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Comparison of Flocculation Measurements in Effluent Processing

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Abstract

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This thesis work was carried out in the water treatment team at the Kemira Espoo R&D Center. The aim of this work was to find some trends and coefficients from jar test parameters that were tested under different conditions with Suomenoja effluents using the device PDA3000.

Eight different sets of jar tests were done. Different coagulant amounts were used for chemical tests using two different coagulant chemicals. For pH adjustment tests, pH adjustment chemicals were added in addition to the coagulants. Different flocculator rapid mixing speeds were compared in the rapid mixing rate test. Different flocculator time settings were compared in the rapid mixing time, slow mixing time and sedimentation time tests. Only one coagulant chemical "chemical-1" was used for the rapid mixing rate, rapid mixing time, slow mixing time and sedimentation time tests. All test samples were measured for pH, zeta potential, turbidity, UV254 absorbance, COD, TOC, DOC and iron or aluminum as well.

Based on the maximum flocculation index, the best results using chemical-1 were 300 μmol dose, 200 rpm for rapid mixing rate, 20 s for rapid mixing time, 30 min for slow mixing time and 20 min for sedimentation time. 150 μmol dose had the best flocculation index in the pH adjustment test. However, considering the other parameters, the 400 μmol dose was better than the 150 μmol dose. 400 μmol dose was best for the chemical-2 test and 300 μmol dose was best for the pH adjustment test using chemical-2. Compared to the other doses, however, the maximum flocculation index differences were not significant.

Keywords: jar test, flocculation, PDA3000, zeta potential

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Opinnäytetyö suoritettiin vesitiimissä Kemiralla Espoossa. Sen tavoitteena oli löytää trendejä ja korrelaatioita saostustestiparametreista, joita testattiin kahdeksassa eri kokeessa Suomenojan lähtevällä vedellä PDA3000-laitteella.

Kemiallisiin kokeisiin käytettiin erilaisia koagulanttimääriä ja kahta erilaista koagulanttikemikaalia. pH:n säätötestejä varten koagulanttien lisäksi lisättiin pH:n säätökemikaaleja. Nopeassa sekoitusnopeustestissä asetettiin flokkulaattori eri nopean sekoituksen nopeuksiin. Flokkulaattorin eri asetustajan vertauksien takia tehtiin nopean sekoitusajan, hitaan sekoitusajan ja sedimentaatioajan testit. Vain yhtä koagulanttikemikaalia, joka oli merkitty "kemikaali-1", käytettiin nopean sekoitusnopeuden, nopean sekoitusajan, hitaan sekoitusajan ja sedimentaatioajan testeihin. Testeissä mitattiin myös pH, zeta-potentiaali, sameus, UV254-absorbanssi, COD, TOC, DOC ja rauta tai alumiini.

Maksimiflokkulaatioindeksin perusteella kemikaali-1:n parhaimmat tulokset olivat 300 $\mu\text{mol:n}$ annos, 200 rpm:n pikasekoituksen nopeus, 20 sekunnin pikasekoituksen aika, 30 minuutin hidassekoituksen aika ja 20 minuutin laskeutusaika. Maksimiflokkulaatioindeksin perusteella 150 $\mu\text{mol:n}$ annos oli paras pH-säätötestissä. Kuitenkin muut parametrit huomioon ottaen 400 $\mu\text{mol:n}$ annos oli parempi kuin 150 $\mu\text{mol:n}$ annos. Kemikaali-2:n testien parhaimmat tulokset olivat 400 $\mu\text{mol:n}$ annos annoskokotestissä ja 300 $\mu\text{mol:n}$ annos pH-säätötestissä. Muihin annoksiin verrattuna maksimiflokkulaatioindeksierot eivät kuitenkaan olleet merkittäviä kemikaali-2:n kohdalla.

Avainsanat: saostuskemikaalien testaus, flokkulaatio, PDA3000, zeta-potentiaali

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List of Abbreviations

AC:	Alternating current
BOD:	Biochemical oxygen demand
COD:	Chemical oxygen demand
DC:	Direct current
DOC:	Dissolved organic carbon
IC:	Inorganic carbon
LED:	Light emitting diode
PE:	Polyethylene
RMS:	Root mean square
RPM:	Revolutions per minute
TC:	Total carbon
TOC:	Total organic carbon
UV:	Ultraviolet

1 Introduction

Water is one of the most important things in the world, as mentioned in the Sustainable Development Goal 6 “Ensure availability and sustainable management of water and sanitation for all” of the United Nations [1]. Water covers 71% of the Earth, although 97.5% of it is seawater, and freshwater is only 2,5%. In addition, not even all of that 2,5% is available to be utilized. Since 1,7 percentage points are glaciers and ice caps, this means only 0,8% of all water is available to share. [2, p. 6.] So, to keep that 0,8% of water usable, wastewater treatment is one key factor.

Water and wastewater treatment have a long history. For example, crushed almonds were smeared around a vessel to remove suspended solids and solid particles from river water in Egypt in 2000 B.C. Also, England officially began using alum for coagulation of public water supplies in 1881. In fact, alum was already used as a coagulant by the early Romans. Even nowadays, coagulation-flocculation process is crucial for water and wastewater treatment. [3, p. 1.]

This thesis work was conducted in the water treatment team of the Kemira Espoo R&D Center. The purpose was to execute a series of chemical treatment tests of treated wastewater, called effluent, under different conditions by jar test. The results were analysed and compared to gain insight into the effects of different parameters on the flocculation process. Jar test is a small-scale test of the coagulation-flocculation process in a water treatment plant to find efficient processing methods and amounts of coagulants [4, p. 1]. Device PDA3000 is based on turbidity fluctuation principle. It was used for searching the tendencies of flowing suspensions with the jar test. [5, p. 9.]

2 Theoretical Background

Water and wastewater treatment are largely divided into four methods: physical, biological, chemical, and physico-chemical. The coagulation-flocculation process belongs to the physico-chemical methods. [2, p. 10.] Coagulation and flocculation are water treatment processes to remove flocs from water [6, p. 1]. A clump called floc is formed in raw water when treatment chemicals react with the suspended solids [3, p. 1].

Coagulation is the process to transform the given suspensions or solutions from a stable to an unstable state. Coagulant chemicals that have opposite charges than the suspended solids, are used to neutralize the solids. The suspended particles start agglomerating from the moment of charge neutralization. Agglomerated particles are still not visible to the naked eye, and these are called microflocs. For good coagulation, rapid mixing with a high energy is required. Following coagulation, flocculation is the process in a gentle mixing stage to accelerate bigger floc formation, in which the particles transition from microflocs to visible size. [3, p. 7; 6, p. 1.]

The fastest way to get flocs is to add coagulants and flocculants. Aluminium and iron salts are generally used as inorganic coagulants. Commonly used flocculants are organic water-soluble polymers. They can be applied at lower doses as coagulant aids in addition to the inorganic coagulants. Although, in terms of cost, polymers are usually several times more expensive than inorganic coagulants. [2, p. 10; 6, p. 5–6.]

2.1 Zeta Potential

Zeta potential is a physical property which is the potential measured at some location close to surfaces of suspended particles [7, p. 1; 8, p. 530]. Figure 1. shows the zeta potential and the distance from a particle surface.

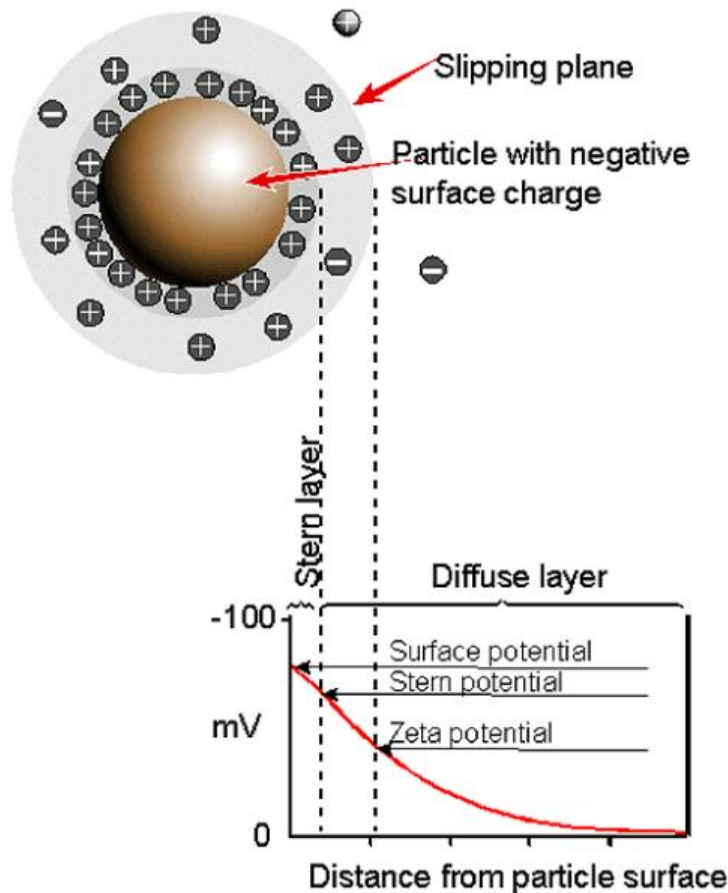


Figure 1. Schematic illustration of the zeta potential with the distance from a particle surface [7, p. 8]

The liquid surrounding a particle has a double layer. Between the inner region and the outer region is hypothetical boundary, which is called stern surface. The ions are strongly bound and stable in the stern layer, which starts from the actual surface. In the outer layer, which is called diffuse layer, the ions' boundaries are weaker than in the stern layer. [7, p. 7; 8, p. 527.] The boundary between the immobilized layer and the mobile fluid is called slipping plane or surface of shear, which is within the diffuse layer. The potential at the slipping plane is the zeta potential. [7, p. 7; 8, p. 541.]

The stability is known from the magnitude of zeta potential. In general, if the zeta potential value is lower than -30 mV or greater than +30 mV, the particles in suspension are stable and repel each other. On the other hand, if the zeta potential value is between -30–+30 mV, the particles are unstable and tend to

gather. [7, p. 8.] In addition, a zeta potential value from -40 mV to -10mV is quite typical for suspended particles in sewage [8, p. 567].

2.2 Parameters of Organics in Water

Organic chemical measuring is an important parameter to determine the amount of organic matter in water. Drinking water and industrial waste streams are regulated based on the oxygen demand. Typical oxygen demand parameters are biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and dissolved organic carbon (DOC). BOD and COD measure directly how much oxygen is consumed in the water through biochemical or chemical means. TOC and DOC measure the amount of CO₂ produced when organic compounds oxidize by chemical means. [2, p. 48–49; 9, p. 3; 10, p. 386.]

BOD measures the amount of organic and biological matter in water that consumes oxygen through the action of bacteria. Bacteria are put to a sample of water, the container is sealed, and it is incubated at 20 °C in the dark for five days (BOD₅) or seven days (BOD₇). Dissolved O₂ is measured before and after the incubation. If the added microorganisms are appropriate to the sample, the BOD test is the closest model of the natural environment. However, microorganisms might die by toxic materials and microorganisms do not oxidize all materials present in water. [2, p. 48; 9, p. 4; 10, p. 386; 11, p. 415.]

COD testing is faster than BOD. It takes about only 1,5–3 hours using a strong chemical oxidant in an acid solution. When the sample-reagent mixture is heated, CO₂ and H₂O are generated from the oxidized organic carbon. After the heating reaction, the oxidant consumption can be measured by titration. Toxic materials do not affect the oxidant in a COD test. However, inorganic oxidation can cause errors. Examples of such substances are chloride, nitrite, hydrogen sulfide, sulfur dioxide, and divalent iron. Mainly there are two oxidants, potassium permanganate (KMnO₄) and potassium dichromate (K₂Cr₂O₇). Measurement with potassium permanganate can be used for certain types of water, especially

discharge waters and clean waters, but not seawater. Permanganate is a weaker oxidizing agent than dichromate. Therefore, some organic substances oxidize incompletely or not at all. Nowadays potassium dichromate is widely used in Europe for COD measurement. [9, p. 4; 10, p. 386; 12, p. 1–2; 13, p. 1–2.]

TOC is a measurement of the dissolved and suspended organic matter concentration in raw water. TOC is usually defined as: TOC = Total carbon (TC) – Inorganic carbon (IC). The main method for measuring TC is burning a sample with a metal catalyst and measuring the amount of produced CO₂. Separately IC can be measured by acidification with a strong acid. CO₃²⁻ and HCO₃⁻ are produced during IC measurement. The filtered TOC sample is used for DOC measurement. DOC is a parameter that characterizes only dissolved organic matter. [2, p. 18; 10, p. 386; 11, p. 417.]

Another organic matter concentration measurement is using ultraviolet (UV) light. Organic contaminants have aromatic organics such as humic acid and fulvic acids. They absorb UV light at a 254 nm wavelength. [2, p. 17; 14, p. 1.]

2.3 PDA3000 Particle & Flocculation Monitor

The PDA3000 is a device to monitor flowing suspensions and emulsions (figure 2) [5, p. 4].



