternatives.

As the main goal of the modifications is to improve the water release after degradation to increase the speed of consolidation, the modified SRF test was used to evaluate the speed of water released from a 250-g MFT sample under a pressure consistent to an applied load of a sand cap. This method provides a description of the relative dewatering rates of MFT in less than 48 h [34] and is suitable for evaluating the degradable flocculant, as its potential benefits are expected to become more evident over time. The base case result for the SRF test is untreated MFT. As shown in Figure 6, the water release with time is slow but reaches a level of 155 g over the course of the 18-h test. Thus, the remaining sludge weighs 95 g, with a measured solids content of 73.5 wt.%.

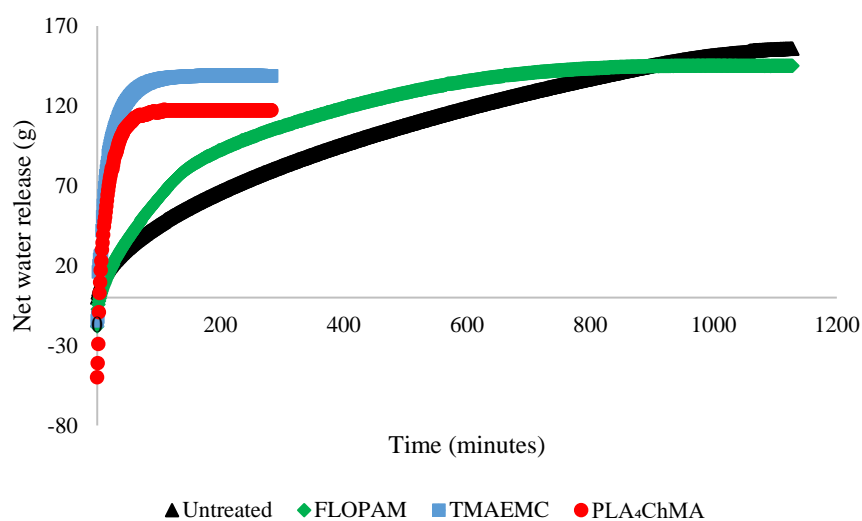


Figure 6. Net water release over time during filtration following flocculation with FLOPAM (1500 ppm), poly(TMAEMC) (10,000 ppm), and poly(PLA₄ChMA) (20,000 ppm).

The net water release curves were corrected for the mass of water added with the flocculant to the 250-g MFT sample. For example, 18.5 g of FLOPAM A3338 solution was added to achieve the 1500-ppm flocculant level; thus, the water release curve starts at a value of -18.5 g. As seen by its curve in Figure 6, FLOPAM A3338 does not offer a faster initial water release during the first hour of filtration compared to the untreated MFT, and the overall water release is lower than untreated MFT, as summarized in Table 1. This result is consistent with the observations by Boxill that A3338-flocculated MFT has the structure of a closed cell foam, highly porous but not very permeable [38]. The cationic flocculants result in much faster initial dewatering than FLOPAM A3338, indicating that they form a structure that will more readily dewater under pressure. This is best demonstrated by the fact that the tailings achieved a solids content of 60% in 52 and 106 min with poly(TMAEMC) and poly(PLA₄ChMA), respectively, compared to 463 min for FLOPAM A338 and 662 min for untreated MFT. The value of 60% is the dewatering target set by the Canada Oil Sands Innovation Alliance (COSIA) clay challenge, and the rapidity with which these cationic polymers achieved the target is promising. However, the overall net water released achieved with the cationic flocculants was lower than that for untreated MFT, suggesting that the undegraded cationic flocculants also cause the solids to retain increased water following treatments. The magnitude of this water retention is likely due to the extremely high doses required. Note that the curves for the tests with the cationic polymers start at a lower initial point, as significant amounts of flocculant solution were added to the MFT in order to achieve the high optimum dosages. While the total amounts of water released after treatment with poly(TMAEMC) and poly(PLA₄ChMA) were similar, the net released by poly(PLA₄ChMA) was lower due to its higher optimum dosage (20,000 vs. 10,000 ppm).

Table 1. Summary of net water releases and cake compactions from filtration experiments. TMAEMC: trimethylaminoethyl methacrylate chloride.

