The microscale flocculation test (MFT) – a high-throughput technique for optimizing separation performance

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Abstract

In this work, a new microscale flocculation test (MFT) method was developed that is ideally-suited for optimizing separation performance. A critical and complicated task in wastewater treatment is to identify the flocculation conditions that yield the optimal separation of water from suspended solid materials. The standard 'jar test' method is inadequate for conducting a full process optimization because a typical set-up only allows for a maximum of 6 tests to be conducted at once, and fairly large volumes of materials (approximately 1 to 2 litres) are needed for each individual test. The microplate-based, parallel processing format of the MFT method allows for many dozens of flocculation tests to be conducted simultaneously, with each test requiring only a few millilitres of material. As a demonstration of the MFT method, ten cationic polymer flocculants were evaluated with various digestate types. The optimal separation performance, as determined by the lowest capillary suction time (CST) measurement, was found by rigorously evaluating the effect of flocculant type (including molecular weight and charge density) and dosage conditions (including total amount added and single versus staged addition). For example, the dose-dependent profiles for certain flocculants exhibited a nearly 10-fold greater decrease in CST compared to other flocculants. Process optimization in environmental separations is not trivial, but rather, is a complicated task that requires an extensive amount of experimental work for which the MFT method is ideally suited.

Keywords: wastewater separation; high-throughput testing; flocculation; microscale processing

Highlights:

- o The conventional jar test was scaled down into a 12-well microplate format

- o Tumble stirrer mixing speed was characterized through video motion tracking

- o The dose-dependent dewatering profile was a strong function of the flocculant type

- o Multi-stage dosing and digestate source can significantly affect dewatering results

- o Our high-throughput approach is ideal for optimizing the flocculant type and dosage

1.0 Introduction

Dewatering processes are important unit operations in various separations applications, including the operation of anaerobic digestion processes, the treatment of industrial wastewaters, and the management of tailings from mining processes. An assortment of flocculants and/or chemical conditioners can be used to promote the aggregation of colloidal particles into larger particles via a combination of both charge neutralization and bridging effects [1]. The liquid fraction can then be removed by mechanical processes such as filter presses and screw thickeners. The ability of a given dewatering process to successfully separate the liquid and solid fractions is influenced by many different factors including the dosage, mixing conditions, and the physicochemical properties of the flocculant. Various synthetic polymers have been used as flocculants including poly(acrylic acid), poly(ethyleneimine), poly(diallyl dimethyl ammonium chloride), poly(acrylamide), and co-polymers of acrylamide and dimethylaminoethyl acrylate (DMAEA) [2]. Numerous suppliers offer an assortment of these water-soluble organic polymers by altering the molecular weight, charge density, structure (e.g. linear, branched, comb), and degree of cross-linking [3]. For example, SNF Floerger sells over forty different versions of their FLOPAM cationic poly(acrylamide) flocculant; the offerings differ in their charge density (low,

medium, high, or very high), molecular weight (low, medium, fairly high, high, or very high) and structure (linear, branched). As well, biopolymer flocculants, including those based on polysaccharides such as chitosan and cellulose, have been developed in response to the need for more environmentally-friendly materials [2].

For any dewatering process, an ongoing challenge involves selecting, from the vast number of possible flocculants, the 'best' one in terms of economics and performance. In our previous work, we found that the dewatering performance of twenty-four different flocculants from three suppliers varied considerably [4]. Notably, for anaerobic wastewater treatment, the cost of the polymer flocculant is the greatest component in the biosolids treatment operation [5]. This leads to two important considerations: first, it is generally understood that there is no workable algorithm to relate flocculant properties to dewatering performance [3]. Secondly, wastewater sources from different treatment plants have diverse dewatering characteristics. So, the exact flocculant type and the optimum dose must be determined on a case-by-case basis for different treatment applications. Yet, the selection of the 'best' flocculant has been described as "one of the most demanding, frustrating, and time-consuming experiences for many operations personnel" [6].

The benefit of optimizing the flocculant dose extends beyond the operating costs for a given treatment facility. Water-soluble polymers have been found to be toxic to aquatic lifeforms, even at low concentrations [7]. Thus, there are valid concerns about the effect of flocculant 'overdosing' in dewatering processes, given the potential for discharge into the aquatic environment, either directly via the liquid fraction, or indirectly via leaching from the solids fraction.

The conventional approach towards flocculant screening and dosage optimization is the jar test procedure. For a typical setup, a set of four to six circular or square vessels (of

approximately 1 to 2 L in capacity) with individual stirrer controls (overhead or magnetic) is used. Many studies have used such systems with varying levels of experimental complexity. For example, Clark and Stephenson [8] employed statistical experimental design strategies to optimize the chemical removal of phosphorus from activated sludge. Ebeling et al. [9] evaluated nineteen different flocculants for reducing the turbidity of aquacultural effluents. Despite widespread use, there are several disadvantages to the jar test approach. First, the method is time-consuming and requires large volumes of the feed water/wastewater source. Thus, only a limited number of tests (with few repeats) are conducted, and often, a decision is made to not fully evaluate all of the possible test conditions. For example, Ebeling et al. [9] used just six of the original nineteen flocculants for a more detailed analysis of dosage effects. Second, the methods used to evaluate the dewatering performance are, at best, semi-quantitative. Thus, the final determination of the optimum flocculant and dose is widely considered to be more of an 'art' rather than a 'science'.

Given the limitations of the conventional jar test approach and the on-going challenge of optimizing flocculation conditions for different treatment applications, we identified a clear need for a high-throughput test that uses a parallel processing format, requires small amounts of sample, uses a quantitative performance metric, and is easy to operate. This idea was principally inspired by the extensive work in the biotechnology industry towards the development of micro-scale test formats for conducting high-throughput screening. For example, Bensch et al. [10] used deep-well plates and robotic equipment to screen the partitioning behaviour of up to 600 different samples of recombinant protein products in various polymer-salt aqueous two-phase systems. The key advantage of microscale techniques are that they allow multiple tests to be run in parallel, and thus, they are ideally suited towards the use of statistical tools such as design-of-experiments (DOE) to identify critical process parameters. This enables the optimization of a

particular measured performance attribute with respect to those parameters. For example, Kang et al. [11] developed a novel cell culture flocculation process using a stimulus-responsive polymer to streamline antibody purification processes via a full-factorial DOE study at a 5 mL culture scale. A recent study developed an automated scaled-down method for optimizing the flocculation of pre-clarified cell broths [12]. These innovations are being driven primarily by the need within the biotechnology industry to minimize the occurrence of process bottlenecks and to bring the pace of development of downstream separation processes in line with the upstream product discoveries [13].