Figure 2. The device PDA3000 Particle & Flocculation Monitor

A transparent flexible tube fits into a slot of the device on the right side of the figure 2. A miniature light-emitting diode (LED) passes the light perpendicularly through the tube of flowing suspension and the light goes into a photodetector. The detector photodiode outputs a voltage, which consists of a large direct current (DC) component and a smaller fluctuating alternating current (AC) component. The DC component is a measure of the average transmitted light intensity, which depends on the turbidity of the flowing suspension. The AC component's random variations are dependent on the number and size of the particles flowing in the suspension, which gives the transmitted light intensity fluctuations. The ratio between the root mean square (RMS) value of the fluctuating AC component and the DC value is marked RMS/DC. It is used as the "flocculation index" indicator. The ratio value increases when flock aggregation occurs and vice versa. [5, p. 4–5.]

The method of the PDA3000 is based on the turbidity fluctuation principle (figure 3) [5, p. 9].

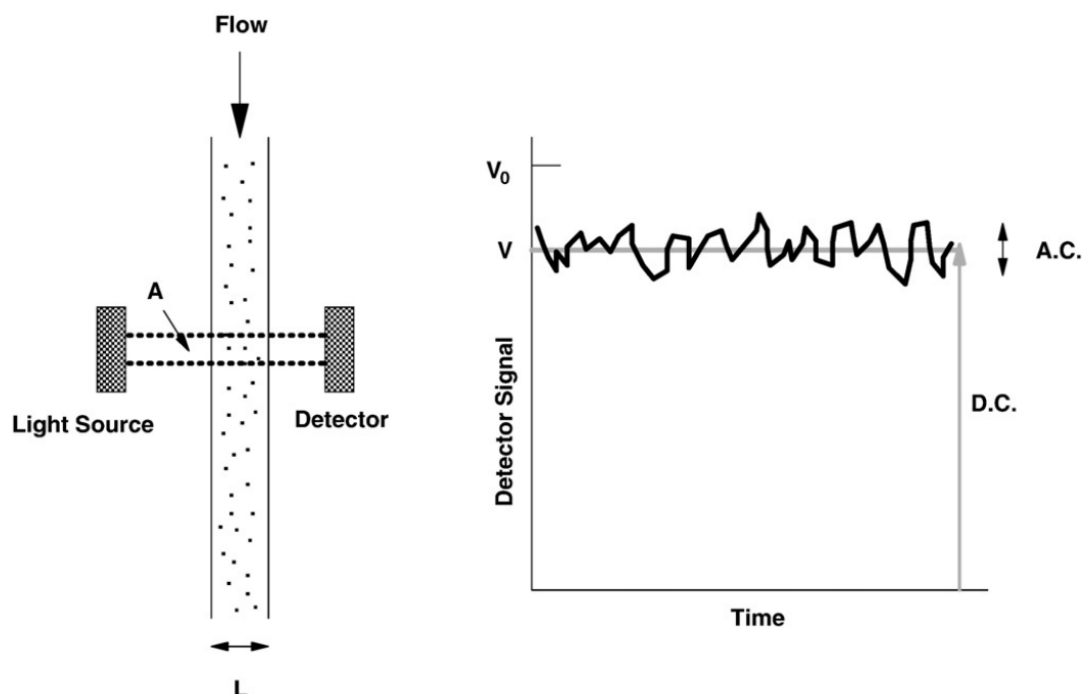


Figure 3. Turbidity fluctuations [5, p. 10]

If the incident light intensity is I_0 , the transmitted light intensity is derived from the Beer-Lambert law:

$$I = I_0 \cdot \exp(-\tau L) \quad (1)$$

Where:

- I: Transmitted light intensity
- I_0 : Incident light intensity
- τ : Turbidity
- L: Optical path length. [5, p. 9.]

Where τ is the turbidity, the expression is:

$$\tau = nC \quad (2)$$

Where:

- τ : Turbidity
- n: Particle number concentration
- C: Scattering cross-section of the particles. [5, p. 9.]

All the particles are assumed to be monodisperse suspensions, which are all the same size. Because the light intensity is converted to a voltage by the photodiode, the expression for the voltage is derived from equation (1) as:

$$V = V_0 \cdot \exp(-\tau L) \quad (3)$$

Where:

- V: Voltage when there are particles in the light beam
- V_0 : Voltage corresponding to the incident light intensity. [5, p. 10.]

As showed in figure 3, the mean value of DC is a few volts, and the fluctuations AC values might be a few mV or less in the detector output. So, V is the average value of a fluctuating voltage and is called the DC value. [5, p. 10.]

The ratio value R is given by:

$$R = \frac{V_{RMS}}{V} = \sqrt{\frac{nL}{A}} C \quad (4)$$

Where:

V_{RMS} : RMS value of the voltage fluctuations

V: Mean DC value

A: Effective cross-sectional area of the light beam. [5, p. 11.]

The ratio value depends only on the square root of the particle concentration (n) because the optical path length (L) and the beam dimensions (A) are constant during the PDA3000 operation. In addition, the scattering cross-section of the particles (C) is based on the assumption of monodisperse suspensions. From equations (2)-(4) the following expression can be derived:

$$nLA = \left(\frac{\ln V_0/V}{R}\right)^2 \quad (5)$$

On the left-hand side of the expression is the sample volume's average particles number in the light beam. The particle number concentration can be determined from the DC and RMS values along with the beam dimensions, and it can be calculated without any information about the light scattering properties of the particles. [5, p. 11.]

Only fluctuations approximately within the 1–350 Hz frequency range are used to calculate RMS. The frequency range of the AC signal is dependent on the flow rate, that is the particles' passage time though the light beam. Tubes of 1-, 3- and 5-mm diameters are fitted to the PDA3000 device, and the suggested ranges of flow rates for the corresponding tube diameters are 0,5–2, 10–40 and 25–100 ml/min. The ratio value is stable within the flow rate range. For lower flow rates, some of the lower frequencies are lost and the measured RMS value is lower than actual value. If the flow rate is too high, some of the upper frequencies are lost, and then again, the measured RMS value is lower than actual value. In

addition, a high flow rate combined with narrow tubes might cause an aggregate breakage and an RMS value reduction. [5, p. 12.]

3 Experimental Part

3.1 Experiment Water Sampling

Effluent samples were taken from the Suomenoja water treatment plant in Espoo on 6 April and 1 Jun 2022. Sediments and moss were seen in the effluents after sampling. Thus, they were filtered out with a 0,5 mm filter on the same days they were picked. The samples were kept in a refrigerator, maintained at 4–6 °C for approximately a month. Every Monday, the required amount of water for the week's testing was taken from the refrigerator and placed in a container on the floor. The excess water was put back in the fridge every Friday. This was done to ensure the tested sample was at room temperature, i.e. 20,1–22,7 °C.

3.2 Experiment of Jar Test

Main equipment and chemicals for the jar test were the following:

- Photometric Dispersion Analyzer PDA3000, Rank Brothers Ltd., England
- Flocculator 2000, Kemira oyj., Finland
- Peristaltic pump Masterflex, Cole-Parmer, United States, Flow rate: 10 ml/min
- Laptop with Rank Brothers Logger application, Sample interval: 10 s, Probe type:3 mm, LED current: 1,70 mA, LED drive: 175
- Intramedic polyethylene (PE) tube (\varnothing 3 mm)
- pH meter Portamess, Knick Elektronische Messgeräte- GmbH & Co. KG, Germany
- Coagulants: chemical-1 and chemical-2
- pH adjustment chemicals: 5% H₂SO₄ and 1M NaOH.

In every experiment, one liter of sample water was poured into a beaker, and the stirrer part of the flocculator was put into the beaker. When the coagulant was added to the sample, the flocculator and the PDA3000 monitoring were turned on. The default setting of the jar test was 30 seconds with 400 revolutions per minute (rpm) for rapid mixing and then 10 minutes with 40 rpm for slow mixing. After that, the stirrer was turned off and the sample was left to settle for 20 minutes. The sample was circulated with the peristaltic pump through a 3 mm tube via the PDA3000 device during the jar tests. The PDA3000 device was connected to a computer and could continuously monitor the flocculation process (figure 4).

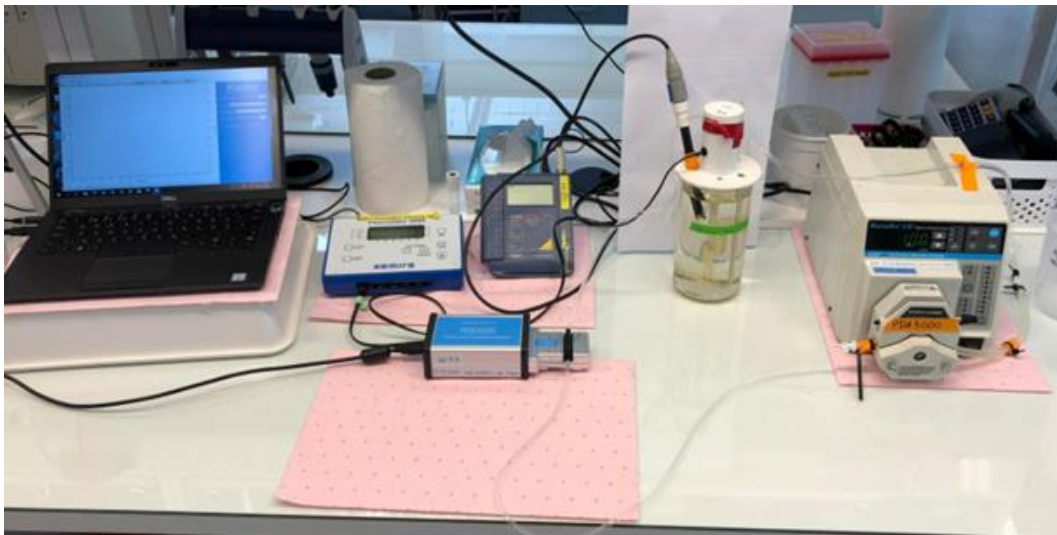


Figure 4. The entire PDA3000 testing arrangement for the jar test

When the buzzer of the flocculator rang at the end, the PDA3000 monitoring was turned off. The tube was rinsed with deionized water between each test. In addition, it was cleaned with dilute hydrochloric acid and rinsed with deionized water at the end of each day.

3.3 Other Analysis than PDA3000

In addition to measuring flocculation, pH was also measured during the slow mixing when the pH was stable. A 300 ml sample was taken with a 100 ml

volumetric pipet after sedimentation from approximately 3 cm below the sample water surface. It was measured for zeta potential, turbidity, UV absorbance, COD, TOC, DOC and iron or aluminium. For measurements of UV absorbance, COD, DOC and iron or aluminium, the samples were sieved with 0.45 µm ion chromatography acrodisc® PSF syringe filters.

Flocks could have been too big for the device Malvern Zetasizer Nano ZS after the settling phase for zeta potential measurement. Therefore, 20 ml of the sample was taken using the previously described procedure, right after rapid mixing every time. Turbidity, spectrometry and COD were measured right after the jar tests, and the samples were frozen to be measured later for zeta potential, TOC, DOC and iron or aluminium analysis.

4 Results and Considerations

Sample effluent characterizations are in table 1.

Table 1. Characterizations of Suomenoja effluent

Pick-up date	6 April 2022	1 Jun 2022
Temperature (°C)	22,0	19,3
pH	7,06	6,87
Redox (mV)	255	236
Conductivity (mS/cm)	517	590
Turbidity unfiltered (NTU)	5,05	2,52
Turbidity filtered (NTU)	0,221	0,274
UV254 absorbance	0,182	0,215
COD unfiltered (mg/l)	35,8	34,9
COD filtered (mg/l)	24,4	27,7
TOC (mg/l)	13	13
DOC (mg/l)	9,3	13
Alkalinity (mmol/l)	0,260	1,15
Zeta potential (mV)	-16,3	-13,7

There were no significant differences between samples taken on 6 April and 1 Jun 2022, although values of filtered COD and alkalinity on 1 Jun were slightly higher than on 6 April.

4.1 Categorization of PDA3000 results

The collected results of the PDA3000 could be categorized into four phases as linear equations (figure 5).