Flocculant	Time to 60% Compaction (min)	Total Net Water Release (g)	Solids Content after Filtration (wt.%)	Filtration after Degradation? (Yes/No)
Untreated	662	155.3	73.5 ± 0.1	N
FLOPAM A3338	463	144.5	69.0 ± 9.0	N
Poly(PLA ₄ ChMA)	106	117.1	65.4 ± 0.2	N
Poly(TMAEMC)	52	139.0	68.1 ± 5.1	N
Poly(PLA ₄ ChMA)	245	127.0	66.8 ± 10.3	Y
Poly(TMAEMC)	52	136.0	64.9 ± 0.8	Y

Thermal degradation studies were also conducted to determine if the enhanced hydrophobicity of poly(PLA₄ChMA) following degradation results in significant improvements in dewaterability during pressure filtration compared to the nondegradable poly(TMAEMC). Immediately after flocculation, the tailings were transferred to an oven set to 75 °C for five days. As expected, an appreciable water release was observed with poly(PLA₄ChMA) after degradation, while little water release was seen with poly(TMAEMC).

No change in the net water release profile was observed before and after the MFT sample treated with poly(TMAEMC) was held under the same degradation conditions, as shown in Figure 7. This finding not only confirms that poly(TMAEMC) does not degrade, it also demonstrates the reproducibility of the SRF test procedure. The amount of water removed from poly(PLA₄ChMA) following degradation resulted in an improved initial net water release, as the total water removed from the sample following degradation exceeded the flocculant volume added to the 250-g MFT sample. However, the subsequent rate of dewatering measured by the pressure filtration test was significantly slower compared to the curve obtained with undegraded poly(PLA₄ChMA). Furthermore, polymer degradation did not result in an improvement in either the overall net water release or the compaction of the sample, as summarized in Table 1. The reduction in the rate of the water release observed after partial poly(PLA₄ChMA) degradation could be attributed to the cleavage

of the cationic functionality of the flocculant during degradation, as previous NMR studies have shown that the choline units containing the cationic functionality are released during degradation [27]. The occurrence of degradation products or residual polymers in the water filtered from the tailings is evident, as a strong yellow color was observed in the tests conducted with poly(PLA₄ChMA) (Figure 8).

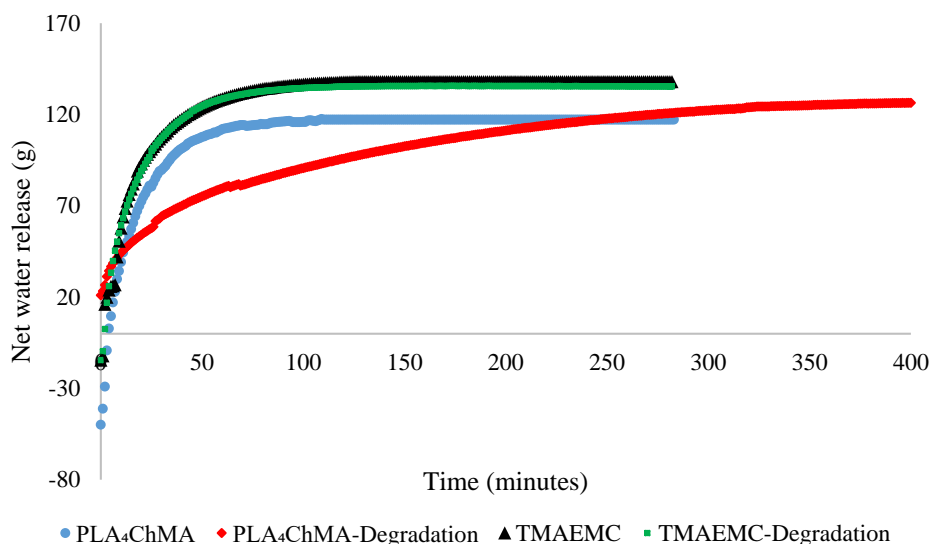


Figure 7. Net water release over time during filtration following flocculation and degradation at 75 °C for 5 days with poly(TMAEMC) and poly(PLA₄ChMA).



Figure 8. Comparison of water released following filtration after treatments with poly(PLA₄ChMA) (left) and poly(TMAEMC) (right).