Despite the considerable advantages of microscale processing techniques towards process development, there have been very few such advances in the field of water/wastewater treatment. Ren et al. [14] developed miniature microbial electrolysis cells to evaluate the effects of the inoculum and the wastewater source on treatment efficiency for a large number of samples with replicates. Mohler et al. [15] developed a high-throughput workflow using sophisticated robotic equipment and automated digital image analysis to evaluate the settling behaviour of oil sands tailings treated with different flocculants. In this study, we focus on the use of polymer flocculants for the dewatering of digestate from anaerobic digestion processes. However, our methods can be used for optimizing the dewatering performance of other coagulant/flocculation aids used on different water/wastewater systems. The microscale flocculation test (MFT) developed is simple to operate, compact (total footprint of approximately 1 square foot) and can be assembled using fairly inexpensive lab equipment.

2. **Experimental**

   2.1 Digestate Sources

The 'municipal' digestate was obtained from the Halton Region wastewater treatment plant in Burlington, Ontario, Canada. Chemical properties of this digestate are shown in Table 1. The 'foodwaste' and 'co-digestion oil' digestates were obtained from the research and development group at Anaergia Inc. (Ontario, Canada). The solids content of all three wastewater sources were measured using the standard total solids test. The measured value for the solids content of the 'municipal' digestate samples was nominally 1.95% (w/w), with the actual values ranging from 1.9% to 2.0%. The corresponding values for the 'foodwaste' and 'co-digestion oil' digestates were nominally 2.1% (w/w). All three digestates were stored in plastic bottles at 4°C for a maximum of twelve weeks. The small volumes (~ 100 to 200 mL) needed to perform a set of flocculation tests were withdrawn from the vessels and then allowed to equilibrate with room temperature. There was no measurable change in the properties of the digestates during storage at 4°C.

Table 1 – Chemical properties of Halton Region municipal digestate

Property	Concentration Range (g/L)
Total Chemical Oxygen Demand	20 – 28
Soluble Chemical Oxygen Demand	1.29 – 1.92
Total Nitrogen	1.50 – 2.05
Total Kjeldahl Nitrogen	1.25 – 1.93
Ammonia	0.84 – 0.95

2.2 Polymer Flocculant Preparation

The flocculants used in this work are from the ZETAG® 'family' of polymer emulsions available from BASF. They are copolymers of polyacrylamide and quaternized-N,N dimethylamino ethylacrylate (DMAEA-Q) and have been widely studied [16]. A total of ten different polymers with various charge densities and molecular weights were evaluated; the polymer properties that were provided by the manufacturer including active content (%), specific

gravity, and qualitative comparisons (e.g. low, medium, high) for both the molecular weight and charge density are given in Table S1 (in the Supporting Information). The stock emulsions were diluted to 0.25% (w/w) via the addition of 50 mM sodium phosphate monobasic solution (pH 4.8) in the same manner as described in our previous work [4]. These active suspensions were typically used within two hours, but not after twenty-four hours following the final dilution step. Control tests were performed by substituting the flocculant for an identical of the 50 mM sodium phosphate monobasic solution, and adding it to the various digestate sources.

2.3 Capillary Suction Time (CST) Tests

Each flocculated sample was analyzed using a capillary suction time (CST) instrument (Triton Electronics), with the circular 'slow-filtering' reservoir insert and standard Whatman #17 chromatographic filter paper, as described in Cobbledick et al. [4]. The only difference is that for this work, the sample volume used varied between 2.5 to 4 mL for each measurement. Sawalha and Scholz [17] give a detailed description of the instrument, including its construction, use, and the underlying principles behind its operation. Although in this work, the CST instrument we used was a single-head type that allows for just one measurement to be made at a time, the same vendor does sell a multi-head CST instrument that would be more appropriate to the parallel screening format of our MFT technique.

3. Results and Discussion

3.1 Design and operation of the microscale flocculation test (MFT)

There are a variety of methods for characterizing dewatering performance in wastewater separations. The CST test was chosen for this work since it is widely used in the industry and is simple to conduct. It was developed nearly 50 years ago [18] and is generally regarded as a

fundamental measure of liquid-solid separation performance [19]. From preliminary tests with buffer solutions and digestate samples, it was determined that the minimum volume of sample needed to obtain a reproducible CST value was 2.5 mL. Based on this value, a standard flat-bottom 12-well microplate proved to be ideal for this study because the maximum volume of each well is approximately 7 mL (22.1 mm diameter, 17.5 mm height). Thus, each well could easily accommodate the required volume of sample, even after the stir bars were added (as described below). Also, a single 12-well plate could be used to run triplicate analysis of four different flocculant-dose-digestate combinations.

It is well known that the dewatering performance of flocculants depends on the mixing conditions [20, 21]. For conducting microscale experiments in multi-well plates, previous studies have used repeated aspiration [10] or orbital shakers [22]. For this work, we chose to use a 'tumble stirrer' (V&P Scientific) that generates a magnetic field that extends radially outwards and can mix multiple vessels at once. It was considered ideal because it can mix all the wells of the microplate to a sufficient degree such that the polymer flocculants can penetrate into high solids-content digestate suspensions. Previous studies have used the same tumble stirrer for microplate studies that screened yeast transformants for their biological activity [23], measured partition coefficients in organic-aqueous mixtures [24], and developed ternary phase diagrams for therapeutic drug candidates [25].

The tumble stirrer was held in a vertical position using a custom-built stand outfitted with horizontal trays to hold the microplates in a fixed position relative to the stirrer; refer to Figure S1 in the Supporting Information for additional details. The stand can hold up to twelve standard 12-well microplates at a time. However, we found it was more practical to work with two 12-well microplates at a time and thus simultaneously conduct triplicate analysis of the dewatering

performance for 8 different flocculant-dose-digestate combinations. The workflow diagram is shown in Figure 1 with the accompanying details given below:

i) A cylindrical magnetic stir bar (measuring 7.9 mm (0.31") in diameter and 12.7 mm (0.5") in length) and a pre-determined volume of digestate (between 2.5 and 4 mL) are added into each well. The vessel from which the digestate is withdrawn is continuously stirred to ensure that a reproducible sample is aliquoted into each well of the microplate.