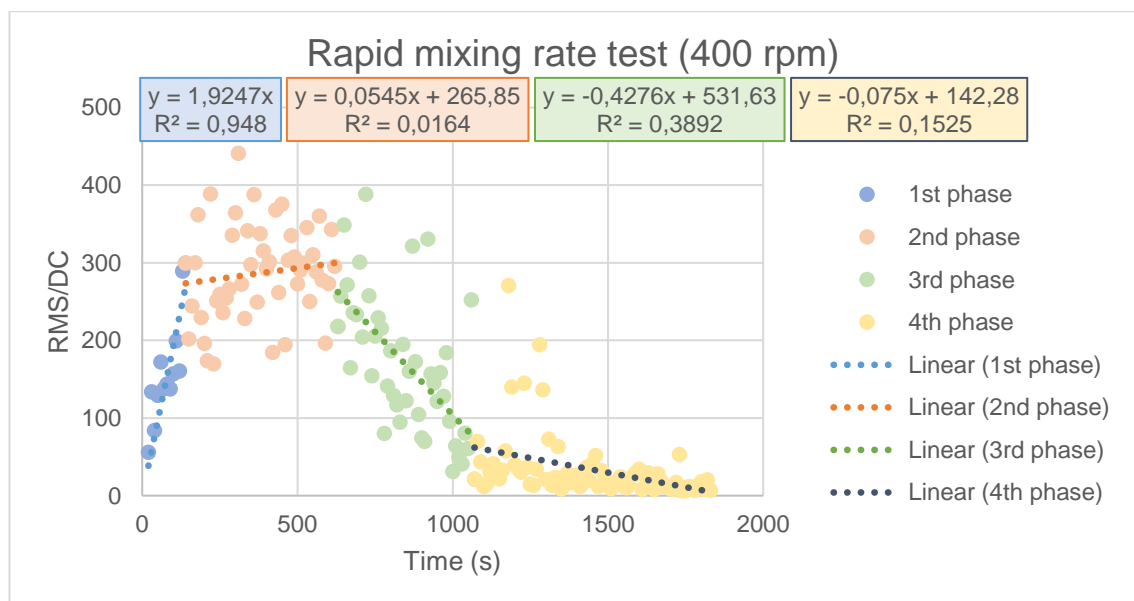


Figure 5. Example of the PDA3000 results, 400 rpm rapid mixing rate test

The four categories were thought of as follows: In the first phase, the slope of the corresponding trend line indicated how rapidly the flocculants formed (blue). The second phase was when the flocculant formation was stable (red). Therefore, the corresponding trend line slope was close to zero, and the intercept showed the maximum flocculation index value. After that, the slope of the corresponding trend line indicated how fast the flocculants settled in the third phase (green). Finally, the fourth phase was again stable (yellow).

4.1.1 Four Phases

All the time and the RMS/DC data used in figure 5 are shown in appendix 1. The RMS/DC data were used from 20 seconds until the end because the results were not stable, especially for the first 20 seconds. The flocculator had 13 seconds of lag between the actual finish time and the buzzer ringing, so the RMS/DC data were used until the actual finish time. The end of the slow mixing time was marked as the beginning of the third phase. There was first an attempt to use derivative calculations to find the beginning of the fourth phase, but no clear trends could be determined. Therefore, the RMS/DC average value for the fourth phase was calculated from the values corresponding to the last half of the sedimentation time. The end of the third phase was marked when the RMS/DC value reached the calculated average.

In order to determine between the first and second phases, first the y-intercept was calculated as a temporary indicator from 200 seconds until the end of the slow mixing. During that time, the PDA3000 data were relatively stable in almost all the jar tests. When the RMS/DC values reached the calculated y-intercept value twice from beginning, the phase was split into two. There were no reliable first phase equation values, when the RMS/DC values reached the y-intercept value only once, because air bubbles would have occasionally made random peaks in the RMD/DC values.

For example, in the 400-rpm rapid mixing rate test, the time setting of the flocculator was the same as default, so the RMS/DC data were used until 1830 seconds, although the data records were continued until 1850 seconds. The RMS/DC average value was calculated to be 27,61 between 1230–1830 seconds. The third phase began at 630 seconds, which was the end of the slow mixing. The RMS/DC value went below 27,61 at 1070 seconds marking the beginning of the fourth phase. The third phase was between 630–1070 seconds, and the fourth phase was between 1070–1830 seconds. The y-intercept was 268,43 between 200–630 seconds. The RMS/DC values reached 268,43 first at 130 seconds and for the second time at 140 seconds from the beginning. So, the

first phase was marked between 20–140 seconds, and the second phase was between 140–630 seconds.

The categorized four phases were shown as linear equations, but only the first phase was a linear equation calculated without using y-intercept setting in Excel. For example, the slopes for the samples of the 40 s and 60 s rapid mixing time tests seemed similar in figure 6.

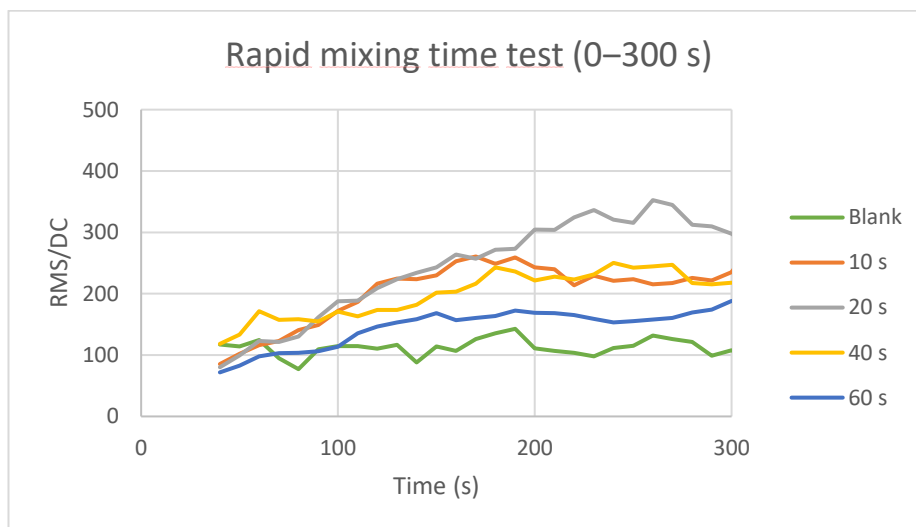


Figure 6. Example of linear equation in the first phase

However, the slope of the 40 s test with the y-intercept was 0,44, which was much smaller than the 60 s test (table 2).

Table 2. Example of linear equation in the first phase

Sample	Equation and R ² in first phase	
	With y-intercept	Without y-intercept
10 s	$y = 1,56x + 56$	$y = 2,23x$
	$R^2 = 0,68$	$R^2 = 0,95$
20 s	$y = 1,37x + 68$	$y = 1,86x$
	$R^2 = 0,73$	$R^2 = 0,95$
40 s	$y = 0,44x + 140$	$y = 1,64x$
	$R^2 = 0,23$	$R^2 = 0,85$
60 s	$y = 0,89x + 59$	$y = 1,58$
	$R^2 = 0,59$	$R^2 = 0,93$

The y-intercept of the 40 s test was 140, which means flocks were formed quickly from the beginning. Thus, the first phase equations were shown without y-intercept, and they had higher correlation coefficients than equations with y-intercept.

4.2 Condition of Zeta Potential Samples

Because of the tight execution schedule, the zeta potential samples were frozen after each jar test and measured at later dates. To know how much frozen condition influenced the samples, two conditions were compared first. One was measured right after jar tests, which was marked original. The other one was marked frozen, and was put to a freezer after jar tests, defrosted to room temperature later and measured (figure 7).

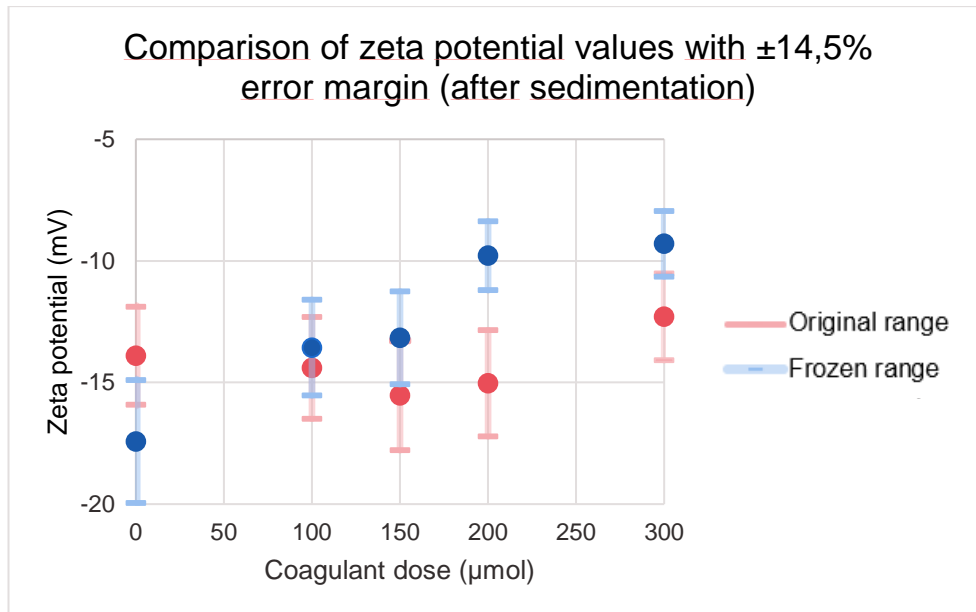


Figure 7. Comparison of zeta potential values with $\pm 14,5\%$ error margin

The error margin $\pm 14,5\%$ was referred from a Malvern zeta potential standard, which was $-40 \text{ mV} \pm 5,8 \text{ mV}$. All the frozen results were closer to 0 mV than the original results except the 0 μmol coagulant results. Both sample error margins were overlapping in 0, 100, 150 and 300 μmol .

Three conditions were compared next. The first two conditions were the same as previously mentioned. The third condition sample was put to a refrigerator maintained at 4–6 °C after jar tests, tempered them to room temperature later and measured (figure 8).

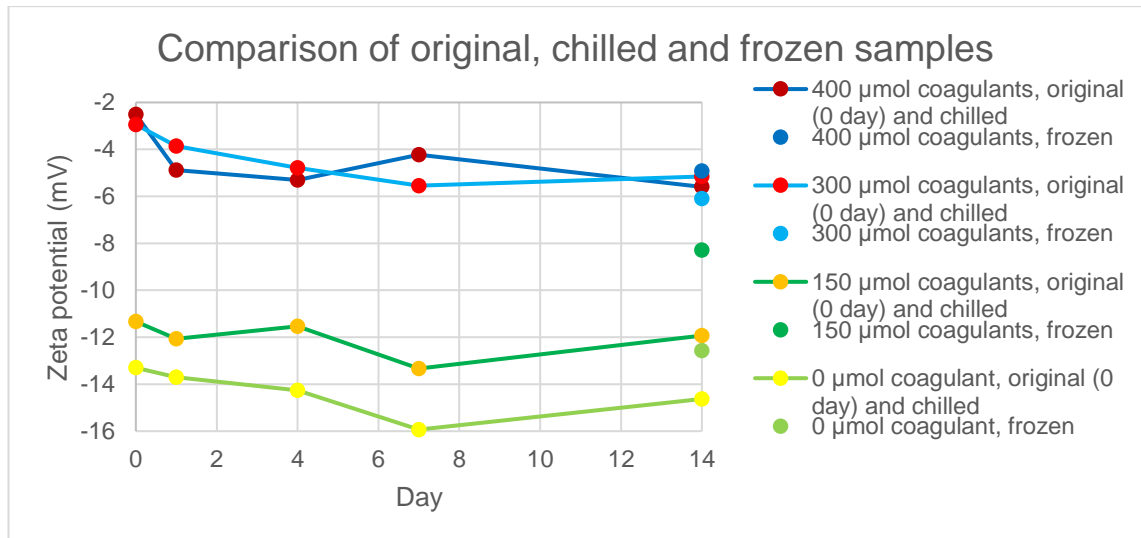


Figure 8. Comparison of original, chilled, and frozen samples

Overall, the chilled sample values variably changed especially 0–7 days, and 14 days chilled sample results were close to the 4 days chilled results. The 300 μmol value was -5,2 mV from the 14 days chilled sample and -6,1 mV from the frozen sample. Otherwise, the other frozen sample values were closer to zero than the 14 days chilled samples.

4.3 Eight Different Jar Test Comparisons

Eight different settings of jar tests were carried out to compare the efficiency of forming flocks. In chemical tests, different dose amounts of different coagulants, marked chemical-1 and chemical-2, were compared. In pH adjustment tests, pH adjustment chemicals were used in addition to the coagulants. The default setting of the jar test was 30 seconds with 400 rpm for rapid mixing, 10 minutes with 40 rpm for slow mixing and 20 minutes with 0 rpm for sedimentation. The rapid mixing rate test was set to 200, 300 and 400 rpm with coagulant chemical-1 for each experiment. Different time settings were also tested separately using the coagulant chemical-1 for rapid mixing, slow mixing, and sedimentation.

Blank samples were measured every experiment day at the beginning of the experiment.

4.3.1 Chemical-1 Test

All pictures of the jar tests are shown in appendix 2. As shown in figure 9, the results of the 300 μmol dose were the most significant smooth mountain type of curve, and there was no ascending phase in the results of the 100 μmol dose.