4. Conclusions

The use of process water to prepare dilute MFT mixtures in place of deionized water leads to significant differences in flocculant performances. Poly(PLA₄ChMA) dosages of 500 ppm achieved similar compactions and supernatant clarities as those obtained using 10,000 ppm in deionized water. The anionic flocculant FLOPAM A3338 offered similar performances as achieved with poly(PLA₄ChMA) after accelerated degradation, while offering ISRs significantly faster than those measured with the novel degradable cationic flocculant. The observed improvements in settling in process water, particularly with anionic flocculants, indicate that the presence of ions in the solution enhance flocculation by acting as salt linkages between the tailings and polymer. These findings indicate that maintaining the water

chemistry of the tailings, even during the dilution of MFT, is critical in evaluating the flocculation characteristics of polymers.

With little advantage found for poly(PLA₄ChMA) compared to anionic FLOPAM A3338 for flocculation of dilute MFT suspensions in process water, a further study was conducted with undiluted MFT using a novel flocculation-filtration technique. Significantly higher dosages were required to achieve the dewatering of undiluted MFT with poly(PLA₄ChMA) and poly(TMAEMC) compared to FLOPAM A3338. The cationic flocculants resulted in much faster rates of water release than FLOPAM A3338 and untreated MFT but did not result in a higher net water release in the absence of polymer degradation. A considerable amount of water was released from the poly(PLA₄ChMA)-treated MFT when held under accelerated degradation conditions, with none observed for the MFT sample flocculated with the nondegradable poly(TMAEMC). However, the hydrolytic degradation of poly(PLA₄ChMA) has a detrimental impact on the rate of MFT dewatering during pressure filtration, likely because the degradation cleaves the cationic functionality from the flocculant.

Thus, the advantage of poly(PLA₄ChMA) in solids consolidation found previously in dilute MFT suspensions prepared in deionized water was greatly reduced in process water and disappeared completely in flocculation-filtration experiments conducted using undiluted MFT. While the result is disappointing, the study demonstrates the importance of moving towards more realistic testing conditions when evaluating new flocculant candidates for MFT treatments. In addition, the much faster initial dewatering under pressure achieved with these cationic flocculants is a promising result that merits further investigation.

Supplementary Materials: NMR spectra from macromonomer synthesis (Figures S1–S3), MFT characterization (Tables S1–S3, Figure S4), and statistical analysis of flocculation results (Tables S4 and S5) are available online at <http://www.mdpi.com/2227-9717/8/6/735/s1>.

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References

1. Masliyah, J.H.; Czarnecki, J.; Xu, Z. Basic Scientific Background. In *Handbook on Theory and Practice of Bitumen Recovery from Athabasca Oil Sands, Volume I: Theoretical Basis*; Kingsley Knowledge Publishing: Calgary, AB, Canada, 2011; pp. 51–125.
2. Loerke, R.; Tan, X.; Liu, Q. Dewatering of Oil Sands Mature Fine Tailings by Dual Polymer Flocculation and Pressure Plate Filtration. *Energy Fuels* **2017**, *31*, 6986–6995. [[CrossRef](#)]
3. Vedoy, D.R.; Soares, J.B. Water-soluble Polymers for Oil Sands Tailing Treatment: A Review. *Can. J. Chem. Eng.* **2015**, *93*, 888–904. [[CrossRef](#)]
4. Alberta Energy Regulator. *Fluid Tailings Management for Oil Sands Mining Projects. Directive 085*; Alberta Energy Regulator: Calgary, AB, Canada, 2017.
5. Sedgwick, A.; Kaminsky, H.; Bouffard, J.F. *Eureka! I Have the Solution to Oil Sand Tailings-Now What?* IOSTC: Edmonton, AB, Canada, 2018.
6. Botha, L.; Soares, J.B. The Influence of Tailings Composition on Flocculation. *Can. J. Chem. Eng.* **2015**, *93*, 1514–1523. [[CrossRef](#)]
7. Kaminsky, H.; Li, Y.; Qureshi, T.; Sedgwick, A.; Moran, K. *Influence of Bitumen Content on Flocculation of FFT*; Titanium Corporation: Edmonton, AB, Canada, 2018.
8. Masliyah, J.H.; Czarnecki, J.; Xu, Z. Colloidal Science in Tailings Management. In *Handbook on Theory and Practice of Bitumen Recovery from Athabasca Oil Sands Volume I: Theoretical Basis*; Kingsley Knowledge Publishing: Calgary, AB, Canada, 2011; pp. 391–448.