ii) The tumble stirrer is turned on (see below for details) and subsequently, the appropriate dose of flocculant suspension is added using a 'repeater' pipette that allows for the rapid dispensing of specified volumes without the need to repeatedly refill the pipette tip. Typically, the total mixing time for the first and last well in a single microplate differs by only approximately 30 seconds due to this rapid sequential dosing. Note that slight differences in the volume of digestate and flocculant solution added are used to compensate for differences in their active contents (see Table S1 in the Supporting Information). For example, the ZETAG 8814 flocculant has an active content of 34% and specific gravity of 1.03. An 8 kg dose of polymer per total tonnes of solids (kg/TTS) corresponds to the addition of 550 µL of 0.25 wt% polymer suspension to 3.0 mL of 2% (w/w) digestate. For each flocculant test, a control experiment involving the addition of the corresponding volume of buffer solution was also conducted. As shown in Figure 1, a single 12-well plate can be used for a triplicate analysis of a single digestate source treated with two different flocculant dosages as well as the corresponding controls.

iii) After the last sample is added, the plate is mixed for an additional one minute. After the removal of the stir bars, a custom plug (shown in the Supporting Information

Figure S2) is inserted into each well to seal the contents inside and to prevent spillage during the subsequent sample transfer step.

iv)   The CST value for the sample in each well is measured by replacing the plug for that well with a custom spout. The plate is then inverted such that the well contents are directed into the circular reservoir insert of the CST instrument.

v)   The CST sensor test head is then cleaned, the chromatographic filter paper is replaced, and the CST instrument is reset for the next measurement.
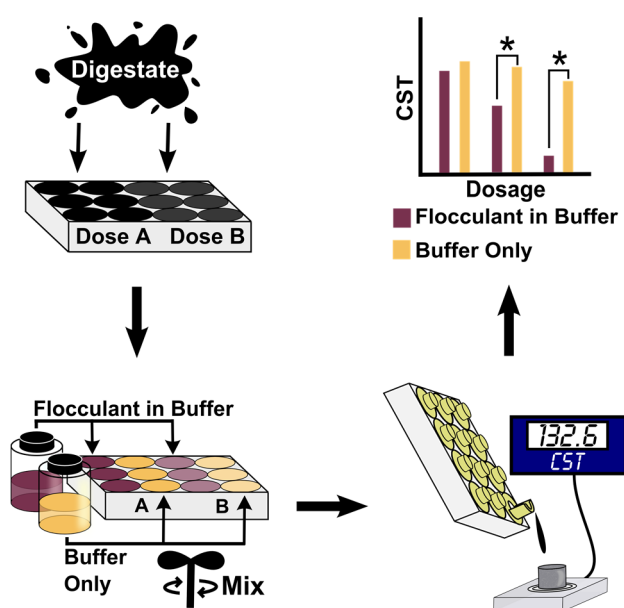
Figure 1: Microscale flocculation test (MFT) workflow for optimizing the flocculant type and dosage conditions. Refer to the text for details on the equipment that was used and individual steps that were performed.

In order to quantify the actual rotational speed of the stir bars in the wells, short video clips were recorded for various 'power levels' of the tumble stirrer and then analyzed using the *Tracker* video analysis tool [http://physlets.org/tracker/]. As shown in Figure 2A, digital markers were affixed to each stir bar and the wells were overlaid with an *xy*-coordinate system for the purpose of displacement calculations. The rotational speed of a stir bar was determined using the best-fit parameters of the sinusoidal function for displacement versus time. A typical data set for

the time-dependent position profile of a stir bar in a well with the tumble stirrer 'power level' set to 40 is shown in Figure 2B. Statistical t-tests at a 95% confidence level confirmed that the mixing speed across all twelve wells is consistent at the power levels investigated. As shown in Figure 2C, the stir bar speed was linearly dependent on the tumble stirrer 'power level'. For all of the work in this study, the microscale flocculation tests were conducted at a stir bar rotational speed of 275 RPM.
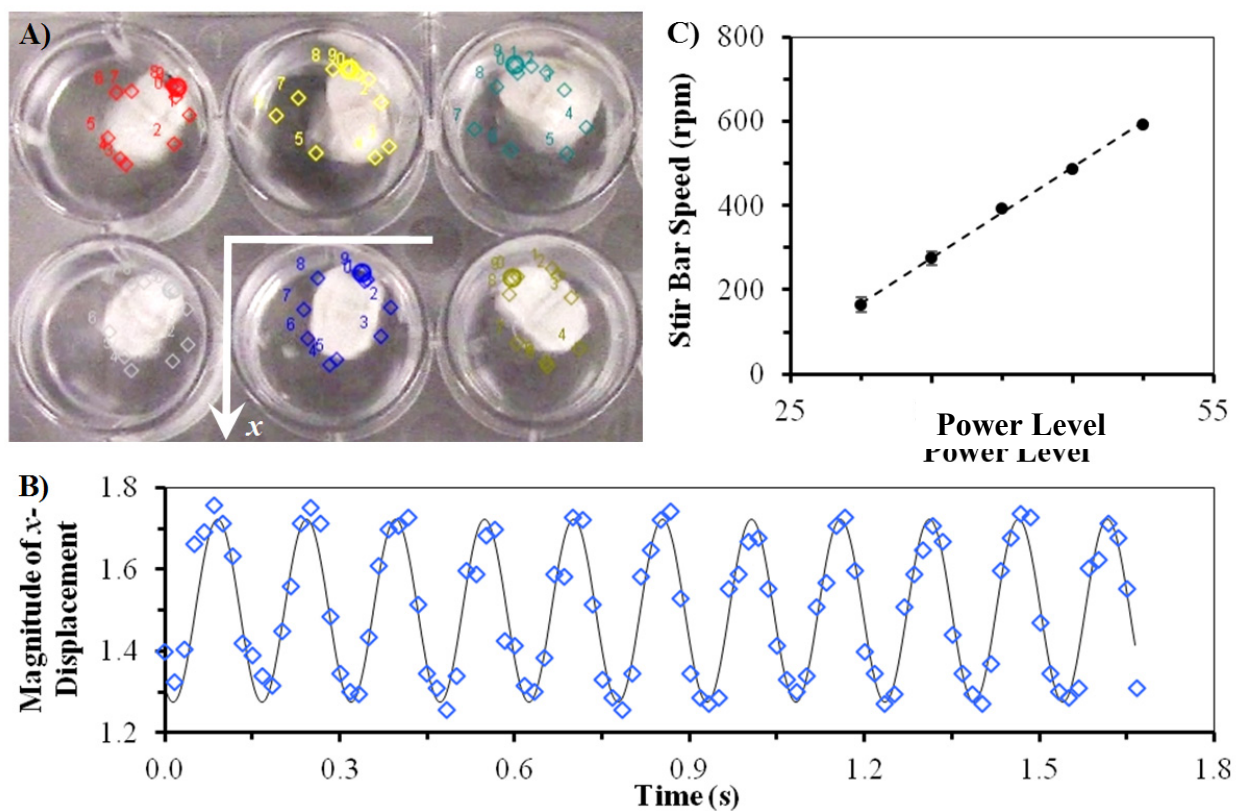
Figure 2: Schematic of the stir bar tracking results. **A)** Using the *Tracker* software, a unique digital marker is placed at the tip of each stir bar and for each frame of the recorded video. The numbered icons represent the locations of each stir bar for the first 10 frames (corresponding to one-sixth of a second) of the recorded video. **B)** Typical data for linear displacement versus time ($\diamond$) and best-fit of the sinusoidal function (—) for a single stir bar at a 'power level' of 40. Note that a displacement of $x = 1$ represents a distance equal to one well diameter (22.1 mm) relative to arbitrarily-set axes. The rotational speed is calculated from the period of the best-fit function. **C)** Average rotational speed across all twelve wells of the microplate versus the tumble stirrer 'power level'. The dashed line represents the linear 'line of best fit'.