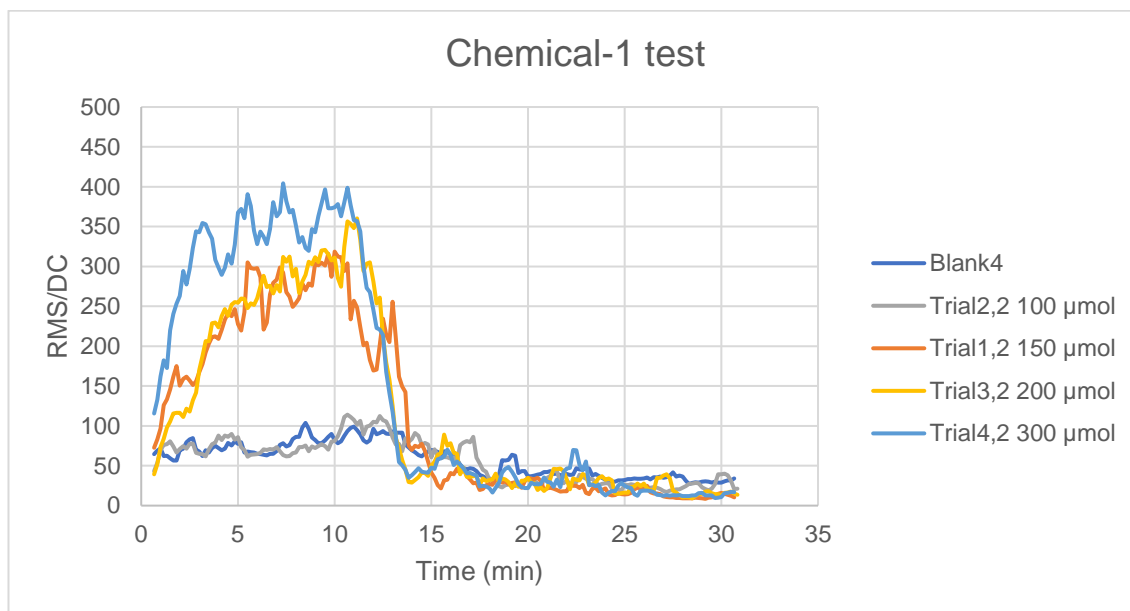


Figure 9. The PDA3000 results of the chemical-1 test with a 5-point moving average

The four phases' equations of figure 9 are shown in table 3.

Table 3. Equations of the PDA3000 results in the chemical-1 test

Sample	1st phase	2nd phase	3rd phase	4th phase
Trial2,2 (100 μmol)	-	$y = 0,02x + 68$	$y = -0,15x + 203$	$y = -0,007x + 37$
Trial1,2 (150 μmol)	$y = 1,28x$	$y = 0,18x + 193$	$y = -0,85x + 807$	$y = -0,03x + 58$
Trial3,2 (200 μmol)	$y = 1,10x$	$y = 0,24x + 184$	$y = -2,32x + 1889$	$y = -0,03x + 75$
Trial4,2 (300 μmol)	$y = 3,46x$	$y = 0,13x + 298$	$y = -2,22x + 1804$	$y = -0,04x + 79$

300 μmol dose's results were the best, which had the considerable slope value in the first phase, the high flocculation index value in the second phase and the small slope value in the third phase. In the second phase, the slope of the Trial1,2 was 0,18, Trial3,2 was 0,24, and Trial4,2 was 0,13, which means flocks were still grown even in the stable phase. Among 100–300 μmol doses, the larger the dose, the better the zeta potential values as well (table 4).

Table 4. Analysis results of the chemical-1 test

Sample		Blank4	Trial2,2	Trial1,2	Trial3,2	Trial4,2
Coagulant dose (μmol)		0	100	150	200	300
Zeta potential (mV)	After rapid mixing	-16	-14	-9,7	-11	-8,6
	After sedimentation	-13	-11	-9,9	-8,3	-5,6
pH (after rapid mixing)		7,1	6,7	6,5	6,4	6,0
Turbidity (NTU)		1,4	0,18	0,15	0,14	0,12
UV254 absorbance		0,21	3,4	1,7	1,5	1,0
COD Unfiltered (mg/l)		35	30	24	23	20
COD Filtered (mg/l)		31	27	23	23	20
TOC (mg/l)		12	10	8,2	8,2	6,9
DOC (mg/l)		12	9,6	8,2	8,0	6,6
Fe ($\mu\text{g}/\text{Kg}$)		69	300	130	110	75

Better coagulation-flocculation test results are usually values that are close to zero except for pH. As shown in table 4, all analysis results were getting close to zero in order of 100, 150, 200 and 300 μmol doses. Iron residues could show how much coagulants remain in the water without forming flocks. Thus, the iron amounts were in inverse proportion to the coagulant doses.

4.3.2 Chemical-2 Test

As shown in figure 10, there was no significant ascending phase.

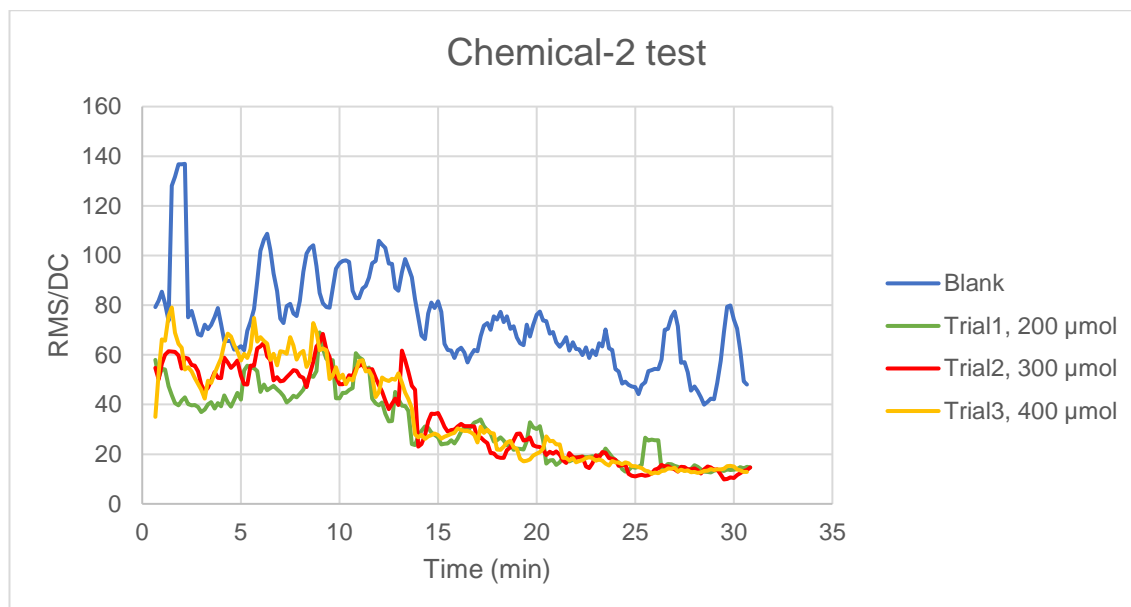


Figure 10. The PDA3000 results of the chemical-2 test with a 5-point moving average

Small peaks were seen from the samples in Trial2 and Trial3 at the beginning, although there were no proper mountain shape curves to calculate. The flocculation index values decreased from the beginning and stabled in approximately the last 5 minutes. Because there were no significant ascending phases, as mentioned in figure 10, results were started from the second phase (table 5).

Table 5. Equations of the PDA3000 results in the chemical-2 test

Sample	1st phase	2nd phase	3rd phase	4th phase
Trial1 (200 µmol)	-	$y = 0,01x + 43$	$y = -0,06x + 89$	$y = -0,01x + 40$
Trial2 (300 µmol)	-	$y = -0,003x + 56$	$y = -0,06x + 87$	$y = -0,01x + 31$
Trial3 (400 µmol)	-	$y = -0,007x + 62$	$y = -0,08x + 103$	$y = -0,01x + 36$

The second and the fourth phases were very stable, although, the scale of the slope in the third phase was also significantly smaller than in the chemical-1 test. All of the flocks in the chemical-2 test were very fine compared to the chemical-1 test. The chemical and physical results are shown in table 6.

Table 6. Analysis results of the chemical-2 test

Sample		Blank	Trial1	Trial2	Trial3
Coagulant dose (μmol)		0	200	300	400
Zeta potential (mV)	After rapid mixing	-13	-9,5	-8,6	-7,3
	After sedimentation	-12	-7,2	-6,2	-5,5
pH (after rapid mixing)		7,2	6,9	6,8	6,9
Turbidity (NTU)		1,4	0,93	0,74	1,0
UV254 absorbance		0,21	0,15	0,14	0,14
COD Unfiltered (mg/l)		32	27	24	24
COD Filtered (mg/l)		30	23	22	22
TOC (mg/l)		12	9,4	9,3	8,9
DOC (mg/l)		12	9,9	8,8	8,9
Al ($\mu\text{g}/\text{kg}$)		17	22	21	20

Among 200–400 μmol doses, the larger dose, the better the zeta potential value. The UV254 absorbance, COD, TOC and DOC results had some similar trends as the zeta potential values.

4.3.3 pH Adjustment Test with Chemical-1

After adding coagulants, the pH values of the samples were aimed to be adjusted to five with pH adjustment chemicals. Because the pH adjustment chemicals were added little by little while checking pH, chemical adding times were variable. Line graphs of the results are shown in figure 11.

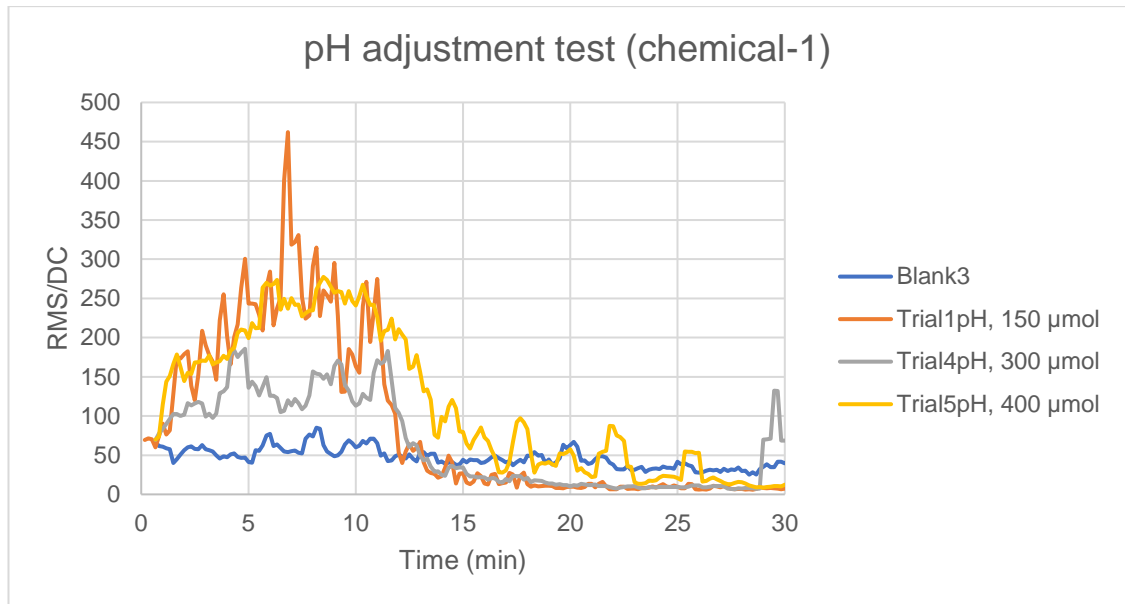


Figure 11. The PDA3000 results of the pH adjustment test (chemical-1) with a 5-point moving average

There was an exceptionally high peak at 6,7 minutes in the 150 μmol dose's curve, which was thought to be due to bubbles. Thus, the high peak was omitted from calculations. Two high peaks were also omitted at 29 and 29,5 minutes from the 300 μmol dose's results. The 300 μmol dose's results were the most minor and unstable curve, although the maximum flocculation index value was 298 with the same dose in section 4.3 Chemical-1 Test. Figure 11 shows that the average flocculation index value seems to be approximately 250 between 6–10 minutes in the 400 μmol dose. However, its maximum flocculation index was 149, which was even smaller than the 300 μmol dose's flocculation index value (table 7).

Table 7. Equations of the PDA3000 results in the pH adjustment test (chemical-1)

Sample	1st phase	2nd phase	3rd phase	4th phase
Trial1pH (150 μmol)	$y = 0,99x$	$y = -0,16x + 313$	$y = -0,40x + 395$	$y = -0,007x + 20$
Trial4pH (300 μmol)	$y = 0,77x$	$y = -0,07x + 169$	$y = -0,41x + 390$	$y = 0,03x + 50$
Trial5pH (400 μmol)	$y = 2,99x$	$y = 0,21x + 149$	$y = -0,63x + 625$	$y = -0,06x + 117$

The 400 μmol dose's slope in the second phase was 0,21, which means flocks were still growing. On the other hand, the 300 μmol dose's slope was -0,07, which was a downward trend. The 150 μmol dose's maximum flocculation index value was 313, the highest number of other experiments. The 150 μmol dose seemed to be one of the effective ways to make flocks. However, according to the other analytical results, the 300 and 400 μmol doses were better than the 150 μmol dose, and also, flock layers of the 300 and 400 μmol doses were thicker than the 150 μmol dose's at the end of each test (table 8).