9. Motta, F.L.; Gaikwad, R.; Botha, L.; Soares, J.B. Quantifying the effect of polyacrylamide dosage, Na^+ and Ca^{2+} concentrations, and clay particle size on the flocculation of mature fine tailings with robust statistical methods. *Chemosphere* **2018**, *208*, 263–272. [[CrossRef](#)]
10. Lu, Q.; Yan, B.; Xie, L.; Huang, J.; Liu, Y.; Zeng, H. A two-step flocculation process on oil sands tailings treatment using oppositely charged polymer flocculants. *Sci. Total Environ.* **2016**, *565*, 369–375. [[CrossRef](#)]
11. Bratby, J. *Treatment with Polymer in Coagulation and Flocculation in Water and Wastewater Treatment*; IWA Publishing: London, UK, 2006; pp. 186–218.
12. Gumfekar, S.P.; Rooney, T.R.; Hutchinson, R.A.; Soares, J.B. Dewatering Oil Sands Tailings with Degradable Polymer Flocculants. *ACS Appl. Mater. Interfaces* **2017**, *9*, 36290–36300. [[CrossRef](#)]
13. Younes, G.; Proper, A.R.; Rooney, T.R.; Hutchinson, R.A.; Gumfekar, S.P.; Soares, J.B. Structure Modifications of Hydrolytically-Degradable Polymer Flocculant for Improved Water Recovery from Mature Fine Tailings. *Ind. Eng. Chem. Res.* **2018**, *57*, 10809–10822. [[CrossRef](#)]
14. Lu, Q.; Yan, B.; Xie, L.; Huang, J.; Liu, Y.; Hongbo, Z. A novel flocculant of $\text{Al}(\text{OH})_3$ -polyacrylamide ionic hybrid. *J. Colloid Interface Sci.* **2004**, *273*, 400–405.
15. Botha, L.; Davey, S.; Nguyen, B.; Swarnakar, A.; Rivard, E.; Soares, J.B. Flocculation of oil sands tailings by hyperbranched functionalized polyethylenes. *Miner. Eng.* **2017**, *108*, 71–82. [[CrossRef](#)]
16. Li, H.; Zhou, J.; Chow, R.; Adegoroye, A.; Najafi, A.S. Enhancing Treatment and Geotechnical Stability of Oil Sands Fine Tailings using Thermo-Sensitive Poly(*n*-Isopropyl Acrylamide). *Can. J. Chem. Eng.* **2015**, *93*, 1780–1786. [[CrossRef](#)]
17. Reis, L.G.; Oliveira, R.S.; Palhares, T.N.; Spinelli, L.S.; Lucas, E.F.; Vedoy, D.R.; Asare, E.; Soares, J.B. Using acrylamide-polypropylene oxide copolymers to dewater and densify mature fine tailings. *Miner. Eng.* **2016**, *95*, 29–39. [[CrossRef](#)]
18. Long, J.; Li, H.; Xu, Z.; Masliyah, J. Role of Colloidal Interactions in Oil Sand Tailings Treatment. *AIChE J.* **2006**, *52*, 371–383. [[CrossRef](#)]
19. Younes, G. Hydrolytically Degradable Cationic Flocculants for Improved Water Recovery from Mature Fine Tailings. Master's Thesis, Queen's University, Kingston, ON, Canada, 2018.
20. Gumfekar, S.P. Multifunctional Water-Soluble Polymers for Dewatering of Oil Sands Tailings. Ph.D. Thesis, University of Alberta, Edmonton, AB, Canada, 2018.
21. Gumfekar, S.P.; Soares, J.B. A novel hydrophobically-modified polyelectrolyte for enhanced dewatering of clay suspension. *Chemosphere* **2018**, *194*, 422–431. [[CrossRef](#)] [[PubMed](#)]
22. Nittala, A.; Gumfekar, S.P.; Soares, J.B. Multifunctional CO_2 -switchable polymers for the flocculation of oil sands tailings. *J. Appl. Polym. Sci.* **2019**, *136*, 47578. [[CrossRef](#)]
23. Yu, Y.; Ferrari, R.; Lattuada, M.; Storti, G.; Morbidelli, M.; Moscatelli, D. PLA-Based Nanoparticles with Tunable Hydrophobicity and degradation kinetics. *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 5191–5200. [[CrossRef](#)]
24. Colombo, C.; Dragoni, L.; Gatti, S.; Pesce, R.; Rooney, T.R.; Mavrouidakis, E.; Ferrari, R.; Moscatelli, D. Tunable Degradation Behavior of PEGylated Polyester-Based Nanoparticles Obtained Through Emulsion Radical Polymerization. *Ind. Eng. Chem. Res.* **2014**, *53*, 9128–9135. [[CrossRef](#)]
25. Rooney, T.R.; Chovancova, A.; Lacik, I.; Hutchinson, R.A. Pulsed laser studies of cationic reactive surfactant radical propagation. *Polymer* **2017**, *130*, 39–49. [[CrossRef](#)]
26. Rooney, T.R.; Moscatelli, D.; Hutchinson, R.A. Polylactic acid macromonomer radical propagation kinetics and degradation behaviour. *React. Chem. Eng.* **2017**, *2*, 487–497. [[CrossRef](#)]
27. Russell, D.; Meunier, L.; Hutchinson, R.A. Characterization of degradation products from a hydrolytically degradable cationic flocculant. *Polym. Degrad. Stabil.* **2020**, *174*, 109097. [[CrossRef](#)]
28. MacKinnon, M.; Matthews, J.; Shaw, W.; Cuddy, R. Water Quality Issues Associated with Composite Tailings (CT) Technology for Managing Oil Sands Tailings. *Int. J. Min. Reclam. Environ.* **2001**, *15*, 235–256. [[CrossRef](#)]
29. Xu, Y.; Dabros, T.; Kan, J. Filterability of oil sands tailings. *Process Saf. Environ.* **2008**, *86*, 268–276. [[CrossRef](#)]
30. Gumfekar, S.P.; Vajihinejad, V.; Soares, J.B. Advanced Polymer Flocculants for Solid-Liquid Separation in Oil Sands Tailings. *Macromol. Rapid Commun.* **2019**, *40*, 1800644. [[CrossRef](#)] [[PubMed](#)]
31. Zhu, Y.; Tan, X.; Liu, Q. Dual Polymer Flocculants for Mature Fine Tailings Dewatering. *Can. J. Chem. Eng.* **2017**, *95*, 3–10. [[CrossRef](#)]
32. Alamgir, A.; Masliyah, J.; Xu, Z. *Al-PAM Assisted Filtration of Mature Fine Tailing*; IOSTC: Edmonton, AB, Canada, 2010.