As part of the initial work to examine the reliability of the MFT technique, all 12 wells of one microplate were filled with the same amount of digestate and ZETAG 8814 flocculant to achieve a dosage of 8 kg/TTS. The collection of CST values from each well ranged from 8.0 to 9.6 seconds with an average (± standard deviation) value of 8.5 (± 0.4) seconds. No spatial variation in CST values was observed, thus, it was determined that the mixing conditions generated by the tumble stirrer were uniform across the microplate.

3.2 High-throughput screening of flocculant type and dose

Figure 3 displays the CST results for municipal digestate dosed with three ZETAG flocculants. Each flocculant was tested at eight different doses, reported as the mass of polymer added per total tonnes of solids (kg/TTS). The CST results were consistent for the triplicate analysis that was done in three wells for each flocculant-dose-digestate combination. For example, the individual CST values for the three wells corresponding to a 5 kg/TTS dose of 8868FS (Panel 3B) were 58.5, 66.3, and 75.5 seconds. The error bars in Figure 3 correspond to plus or minus one standard deviation about the average CST value. Overall, the CST values ranged from 211 (± 12) seconds for 8868FS at 1 kg/TTS dose to 7.4 (± 0.3) seconds for 8814 at 10 kg/TTS dose; the values in parentheses, again, represent one standard deviation. For comparison, the CST values for the unmodified municipal digestate and the sodium phosphate monobasic buffer solution were approximately 250 and 5 seconds, respectively. It is readily apparent that the dose-dependent dewatering profile is a strong function of the flocculant type. At the 3 kg/TTS dosage, the average CST values for the 8814 (Panel 3A), 8868FS (Panel 3B), and 8816 (Panel 3C) flocculants were 28 (± 3), 169 (± 10), and 78 (± 7) seconds, respectively. Within each panel, the recorded CST values when the municipal digestate was diluted with the sodium phosphate monobasic buffer solution are shown. The results are displayed in terms of the

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equivalent volume of the 0.25 wt% flocculant solutions that were added for the dosing studies. It was found that the simple dilution of digestate had a statistically significant effect on the CST values. Figure S3 in the Supporting Information shows that the CST decreases by approximately 120 seconds for every weight percent decrease in the solids content of the digestate due to the addition of the buffer solution used to suspend the flocculants.

The 8814 flocculant (Panel 3A) was found to be effective across the entire dose range. At all doses greater than or equal to 4 kg/TTS, the average CST values were less than 20 seconds. Even at the lowest dosage that was tested (1 kg/TTS), the average CST value was approximately half the magnitude of the value representing the undiluted digestate. The 8868FS (Panel 3B) exhibited the strongest dependence of CST on dose. Only at the highest dose that was tested (10 kg/TTS) did the average CST value fall below 20 seconds. Towards the lowest dose of 1 kg/TTS, the 8868FS flocculant had barely an effect on dewatering performance. The 8816 flocculant (Panel 3C) was found to give similar CST values to those obtained with the 8814 at the lower dose conditions; however it had a much lower impact on CST as the dose was increased. Even at the highest dose tested in this work, the average CST value was greater than 25 seconds. It is apparent that our MFT approach is ideally-suited for determining these dose-dependent dewatering profiles, and thus allowing for the making of quantitative comparisons of different flocculant types and doses.

For the high dose range from 5 to 10 kg/TTS, a simple regression analysis of the results for the 8868FS flocculant showed that a linear model with the best-fit value of the slope of -9.2 seconds per kg/TTS (p-value < 0.0001) was appropriate for predicting CST as a function of dose; the 95% confidence interval for the slope was -6.2 to -12.2 seconds per kg/TTS. In comparison, for the 8814 flocculant, the same analysis indicated that a linear model with the best-fit value of the slope of -1.3 seconds per kg/TTS (p-value < 0.0001) was appropriate; the 95% confidence

interval for the slope was -1.0 to -1.5 seconds per kg/TTS. Thus, it is shown that the 8868FS flocculant exhibited a nearly 10-fold greater change in CST for every 1 kg/TTS dose increase than the 8814 flocculant. The results presented above prove the usefulness of the MFT approach to reduce operating costs by optimizing the flocculant type and dose. For the 8816 flocculant, the same analysis indicated that the best-fit value of the slope was not statistically different than zero (p-value = 0.63) and thus, there was no dependence of the CST on dose.