Table 8. Analysis results of the pH adjustment test (chemical-1)

Sample		Blank3	Trial1pH	Trial4pH	Trial5pH
Coagulant dose (μmol)		0	150	300	400
Zeta potential (mV)	After rapid mixing	-14	-9,9	-6,9	-7,4
	After sedimentation	-13	-8,3	-6,1	-4,9
pH (after rapid mixing)		6,7	5,8	4,8	5,3
Turbidity (NTU)		1,2	1,1	1,6	1,4
UV254 absorbance		0,18	0,10	0,079	0,076
COD Unfiltered (mg/l)		26	18	14	14
COD Filtered (mg/l)		25	15	13	13
TOC (mg/l)		9,9	6,6	5,0	5,0
DOC (mg/l)		9,6	6,5	4,9	4,9
Fe ($\mu\text{g/Kg}$)		43	77	100	93

A 20 ml sample was taken right after rapid mixing in every jar test except for the pH adjustment tests. In these when pH was stable during slow mixing, a 20 ml sample was taken for the zeta potential measurements. Only the pH of the 300 μmol dose went to under five after the rapid mixing, and it was too acid to form flocks for the Suomenoja effluent. For this reason, the flocculation curve shape was the exception.

4.3.4 pH Adjustment Test with Chemical-2

After adding coagulants, pH values of the samples were aimed to be adjusted six with pH adjustment chemicals. Chemical adding times were variable as same as in chapter 4.3.3. As shown in figure 12, the peaks of this test were similar to figure 10 except for some peaks, that showed up between 10–13 minutes after the rapid mixing. In addition, all the RMS/DC values were approximately 20 or above in the last five minutes.

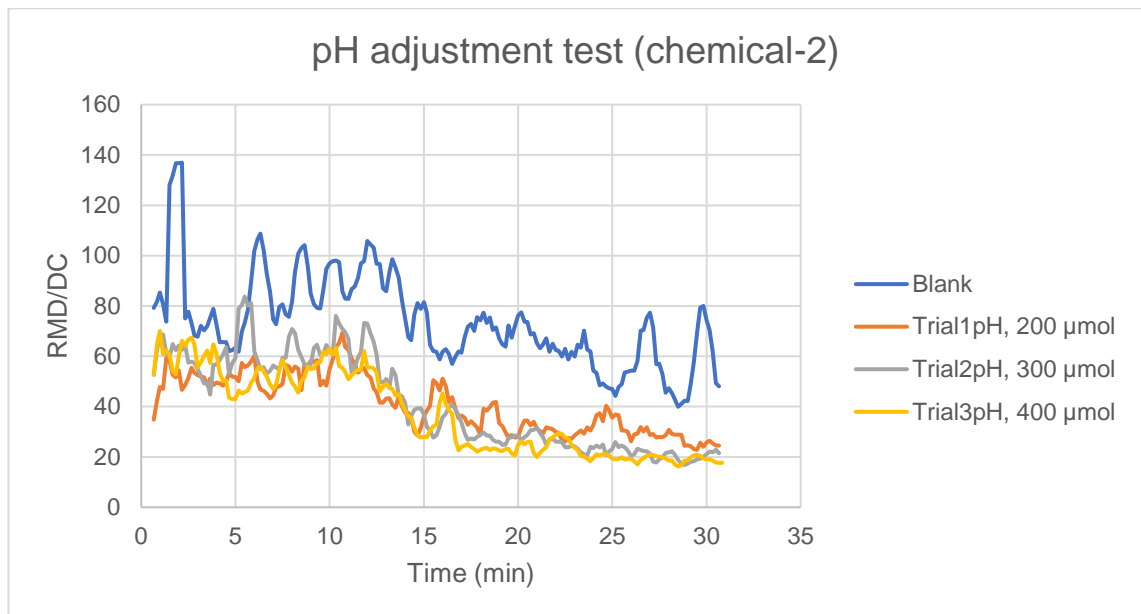


Figure 12. The PDA3000 results of the pH adjustment test (chemical-2) with a 5-point moving average

When the four phase's equations of this test were compared to the equations of the chemical-2 test, there were no significant differences (table 9).

Table 9. Equations of the PDA3000 results in the pH adjustment test (chemical-2)

Sample	1st phase	2nd phase	3rd phase	4th phase
Trial1pH (200 μmol)	-	$y = 0,01x + 48$	$y = -0,1x + 143$	$y = -0,01x + 50$
Trial2pH (300 μmol)	-	$y = 0,007x + 60$	$y = -0,09x + 119$	$y = -0,01x + 41$
Trial3pH (400 μmol)	-	$y = -0,01x + 61$	$y = -0,07x + 100$	$y = -0,008x + 32$

The chemical and physical results are shown in table 10.

Table 10. Analysis results of the pH adjustment test (chemical-2)

Sample		Blank	Trial1pH	Trial2pH	Trial3pH
Coagulant dose (μmol)		0	200	300	400
Zeta potential (mV)	After rapid mixing	-13	-10	-6,0	-6,8
	After sedimentation	-12	-7,4	-7,2	-6,1
pH (after rapid mixing)		7,2	6,3	6,1	5,9
Turbidity (NTU)		1,4	1,2	1,7	2,5
UV254 absorbance		0,21	0,15	0,15	0,14
COD Unfiltered (mg/l)		32	25	27	24
COD Filtered (mg/l)		30	23	23	21
TOC (mg/l)		12	8,8	8,3	8,0
DOC (mg/l)		12	8,6	8,1	7,8
Al ($\mu\text{g}/\text{Kg}$)		17	25	36	96

Same as in the previous chapter, when the pH was stable during slow mixing, a 20 ml sample was taken for the zeta potential measurements. The trends were similar as chemical-2 test results in zeta potential, UV254 absorbance, filtered COD, TOC and DOC.

4.3.5 Rapid Mixing Rate Test with Chemical-1

Based on the chemical-1 test results, chemical-1 dose of 300 μmol was decided to be used for rapid mixing rate, rapid mixing time, slow mixing time and sedimentation time tests. As shown in figure 13, the results of the 200-rpm test were the highest curve, and the 400-rpm curve was gentle, especially between approximately 13–23 minutes.

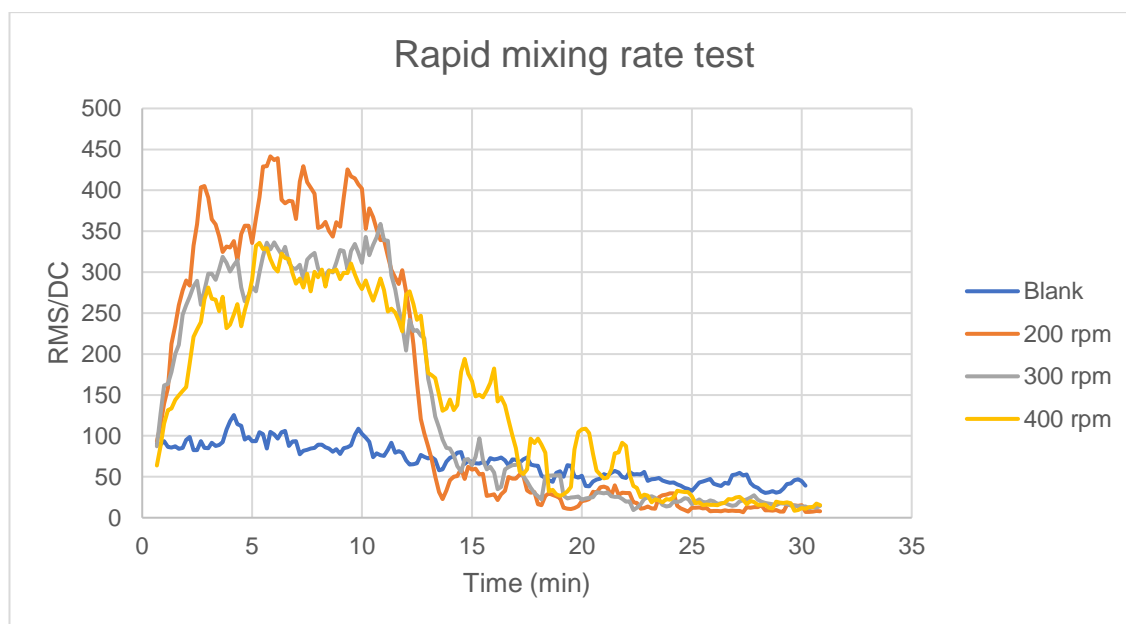


Figure 13. The PDA3000 results of the rapid mixing rate test with a 5-point moving average

The four phases' equations of figure 13 are shown in table 11.

Table 11. Equations of the PDA3000 results in the rapid mixing rate test

Sample	1st phase	2nd phase	3rd phase	4th phase
200 rpm	$y = 3,01x$	$y = 0,01x + 376$	$y = -2,16x + 1744$	$y = -0,04x + 71$
300 rpm	$y = 2,39x$	$y = 0,08x + 280$	$y = -1,03x + 964$	$y = -0,04x + 75$
400 rpm	$y = 1,92x$	$y = 0,05x + 266$	$y = -0,43x + 532$	$y = -0,08x + 142$

The slope of the first phase steepened in the order of 400, 300 and 200 rpm and the values of the y-intercept followed the same pattern in the second phase. In the third phase, the slope got flatter in the order of 200, 300 and 400 rpm. As shown in table 12, the 200 rpm results were also the most efficient and followed by the 300 and 400 rpm.

Table 12. Analysis results of the rapid mixing rate test

Sample		Blank	200 rpm	300 rpm	400 rpm
Coagulant dose (μmol)		0	300	300	300
Zeta potential (mV)	After rapid mixing	-18	-7,9	-8,6	-7,5
	After sedimentation	-14	-6,8	-7,3	-7,6
pH (after rapid mixing)		7,0	5,5	5,7	5,9
Turbidity (NTU)		1,1	1,1	1,0	1,4
UV254 absorbance		0,18	0,080	0,084	0,090
COD Unfiltered (mg/l)		27	14	14	17
COD Filtered (mg/l)		25	13	15	16
TOC (mg/l)		10	5,4	5,5	5,7
DOC (mg/l)		9,1	5,2	5,6	5,9
Fe ($\mu\text{g}/\text{Kg}$)		44	73	73	73

The 400-rpm rapid mixing was too fast, and some formed flocks might have broken down.

4.3.6 Rapid Mixing Time Test with Chemical-1

Curves of smooth mountain type increased in the order of 60 s, 40 s, 10 s and 20 s (figure 14).

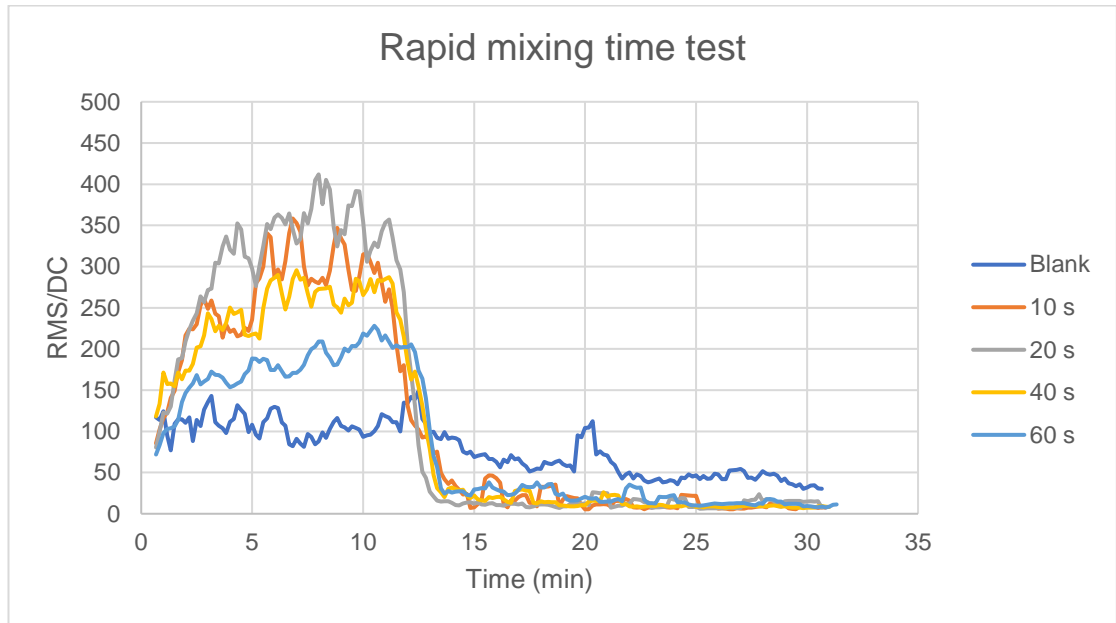


Figure 14. The PDA3000 results of the rapid mixing time test with a 5-point moving average

Apparently 60 s was too long for rapid mixing and affected for formation flocks. As shown in table 13, the 10 s was most efficient for growing flocks in the first phase, and the 20 s was the largest maximum flocculation index in the second phase.

Table 13. Equations of the PDA3000 results in the rapid mixing time test

Sample	1st phase	2nd phase	3rd phase	4th phase
10 s	$y = 2,23x$	$y = 0,18x + 218$	$y = -1,33x + 1097$	$y = -0,02x + 42$
20 s	$y = 1,86x$	$y = 0,07x + 319$	$y = -2,85x + 2192$	$y = 0,0008x + 11$
40 s	$y = 1,64x$	$y = 0,11x + 216$	$y = -1,48x + 1233$	$y = -0,01x + 31$
60 s	$y = 1,58x$	$y = 0,12x + 140$	$y = -1,33x + 1120$	$y = -0,02x + 49$

The chemical and physical results are shown in table 14.