33. Pennetta de Oliveira, L.; Gumfekar, S.P.; Motta, F.; Soares, J.B. Dewatering of Oil Sands Tailings with Novel Chitosan-Based Flocculants. *Energy Fuel* **2018**, *32*, 5271–5278. [[CrossRef](#)]
34. Li, Y.; Kaminsky, H.; Romaniuk, N.; Tate, M. *Filter Press Modification to Assess Dewatering Performance of Fluid Fine Tailings*; IOSTC: Edmonton, AB, Canada, 2018.
35. Ezenwajiaku, I.H.; Chovancová, A.; Lister, K.C.; Lacík, I.; Hutchinson, R.A. Experimental and Modeling Investigation of Radical Homopolymerization of 2-(Methacryloyloxyethyl) Trimethylammonium Chloride in Aqueous Solution. *Macromol. React. Eng.* **2020**, *14*, 1900033. [[CrossRef](#)]
36. Lister, K.C. Evaluation of a Novel Polymeric Flocculant for Enhanced Water Recovery of Mature Fine Tailings. Master's Thesis, Queen's University, Kingston, ON, Canada, 2020.
37. Sadighian, A.; Revington, A.; Kaminsky, H.; Moyls, B.; Li, Y.; Omotoso, O. *A New Protocol to Assess the Quality of Tailings Flocculation/Coagulation: A Collaboration to Improve Tailings Treatment at Suncor Energy*; IOSTC: Edmonton, AB, Canada, 2018.
38. Boxill, L. The Impact of Fabric and Surface Characteristics on the Engineering Behaviour of Polymer-Amended Mature Fine Tailings. Ph.D. Thesis, University of British Columbia, Vancouver, BC, Canada, 2016.



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