The proposed MFT technique has shown to require a significantly smaller volume of materials in comparison to the standard jar test approach. The entire data set presented in Figure 3 was obtained using approximately 300 to 400 mL of municipal digestate, approximately 10 mL of each diluted flocculant suspension, and just eight 12-well microplates. For comparison, the same set of results would require running 96 individual jar test trials according to the conventional dewatering test technique, with approximately 144 L of digestate and 5 L of flocculant suspension needed to complete the tests. The same volume must be disposed of afterwards. As a result, the MFT approach is ideally suited for cases when source samples are limited such as with lab-scale digesters working with unique feed sources, or in cases where only a small volume of sample can be shipped at one time.
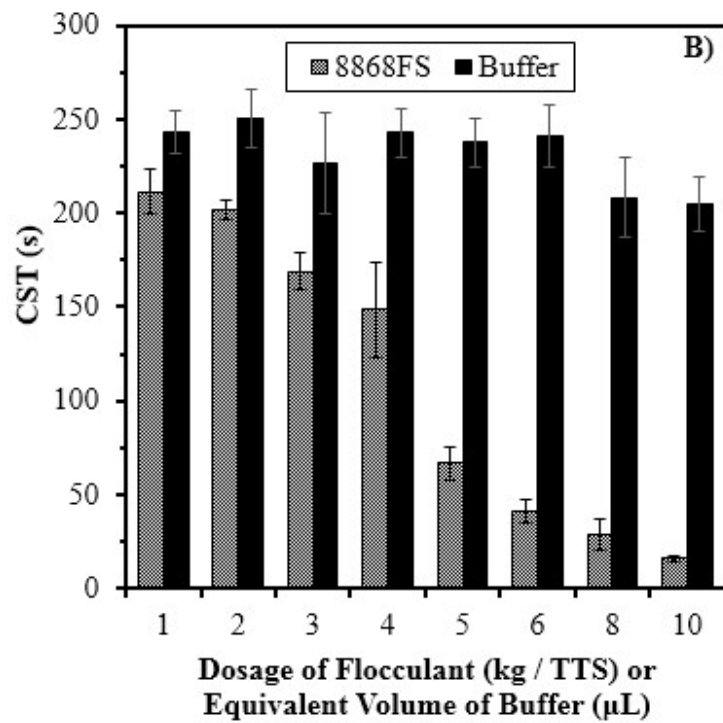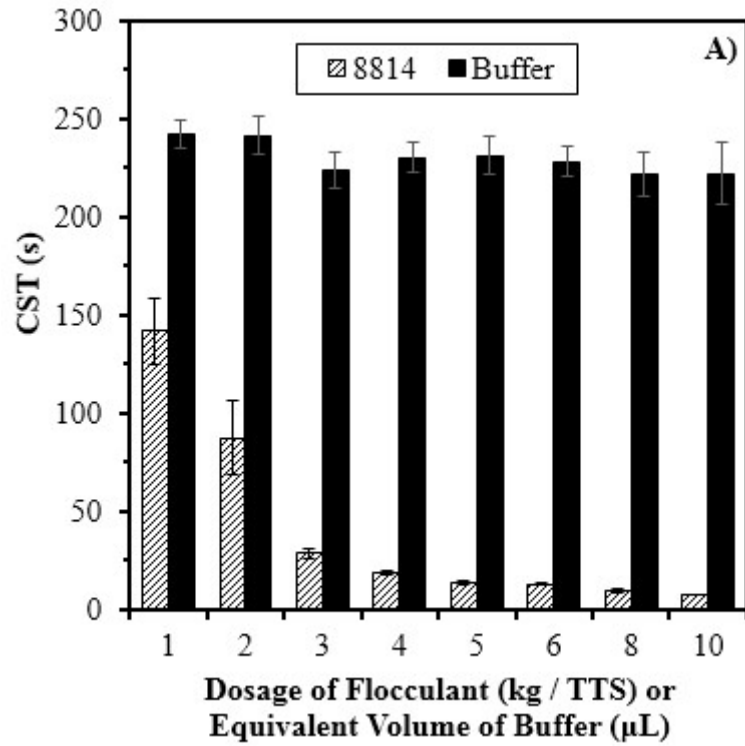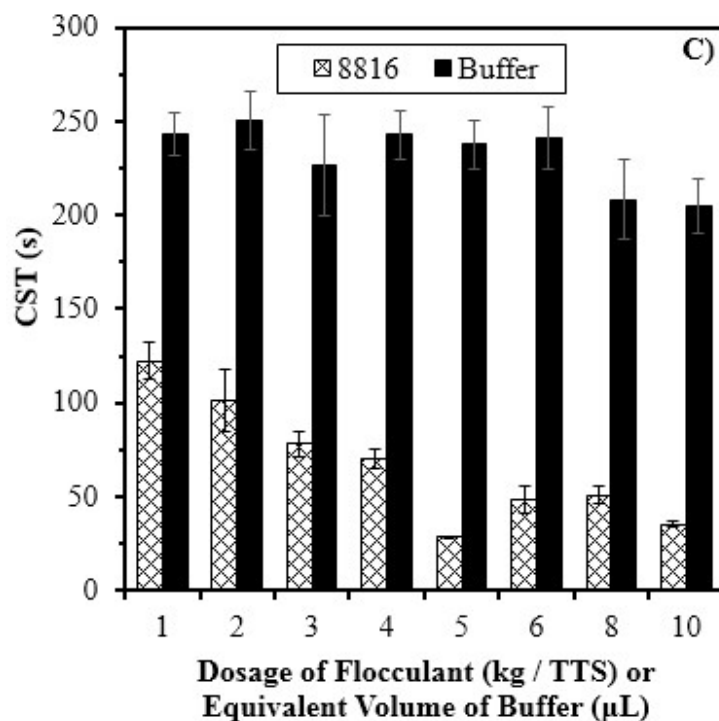
Figure 3: Comparison of the dose-dependent dewatering profile for three flocculants: ZETAG® 8814 (Panel A), ZETAG® 8868FS (Panel B), and ZETAG® 8816 (Panel C). The solid bars represent CST results obtained by adding the 'equivalent volume of buffer' at that particular dosage, and are included to differentiate the actual flocculant effects from simple dilution effects.

For the other seven flocculants that were examined in this work, similar dose-dependent dewatering profiles to those shown in Figure 3 were obtained. A comparison of the performance of all ten ZETAG flocculants is shown in Figure 4 for two dosages: 3 kg/TTS (Panel 4A) and 8 kg/TTS (Panel 4B). At each dose, the flocculants are organized into two 'bins' based on their different active content values (see Supporting Information, Table S1). This was done for the reason that in each bin, a different volume of sodium phosphate monobasic solution must be used for the buffer control experiments due to the differing polymer active contents. At the 3 kg/TTS dose, the 8814 flocculant was clearly the best flocculant of the ten tested; the average CST of 28 ($\pm$ 3) seconds is less than half of the next three lowest CST values of 72 ($\pm$ 27), 78 ($\pm$ 7), and 84 ($\pm$ 16) seconds for the 8849FS, 8816, and 8844FS flocculants, respectively. The 8848FS

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flocculant was clearly the worst-performing additive tested at this dosage. Its average CST of 196 ($\pm$ 14) seconds was only slightly lower, yet still significantly different (p-value = 0.02), than that obtained by simply adding an equivalent volume of buffer solution. At the higher 8 kg/TTS dose, the 8814 flocculant was also found to give the lowest average CST (9.6 ± 0.9 seconds). Also at the higher dose, it was the 8857FSB flocculant that gave the highest CST values and thus, was the worst additive of the ten tested. The average CST of 76 ($\pm$ 9) seconds for 8857FSB is one and half-times higher than the next highest CST value (51 ± 5 seconds for the 8816 flocculant). It is important to recognize that the performance of a flocculant relative to other flocculants at a particular dosage level is clearly not indicative of its relative performance at another dosage level.