Table 14. Analysis results of the rapid mixing time test

Sample		Blank	10 s	20 s	40 s	60 s
Coagulant dose (μmol)		0	300	300	300	300
Zeta potential (mV)	After rapid mixing	-14	-6,4	-6,6	-7,6	-4,5
	After sedimentation	-14	-5,4	-6,2	-7,1	-8,3
pH (after rapid mixing)		6,6	5,3	5,4	5,4	5,4
Turbidity (NTU)		1,3	1,0	1,5	0,97	0,89
UV254 absorbance		0,18	0,077	0,077	0,077	0,078
COD Unfiltered (mg/l)		28	14	14	14	15
COD Filtered (mg/l)		25	13	13	13	14
TOC (mg/l)		9,5	5,3	5,0	5,1	5,0
DOC (mg/l)		9,4	5,1	5,0	5,0	4,8
Fe ($\mu\text{g/Kg}$)		49	83	86	76	81

The zeta potential values after rapid mixing were variable. However, there was a trend in the zeta potential values after sedimentation. More specifically, the zeta potential values got closer to zero in order of 60 s, 40 s, 20 s and 10 s. Otherwise, the other results in the table were almost similar.

4.3.7 Slow Mixing Time Test with Chemical-1

Because of a computer problem, the PDA300 data of the 20 minutes sample could not be saved (figure 15).

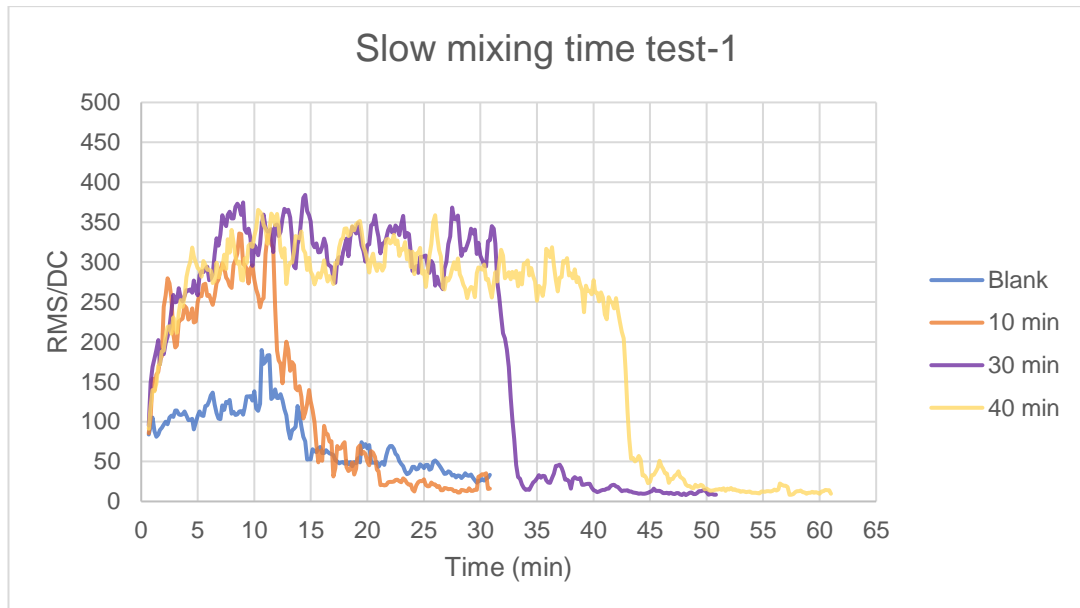


Figure 15. The PDA3000 results of the slow mixing time test-1 with a 5-point moving average

Flocks went to the bottom of beakers in all slow mixing time tests except in the 10- and 20-minutes tests on 29 April. One reason could be that some detergent residue might affect the results. The effluent was poured from a 20-liter canister into beakers for the tests of the blank, 30 and 40 minutes. For the 10- and 20-minutes tests, the effluent was poured from a ten-liter bucket, which was washed with detergent and rinsed properly. Thus, the 10- and 20-minutes samples were tested again on 4 May, and these flocks went to the bottom of the beakers (figure 16).

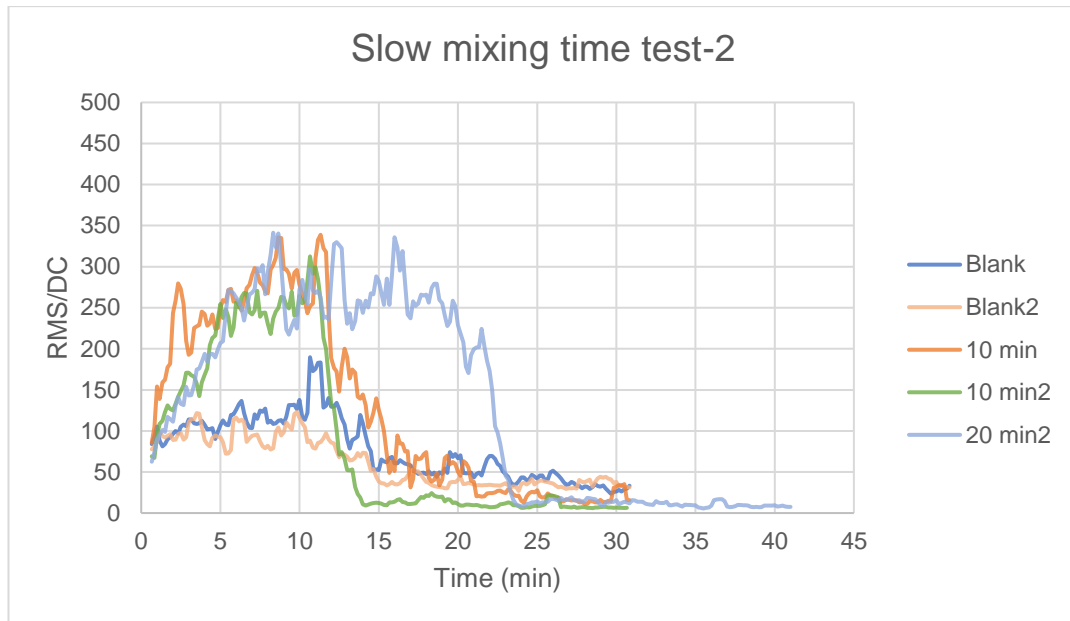


Figure 16. The PDA3000 results of the slow mixing time test-2 with a 5-point moving average

The RMS/DC value of the 10 minutes sample raised sharper than the samples of the 10 min2 and the 20 min2. Furthermore, the RMS/DC values of the sample 10 min dropped gently between approximately 10–20 minutes. Equations of four phases are shown in table 15.

Table 15. Equations of the PDA3000 results in the slow mixing time test

Sample	1st phase	2nd phase	3rd phase	4th phase
10 min	$y = 2,33x$	$y = 0,09x + 231$	$y = -0,79x + 796$	$y = -0,06x + 117$
30 min	$y = 1,03x$	$y = -0,03x + 358$	$y = -2,11x + 4228$	$y = -0,02x + 75$
40 min	$y = 1,43x$	$y = -0,02x + 327$	$y = -1,16x + 3099$	$y = -0,02x + 93$
10 min2	$y = 1,25x$	$y = 0,20x + 156$	$y = -1,66x + 1333$	$y = -0,008x + 21$
20 min2	$y = 0,87x$	$y = -0,04x + 293$	$y = -1,41x + 1982$	$y = -0,007x + 24$

There were no clear trends in the first and third phases. In the second phase, the samples of the 30 min and 40 min had higher maximum flocculation indexes than

the results of the 10 min, 10 min² and 20 min². In addition, the maximum flocculation index of the 10 min² sample was conspicuously lower than others because the slope value was 0,20 in the second phase.

The slower the mixing time, the better the results were, between 10–40 minutes in the chemical and physical results on 29 April (table 16).

Table 16. Analysis results of the slow mixing time test-1

Sample		Blank	10 min	20 min	30 min	40 min
Coagulant dose (μmol)		0	300	300	300	300
Zeta potential (mV)	After rapid mixing	-18	-7,7	-6,2	-5,6	-5,5
	After sedimentation	-14	-7,0	-6,0	-6,0	-5,9
pH (after rapid mixing)		6,8	5,7	5,5	5,3	5,3
Turbidity (NTU)		1,3	2,2	1,9	0,5	0,4
UV254 absorbance		0,18	0,084	0,078	0,076	0,075
COD Unfiltered (mg/l)		26	16	16	14	13
COD Filtered (mg/l)		24	15	14	12	12
TOC (mg/l)		9,4	5,5	4,9	4,8	4,9
DOC (mg/l)		9	5,5	5,1	4,9	4,7
Fe ($\mu\text{g/Kg}$)		41	58	66	57	58

Compared to the results on 4 May, there were relatively similar results in pH, turbidity, spectrometry, COD, TOC, and DOC (table 17).

Table 17. Analysis results of the slow mixing time test-2

Sample		Blank2	10 min2	20 min2
Coagulant dose (μmol)		0	300	300
Zeta potential (mV)	After rapid mixing	-15	-6,7	-7,9
	After sedimentation	-14	-8,4	-7,8
pH (after rapid mixing)		6,5	5,4	5,4
Turbidity (NTU)		1,3	1,2	1,0
UV254 absorbance		0,18	0,082	0,080
COD Unfiltered (mg/l)		25	13	15
COD Filtered (mg/l)		24	14	13
TOC (mg/l)		9,6	5,3	5,2
DOC (mg/l)		9,4	5,3	5,1
Fe ($\mu\text{g/Kg}$)		50	89	85

Even though most of the results were similar, there were 31 and 19 $\mu\text{g/Kg}$ differences in the iron amount and 1–1,8 mV differences in the zeta potential results. The detergent residue might have affected the results, or the deviation in repeatability might have been high.

4.3.8 Sedimentation-Time Test with Chemical-1

The PDA3000 results are shown in figure 17.

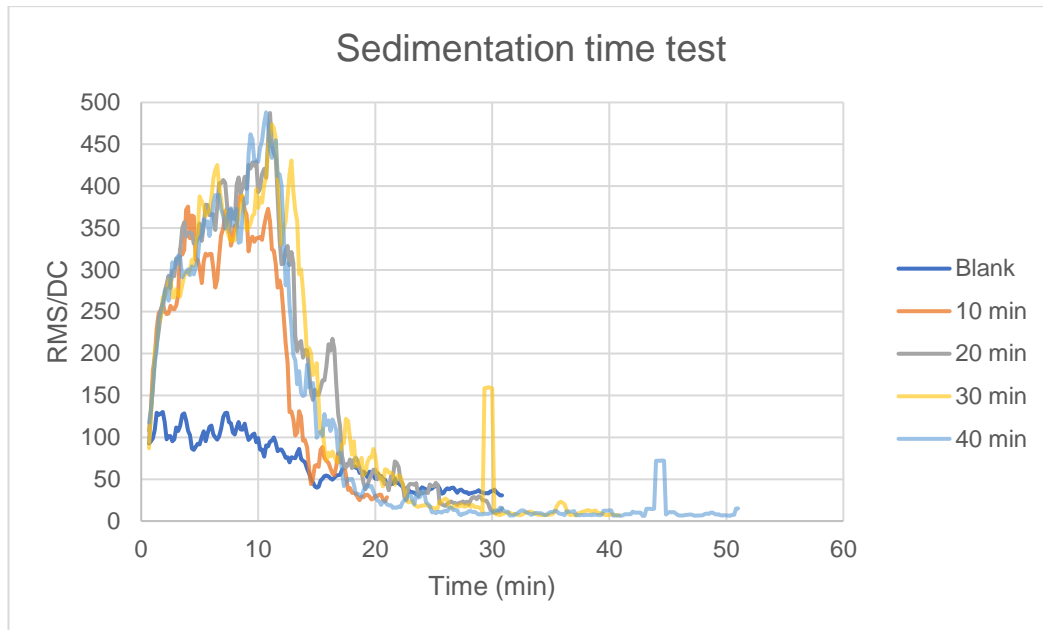


Figure 17. The PDA3000 results of the sedimentation time test with a 5-point moving average

From the figure, it can be said that the peaks were still ascending between approximately 2–10 minutes and there were big scatters even though same settings were used between 0–20,5 minutes. Two high peaks were omitted from calculations at 29,3 minutes in the 30 minutes results and at 44 minutes from the 40 minutes results due to possible bubbles (table 18).

Table 18. Equations of the PDA3000 results in the sedimentation time test

Sample	1st phase	2nd phase	3rd phase	4th phase
10 min	$y = 1,89x$	$y = 0,06x + 317$	$y = -1,95x + 1616$	$y = -0,16x + 214$
20 min	$y = 2,92x$	$y = 0,23x + 285$	$y = -0,76x + 870$	$y = -0,06x + 117$
30 min	$y = 2,63x$	$y = 0,20x + 275$	$y = -0,55x + 713$	$y = -0,06x + 144$
40 min	$y = 3,73x$	$y = 0,34x + 234$	$y = -0,65x + 753$	$y = -0,003x + 19$

There were no similarities in the first and second phases, even with the same rapid and slow mixing as in figure 17. When longer sedimentation times, the y-

intercepts got lower in the fourth phase. The chemical and physical results are shown in table 19.

Table 19. Analysis results of the sedimentation time test

Sample		Blank	10 min	20 min	30 min	40 min
Coagulant dose (μmol)		0	300	300	300	300
Zeta potential (mV)	After rapid mixing	-14	-5,6	-8,1	-6,8	-8,1
	After sedimentation	-13	-5,3	-8,5	-8,2	-7,8
pH (after rapid mixing)		6,5	5,5	5,6	5,6	5,6
Turbidity (NTU)		1,5	1,3	1,6	1,6	0,83
UV254 absorbance		0,18	0,083	0,084	0,083	0,082
COD Unfiltered (mg/l)		27	14	18	16	15
COD Filtered (mg/l)		25	14	13	14	16
TOC (mg/l)		10	5,5	5,4	5,5	5,4
DOC (mg/l)		10	5,4	5,3	5,4	5,3
Fe ($\mu\text{g/Kg}$)		52	74	67	58	77

The 10 min sample zeta potential values were approximately -5,5 and the others were approximately -8. Otherwise, the other chemical and physical results were relatively similar, so there were no significant trends.

4.4 Maximum Flocculation Index

Because the slope values were not always close to zero in the second phase, the y-intercept values did not clearly indicate the maximum flocculation index. Therefore, the linear equations and the RMS/DC average values were compared in the second phase (table 20).

Table 20. Comparison of the y-intercept values and the RMS/DC average values in the second phase

Test	Sample	2nd phase	
		Linear equation	RMS/DC average
Chemical-1	Trial2,2 (100 μ mol)	$y = 0,02x + 68$	76
	Trial1,2 (150 μ mol)	$y = 0,18x + 193$	268
	Trial3,2 (200 μ mol)	$y = 0,24x + 184$	280
	Trial4,2 (300 μ mol)	$y = 0,13x + 298$	345
Chemical-2	Trial1 (200 μ mol)	$y = 0,01x + 43$	47
	Trial2 (300 μ mol)	$y = -0,003x + 56$	55
	Trial3 (400 μ mol)	$y = -0,007x + 62$	59
pH adjustment with chemical-1	Trial1pH (150 μ mol)	$y = -0,16x + 313$	242
	Trial4pH (300 μ mol)	$y = -0,07x + 169$	139
	Trial5pH (400 μ mol)	$y = 0,21x + 149$	221
pH adjustment with chemical-2	Trial1pH (200 μ mol)	$y = 0,01x + 48$	53
	Trial2pH (300 μ mol)	$y = 0,007x + 60$	62
	Trial3pH (400 μ mol)	$y = -0,01x + 61$	56
Rapid mixing rate	200 rpm	$y = 0,01x + 376$	380
	300 rpm	$y = 0,08x + 280$	312
	400 rpm	$y = 0,05x + 266$	287
Rapid mixing time	10 s	$y = 0,18x + 218$	283
	20 s	$y = 0,07x + 319$	347
	40 s	$y = 0,11x + 216$	260
	60 s	$y = 0,12x + 140$	185
Slow mixing time	10 min	$y = 0,09x + 231$	265
	30 min	$y = -0,03x + 358$	327
	40 min	$y = -0,02x + 327$	299
	10 min ²	$y = 0,20x + 156$	235
	20 min ²	$y = -0,04x + 293$	264
Sedimentation time	10 min	$y = 0,06x + 317$	342
	20 min	$y = 0,23x + 285$	371
	30 min	$y = 0,20x + 275$	352
	40 min	$y = 0,34x + 234$	354

When the slope values were close to zero, the RMS/DC average values were also similar to the y-intercept values. When the RMS/DC average values were compared to the graphs of the PDA3000 results, the RMS/DC average values indicated the maximum flocculation index more accurately than the y-intercepts in the charts. The RMS/DC average proved especially useful in interpreting the sample Trial4pH and Trial5pH results in pH adjustment test (chemical-1).

4.5 Correlations

It was thought that there was some correlation between the y-intercept values in the fourth phase and the turbidity values. These correlation coefficients are shown in table 21.

Table 21. Correlation between the y-intercept values in the fourth phase and the turbidity values

Test	Sample	Intercept 4th phase	Turbidity (NTU)	Correlation coefficient
Chemical-1	Trial2,2 (100 μ mol)	37	0,18	-0,96
	Trial1,2 (150 μ mol)	58	0,15	
	Trial3,2 (200 μ mol)	75	0,14	
	Trial4,2 (300 μ mol)	79	0,12	
Chemical-2	Trial1 (200 μ mol)	40	0,93	0,72
	Trial2 (300 μ mol)	31	0,74	
	Trial3 (400 μ mol)	36	1,0	
pH adjustment with chemical-1	Trial1pH (150 μ mol)	20	1,1	0,45
	Trial4pH (300 μ mol)	50	1,6	
	Trial5pH (400 μ mol)	117	1,4	
pH adjustment with chemical-2	Trial1pH (200 μ mol)	50	1,2	-0,99
	Trial2pH (300 μ mol)	41	1,7	
	Trial3pH (400 μ mol)	32	2,5	
Rapid mixing rate	200 rpm	71	1,1	0,98
	300 rpm	75	1,0	
	400 rpm	142	1,4	
Rapid mixing time	10 s	42	1,0	-0,93
	20 s	11	1,5	
	40 s	31	0,97	
	60 s	49	0,89	
Slow mixing time	10 min	117	2,2	0,91
	30 min	75	1,2	
	40 min	93	1,0	
	10 min ²	21	0,48	
	20 min ²	24	0,41	
Sedimentation time	10 min	214	1,3	0,56
	20 min	117	1,6	
	30 min	144	1,6	
	40 min	19	0,83	

Some tests had low correlation coefficients and a trend could not be found from the correlation coefficient itself. However, the correlation coefficients of the rapid mixing rate and slow mixing time tests were over 0,9. In addition to that, the correlation coefficients were close to -1 in the chemical-1, pH adjustment (chemical-2) and rapid mixing time tests. As shown in table 22, there were some correlations between the zeta potential and the maximum flocculation index as well.

Table 22. Correlation between the zeta potential values and the maximum flocculation index values

Test	Sample	Zeta potential (mV)	2nd phase	Correlation coefficient
		After sedimentation	RMS/DC average	
Chemical-1	Trial2,2 (100 μmol)	-11	76	0,81
	Trial1,2 (150 μmol)	-10	268	
	Trial3,2 (200 μmol)	-8,3	280	
	Trial4,2 (300 μmol)	-5,6	345	
Chemical-2	Trial1 (200 μmol)	-7,2	47	1,0
	Trial2 (300 μmol)	-6,2	55	
	Trial3 (400 μmol)	-5,5	59	
pH adjustment with chemical-1	Trial1pH (150 μmol)	-8,3	242	-0,36
	Trial4pH (300 μmol)	-6,1	139	
	Trial5pH (400 μmol)	-4,9	221	
pH adjustment with chemical-2	Trial1pH (200 μmol)	-7,4	53	-0,047
	Trial2pH (300 μmol)	-7,2	62	
	Trial3pH (400 μmol)	-6,1	56	
Rapid mixing rate	200 rpm	-6,8	380	0,99
	300 rpm	-7,3	312	
	400 rpm	-7,6	287	
Rapid mixing time	10 s	-5,4	283	0,79
	20 s	-6,2	347	
	40 s	-7,1	260	
	60 s	-8,3	185	
Slow mixing time	10 min	-7,0	265	0,92
	30 min	-6,0	327	
	40 min	-5,9	299	
	10 min ²	-8,4	235	
	20 min ²	-7,8	264	
Sedimentation time	10 min	-5,3	342	-0,81
	20 min	-8,5	371	
	30 min	-8,2	352	
	40 min	-7,8	354	

The zeta potential values measured after sedimentation were used for the comparison because they had more clear trends than the values measured after rapid mixing. The pH adjustment and sedimentation tests were variable, but they had relatively high correlation coefficients. The zeta potential values (after sedimentation) and others correlation details are shown in appendix 3.

5 Conclusion

The PDA3000 results were divided into four phases. In the first phase, the slope showed how fast flocks formed, and the equation must have no y-intercept. In the second phase, the RMS/DC average value showed the maximum flocculation index, which indicates how big flocks were formed. The slope could be used to determine whether the flocks were still growing or not. In the third phase, the slope indicated how fast flocks settled. There might be some correlation between the y-intercept and turbidity under specific conditions in the fourth phase.

Among 100–400 μmol doses, the larger dose, the better the chemical and physical results especially zeta potential values. There were no clear trends in the sedimentation time test results, although there were some correlations in the rapid mixing time and slow mixing time test. The zeta potential values were closer to zero with shorter rapid mixing time and longer slow mixing time. In addition to that, the 200-rpm rapid mixing rate had the lowest zeta potential, and the 400-rpm test had the highest. Overall, the zeta potential values after sedimentation were closer to zero than the values from just after rapid mixing in the most results. So, the particle charges were neutralized, and the after-sedimentation samples were more unstable suspensions.

In addition to other parameters, the chemical-1 pH adjustment test had to take into account the time it takes to add the pH adjustment chemical and for the pH value to stabilize. Thus, the shape and trends of the PDA3000 results were different in that test than the other tests using chemical-1. The 4-phase idea arising from the chemical-1 tests results might not have been suitable for chemical-2, and the repeatability might be a problem. Jar tests were primarily measured once for each setting. Although some tests used the same flocculator settings, and only the execution dates were different, there were differences in the tests results, e.g., in the 300 μmol dose chemical-1 test and the 400-rpm rapid mixing rate test.

Equations of the four phases were valuable indicators for understanding the state of the flocks. However, the equations alone could not always fully describe the state of the flocks. It is always necessary to compare the graph of the PDA3000 results and the equations to supplement the parts where the equations alone are not as clear as necessary.

References

- 1 Sustainable Development. Online material. United Nations. <<https://sdgs.un.org/goals/goal6>>. Read 28.7.2022.
- 2 Valanko, Rasmus; Shestakova, Marina; Pekonen, Pentti; Hesampour, Mehrdad; Hansen, Bengt; Halttunen, Sakari; Hofmann, Reinhard; Pretorius, Ruan; Penttinen, Matias; Recktenwald, Michael; Karpova, Tatjana; van Rossum, Ronald; Grönfors, Outi; Mattsson, Eva; Ahlgren, Jonni; Nilsson, Britt; Leen, Paul; Havansi, Hannele & Abinet, Roderick. About water treatment. Online material. Kemira Oyj. <<https://www.kemira.com/insights/water-handbook-2020/>>. Read 22.7.2022.
- 3 Bratby, John. 2016. Coagulation and Flocculation in Water and Wastewater Treatment. 3rd edition. E-book. IWA Publishing.
- 4 Satterfield, Zane. Jar Testing. Online material. National environmental services center. <https://sswm.info/sites/default/files/reference_attachments/SATTERFIELD%202009.%20Tech%20brief%20-%20Jar%20Testing.pdf#:~:text=Jar%20testing%20is%20a%20method%20of%20simulating%20a,operate%20with%20a%20particular%20type%20of%20raw%20water>. Read 22.7.2022.
- 5 PDA3000 Particle & Flocculation Monitor, Operating Manual. Online material. Rank Brothers Ltd. <<https://www.rankbrothers.co.uk/downloads/PDA3000.pdf>>. Read 22.7.2022.
- 6 Coagulation and Flocculation. Online material. Rural water association. <<https://www.mrwa.com/WaterWorksMnl/Chapter%2012%20Coagulation.pdf>>. Read 1.9.2022.
- 7 Zeta potential - An introduction in 30 minutes. Online material. Malvern Instruments Limited. <<https://www.research.colostate.edu/wp-content/uploads/2018/11/ZetaPotential-Introduction-in-30min-Malvern.pdf>>. Read 1.9.2022.
- 8 C. Hiemenz, Paul & Rajagopalan, Raj. 1997. Principles of Colloid and Surface Chemistry. Boca Raton: Taylor & Francis Group.
- 9 Boyles, Wayne. 1997. The Science of Chemical Oxygen Demand Technical indormation Series, Booklet No. 9. Online material. Hach Company. <<https://www.hach.com/asset-get.download-en.jsa?code=61786>>. Read 25.9.2022.

- 10 C. Harris, Daniel. 2016. Quantitative Chemical Analysis. Ninth Edition. New York: W. H. Freeman and Company.
- 11 Baird, Colin & Cann, Michael. 2012. Environmental Chemistry. Fifth Edition. New York: W. H. Freeman and Company.
- 12 SFS 3036 Determination of chemical oxygen demand (COD_{Mn} -value or KMnO₄ -number) in water, oxidation with permanganate. 1981. Second edition. Suomen standardisoimisliitto.
- 13 SFS 5504 Determination of chemical oxygen demand (COD_{Cr}) in water with the closed tube method, oxidation with dichromate. 1988. Suomen standardisoimisliitto.
- 14 UV254 online analyzer. Online material. Real Tech Inc. <https://realtechwater.com/w_p/wp-content/uploads/2018/07/UV254-Analyzer-M-Series-Specification-Sheet-Real-Tech-1.pdf>. Read 26.9.2022.