At the 8 kg/TTS dose, the four flocculants that gave the lowest average CST values (all less than 20 seconds) were characterized as follows: very high molecular weight, medium charge density (8814); very high molecular weight, high charge density (8818); high molecular weight, medium charge density (8844FS); high molecular weight, very-high charge density (8849FS). However, the second highest average CST was obtained for the 8816 flocculant which is characterized as very high molecular weight, medium-high charge density. Thus, it proved to be impossible to extract any particular correlation between dewatering performance and flocculant properties. A number of previous studies, including Dentel et al. [3], have reported similar observations. These results demonstrate the advantage of the rapid-but-exhaustive evaluation of polymer flocculant candidates using our MFT approach and caution users against trying to predict flocculant-dose-digestate combination performance based on limited tests. It is apparent that flocculant selection for dewatering processes is not a trivial practice, but rather, a complicated task that requires an extensive amount of experimental work; the MFT technique developed in this work is ideally suited for this task.
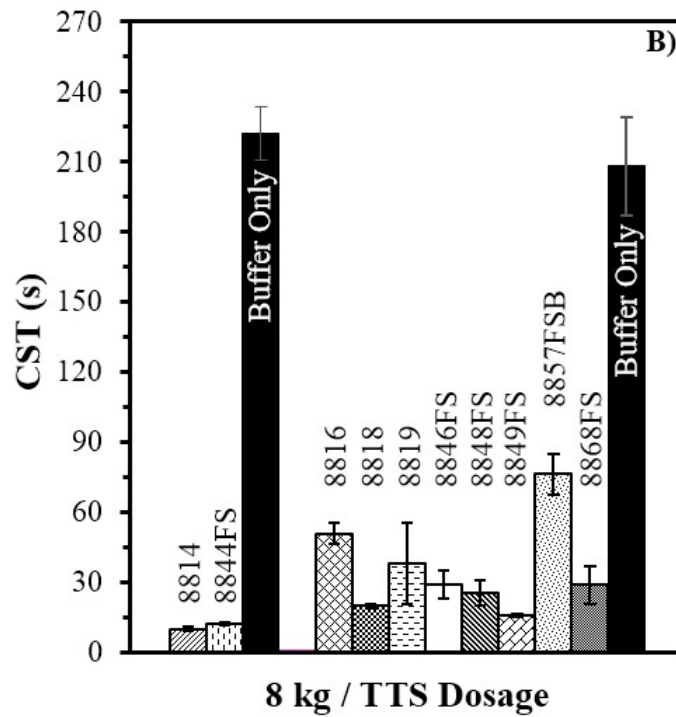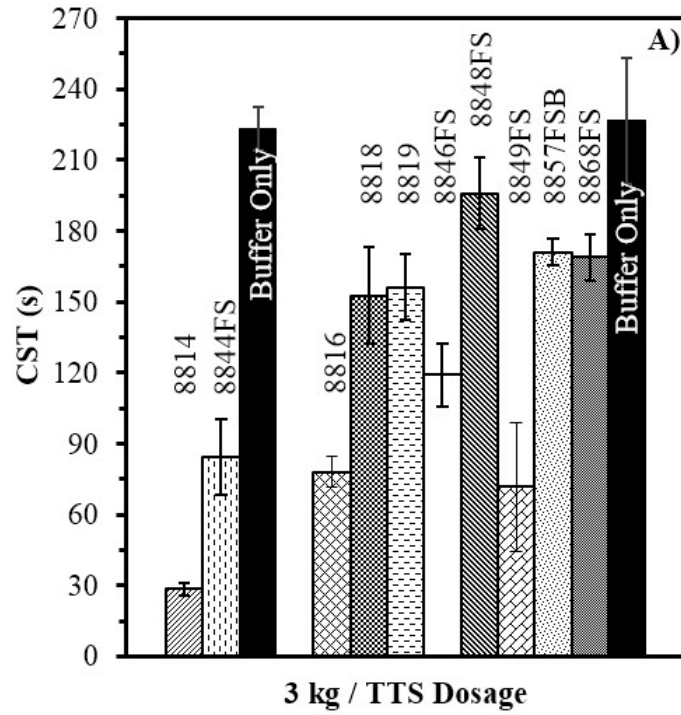
Figure 4: Comparison of the effectiveness of ten ZETAG® flocculants at the 3 kg/TTS (Panel A) and 8 kg/TTS (Panel B) dosage levels. The results are sorted into two bins with different 'buffer only' results due to the differences in the active contents of the flocculants; refer to Supporting Information, Table S1 for additional details.

3.3   Evaluation of flocculant multi-dosing effects

Previous studies have proposed multi-stage dosing to improve the overall dewatering performance of flocculants. Gregory and Guibai [26] examined the dosage of a high molecular weight cationic polymer flocculant into clay suspensions and reported that repeated doses of the flocculant produced larger flocs than those obtained with a single, larger, dose. Sengupta et al. [27] evaluated multi-stage addition on a similar clay suspension for up to eight different doses. Both of these early studies were performed in large beakers of approximately 1 L. In order to examine this effect using the MFT approach, we selected two flocculants (8818 and 8844FS) from our initial screening tests that had reasonably high CST values (greater than 40 seconds) at an intermediate dose of 5 kg/TTS. This was to ensure that the potential for improvement existed. The same microplate procedure was used, except that the flocculant addition step was split into two doses, where the second dose was added 60 seconds following the first addition. For example, the 400 µL of 8844FS flocculant was added as two separate additions of 100 and 300 µL, 200 and 200 µL, or 300 and 100 µL to achieve the 25%-75%, 50%-50%, and 75%-25% fractional doses shown in Figure 5.

The results from this test show that the observed 'multi-dosing effect' is flocculant-specific. The CST results for the 8818 flocculant were not statistically different for the four different dosage conditions. However, this was not the case for the 8844FS flocculant. The average CST values for the tests performed with the 50%-50% and 25%-75% staged addition were significantly lower (both p-values <0.002) than those obtained for a single dose of the same total volume of flocculant (i.e. the 100%-0% split fraction). The exact mechanism for this behaviour is unknown and thus additional studies are needed to better understand this effect. This preliminary work exemplifies the usefulness of the MFT approach, especially when evaluating

more complicated dosage strategies that may involve the staged addition of different coagulants and flocculants [28].
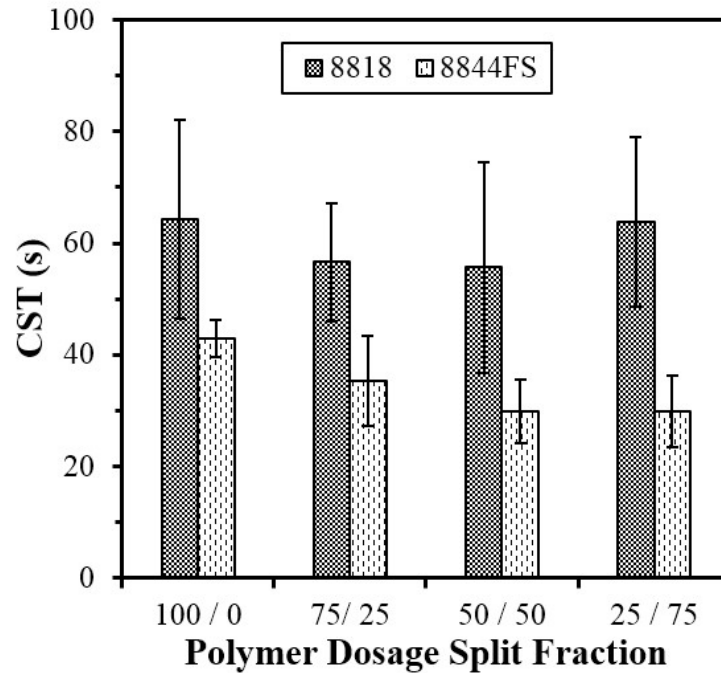

Figure 5: The effect of performing a staged addition of a flocculant dose (i.e. multi-dosing) on the dewaterability of flocculated digestate. The flocculant dosage split fraction represents how the total dose of polymer is divided into two separate additions at a 5 kg/TTS dose.

3.4   Evaluation of the effect of digestate source

In order to further demonstrate the utility of the MFT technique, we evaluated the effect of the digestate source on flocculant-based dewatering performance. The three digestates used in this study had nearly identical solid weight percentages, but quite different CST values. The average unflocculated CSTs for the 'foodwaste' and 'co-digestion oil' digestates were approximately 700 seconds, nearly three times the corresponding value for the municipal digestate. The 8814 and 8868FS flocculants were chosen for these tests because they have significantly different properties. 8814 is characterized as very high molecular weight and

medium charge density while 8868FS is characterized as low molecular weight and high charge density. As shown in Figure 6, each flocculant was evaluated at a 'low' (3 kg/TTS) and 'high' (8 kg/TTS) dose. Thus for the triplicate analysis of each flocculant-dose-digestate combination, a total of 36 individual CST measurements were made. For all three digestates, the 8814 flocculant consistently produced significantly lower CST values than the 8868FS flocculant. For the 'foodwaste' digestate, the addition of the 8814 flocculant caused a dramatic reduction in the average CST to 65 ($\pm$ 5) and 32 ($\pm$ 4) seconds for the 3 and 8 kg/TTS doses, respectively. However, neither flocculant was particularly effective as a dewatering aid for the 'co-digestion oil' digestate. The lowest average CST value obtained was 120 ($\pm$ 38) seconds for the 8814 flocculant at an 8 kg/TTS dose. It is known that this digestate has a higher content of volatile fatty acids than the other digestates, which may contribute to the ineffective dewatering performance. Clearly, more studies should be conducted with the 'co-digestion oil' digestate to determine the optimum flocculant and the dose that produces the most efficient dewatering separation. The MFT technique developed in this work is ideally suited for such a task.
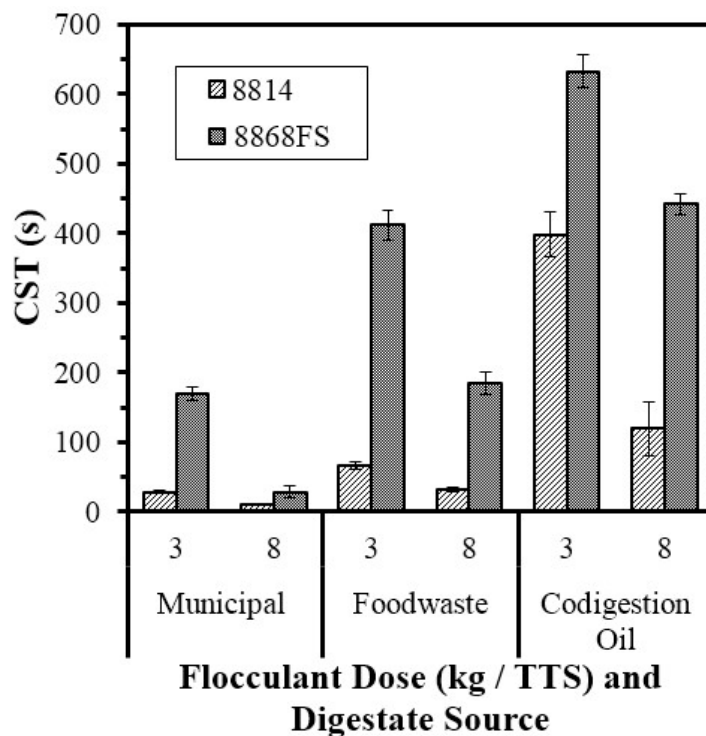
Figure 6: The effect of the digestate source on the flocculation and dewaterability of the resulting digestates using the 8814 and 8868FS flocculants.

4. Conclusions

The MFT developed in this work has been shown to be an effective technique for optimizing the flocculant type and dosage conditions in wastewater separation applications. In contrast with the tradition 'jar test' approach, the MFT's minimal volumes of materials required and parallel processing approach allow for a more facile determination of the dewatering performance over a range of operating conditions. The MFT is simple to conduct, uses simple laboratory equipment and well-established performance metrics, and allows for quantitative comparisons to be made via rigorous statistical tests. A review of the key findings from the application of the MFT method to polymer-induced flocculation of digestate is given below:

- o All ten of the ZETAG polymer flocculants showed a decrease in CST with increasing dosage. The dose-dependent dewatering profile is a strong function of the flocculant type,

however, it was not possible to correlate the flocculant properties with their dewatering performance.

- o Regression analysis of the experimental results revealed that for certain flocculants, the dose could be reduced without any dramatic change in the CST results. However, this was not true for all flocculants and must be assessed on a case-by-case basis.
- o The effects of multi-stage dosing on dewatering performance are also flocculant-specific and again, must be determined on a case-by-case basis.

In this study, we focused on the use of polymer flocculants for the dewatering of digestate from anaerobic digestion processes, however, our methods are applicable for optimizing various others coagulant/flocculation aids used on different water/wastewater sources. By extension, this parallel-processing approach could be applied to the investigation of a wide range of separations processes, including floatation and precipitation, merely by modifying a few method parameters. Further applications of this protocol will be investigated in the future.

Overall, the results in this work confirm that identifying the optimum dewatering conditions for given wastewater source is a complicated task that requires an extensive amount of experimental work, and that the MFT technique developed in this work is ideally suited for this task.

Supporting Information

Additional information as noted in the text will be published online alongside the electronic version.

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Supporting Information

The microscale flocculation test (MFT) – a high-throughput technique for optimizing separation performance

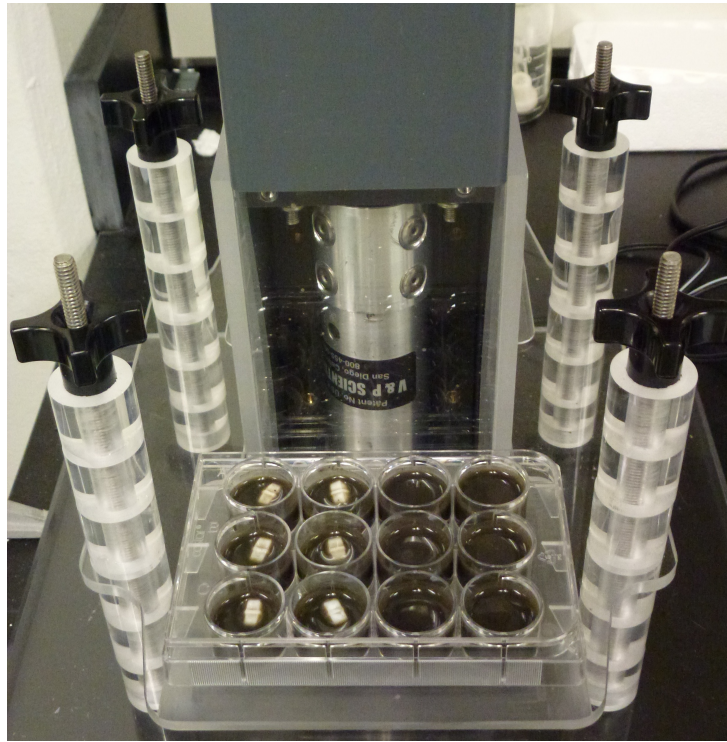Ryan J. LaRue, Jeffrey Cobbledick, Nicholas Aubry, Emily D. Cranston, David R. Latulippe*

Figure S1 – Experimental setup involving the tumble stirrer, custom-built stand, 12-well microplate, digestate/flocculant samples and magnetic stir beads. In this image, it can be clearly seen that the first two columns of the microplate are employed to test one dosage, while the second two columns are contain a separate dosage.

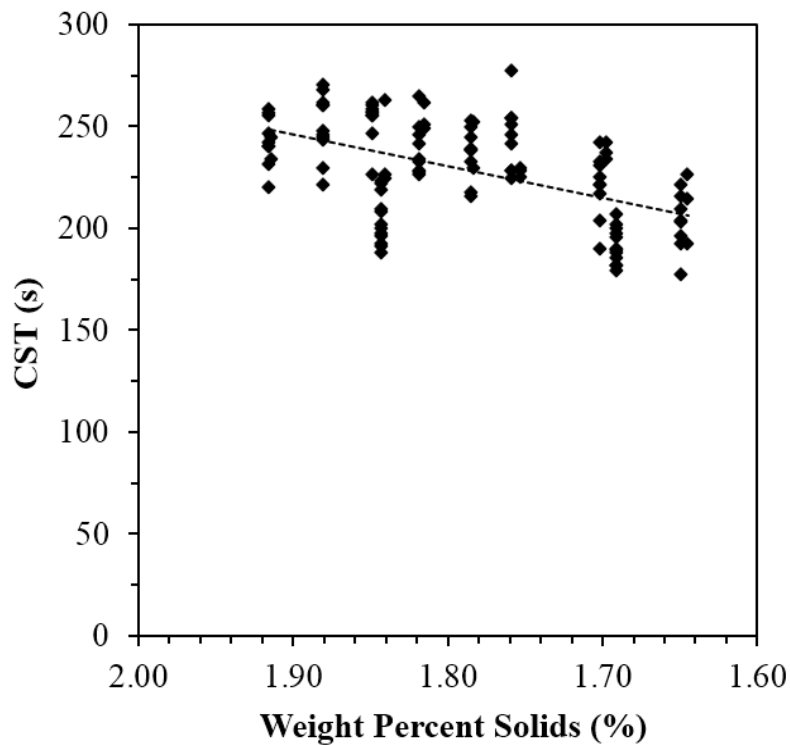Figure S2 – A 12-well microplate fitted with plugs and a pouring spout.

Figure S3 – The "diluting effect" of sodium phosphate monobasic buffer solution, used to suspend the ZETAG® flocculants. Decreasing the weight percent of the digestate via the addition of buffer (alone) causes a statistically-significant drop in CST. Intrinsically, higher doses of buffer result in lower CST values. Regression analysis of CST results, including data from all ten ZETAG® flocculants investigated, yields a linear best-fit model with positive slope of 121.5 seconds per weight percent and an intercept of 12.5 seconds. The slope is significantly different than zero (p-value $< 10^{-10}$).

Table S1 – Technical information for ZETAG polymer as provided by BASF

Emulsion Series	Emulsion ID	Molecular Weight	Charge Density	Specific Gravity	Active Content (%)
ZETAG	8814	Very High	Medium	1.03	34
	8816	Very High	Medium-High	1.03	40
	8818	Very High	High	1.03	40
	8819	Very High	Very High	1.03	40
	8844 FS	High	Medium	1.03	34
	8846 FS	High	Medium-High	1.03	40
	8848 FS	High	High	1.03	40
	8849 FS	High	Very High	1.03	40
	8857 FSB	Medium	High	1.03	40
	8868 FS	Low	High	1.03	40