Results of 400 rpm rapid mixing rate test

Phase	Time (s)	RMS/DC
	0	9,31
	10	36,33
1	20	55,87
1	30	133,87
1	40	83,81
1	50	129,15
1	60	172,15
1	70	137,81
1	80	143,55
1	90	137,45
1	100	156,63
1	110	199,43
1	120	160,70
1	130	289,15
2	140	299,43
2	150	201,79
2	160	244,08
2	170	300,08
2	180	361,77
2	190	229,52
2	200	195,93
2	210	173,65
2	220	388,59
2	230	169,65
2	240	251,02
2	250	259,27
2	260	235,41
2	270	254,39
2	280	265,93
2	290	335,52
2	300	364,08
2	310	440,98
2	320	272,36
2	330	227,94
2	340	341,23
2	350	297,51
2	360	387,55
2	370	249,08
2	380	337,30
2	390	315,21
2	400	291,97
2	410	301,19

Phase	Time (s)	RMS/DC
2	420	184,45
2	430	367,93
2	440	261,63
2	450	375,21
2	460	194,47
2	470	303,27
2	480	335,11
2	490	307,16
2	500	272,65
2	510	290,44
2	520	299,43
2	530	345,24
2	540	249,80
2	550	310,40
2	560	288,52
2	570	359,89
2	580	277,55
2	590	196,58
2	600	273,28
2	610	342,76
2	620	295,22
3	630	217,92
3	640	257,04
3	650	348,47
3	660	271,24
3	670	164,63
3	680	235,63
3	690	232,90
3	700	300,78
3	710	204,15
3	720	388,27
3	730	257,24
3	740	154,47
3	750	205,30
3	760	228,89
3	770	215,57
3	780	79,98
3	790	141,00
3	800	186,59
3	810	128,81
3	820	116,67
3	830	94,64

Phase	Time (s)	RMS/DC
3	840	194,63
3	850	122,21
3	860	160,23
3	870	321,20
3	880	172,36
3	890	104,34
3	900	74,30
3	910	69,78
3	920	330,21
3	930	157,00
3	940	144,77
3	950	121,30
3	960	158,28
3	970	127,84
3	980	184,07
3	990	95,74
3	1000	31,20
3	1010	64,05
3	1020	49,03
3	1030	40,94
3	1040	80,67
3	1050	60,83
3	1060	251,93
4	1070	21,08
4	1080	69,72
4	1090	43,37
4	1100	11,75
4	1110	15,40
4	1120	30,81
4	1130	40,94
4	1140	34,46
4	1150	21,48
4	1160	32,83
4	1170	57,56
4	1180	270,80
4	1190	139,78
4	1200	39,72
4	1210	35,28
4	1220	30,40
4	1230	144,95
4	1240	36,89
4	1250	14,59
4	1260	13,38
4	1270	34,05

Phase	Time (s)	RMS/DC
4	1280	194,54
4	1290	136,36
4	1300	20,67
4	1310	72,62
4	1320	13,37
4	1330	23,51
4	1340	63,24
4	1350	8,51
4	1360	17,43
4	1370	29,19
4	1380	16,62
4	1390	22,29
4	1400	25,94
4	1410	11,76
4	1420	17,43
4	1430	36,09
4	1440	19,46
4	1450	40,94
4	1460	51,52
4	1470	11,76
4	1480	32,43
4	1490	21,08
4	1500	14,19
4	1510	8,92
4	1520	16,62
4	1530	16,21
4	1540	23,92
4	1550	12,16
4	1560	10,13
4	1570	14,59
4	1580	25,14
4	1590	30,01
4	1600	34,06
4	1610	8,11
4	1620	25,94
4	1630	29,60
4	1640	11,35
4	1650	8,11
4	1660	27,98
4	1670	19,87
4	1680	11,76
4	1690	11,76
4	1700	8,92
4	1710	8,11

Phase	Time (s)	RMS/DC
4	1720	17,03
4	1730	52,72
4	1740	6,08
4	1750	6,49
4	1760	11,76
4	1770	11,35
4	1780	6,89

Phase	Time (s)	RMS/DC
4	1790	10,95
4	1800	17,84
4	1810	8,11
4	1820	20,28
4	1830	6,89
	1840	33,25
	1850	7,71

Pictures of Jar tests

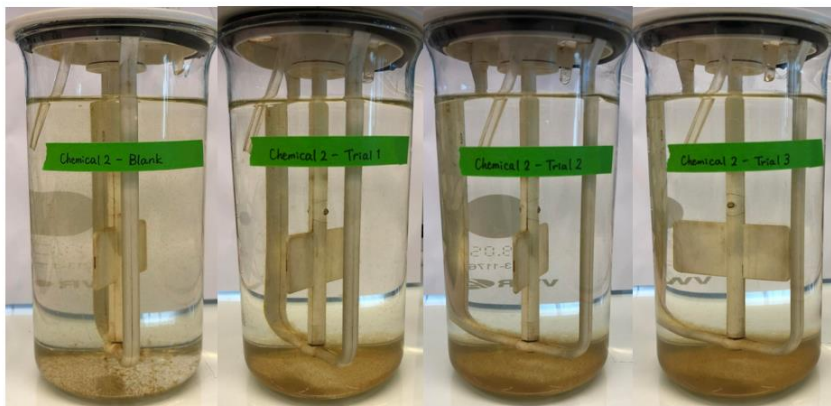
Chemical-1 test

Blank4 Trial2,2 Trial1,2 Trial3,2 Trial4,2



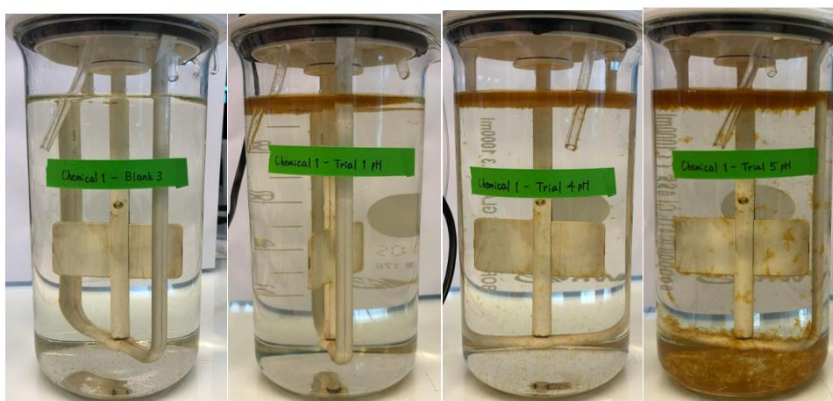
Chemical-2 test

Blank Trial1 Trial2 Trial3



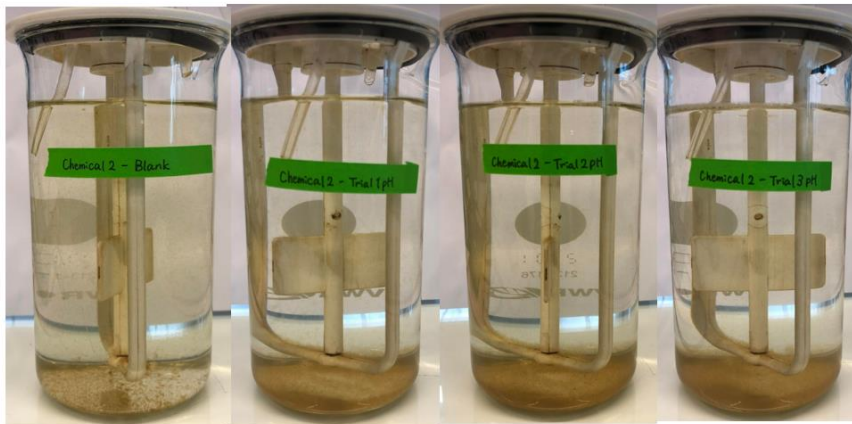
pH adjustment test (chemical-1)

Blank3 Trial1pH Trial2pH Trial3pH



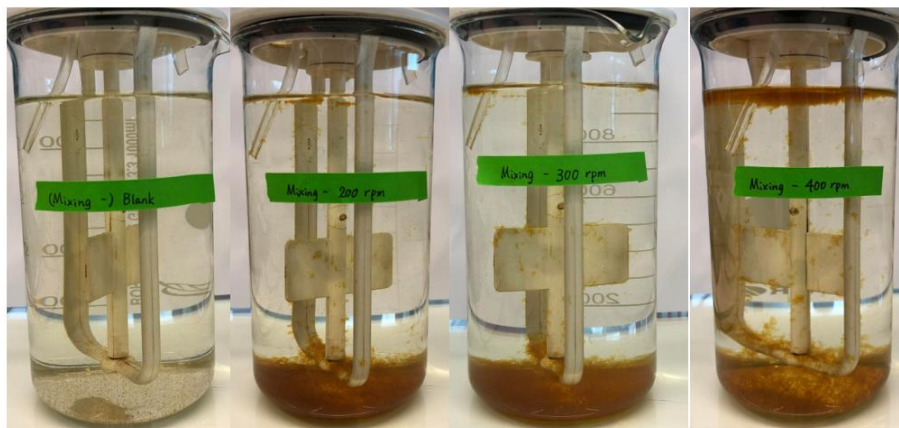
pH adjustment test (chemical-2)

Blank Trial1pH Trial2pH Trial3pH



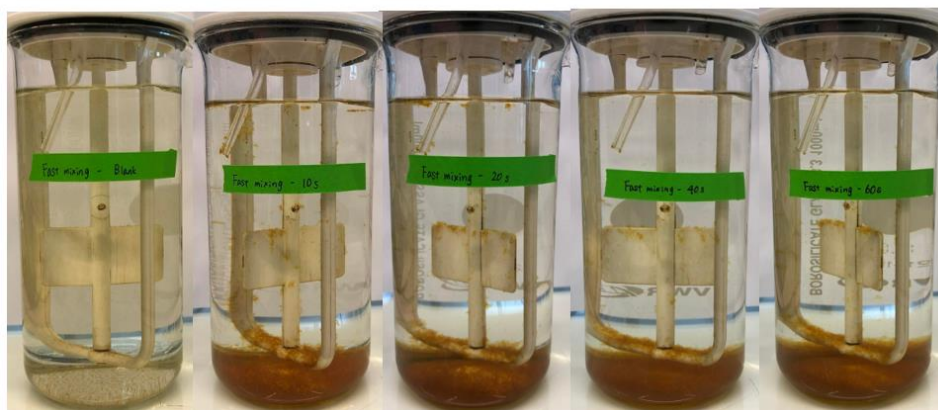
Rapid mixing rate test

Blank 200rpm 300rpm 400rpm

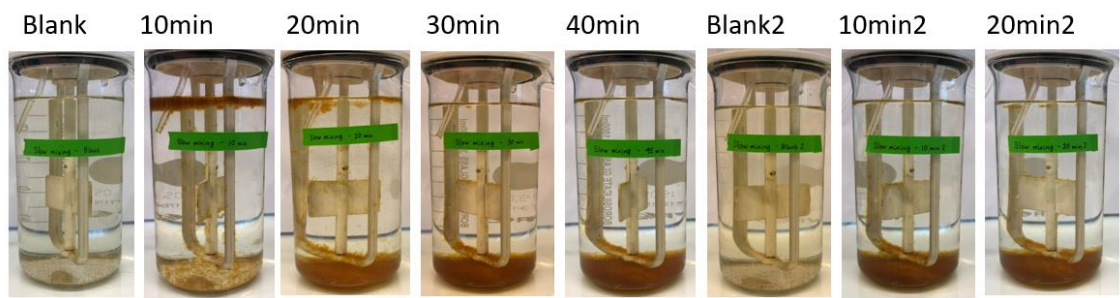


Rapid mixing rate test

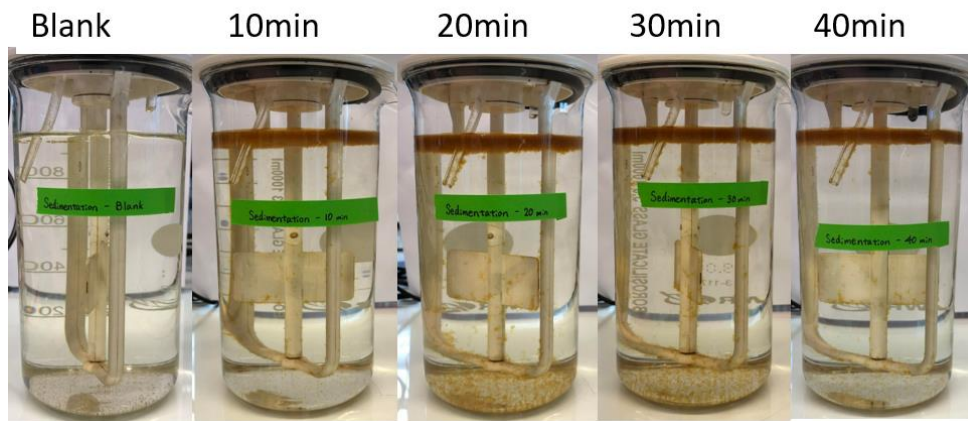
Blank 10s 20s 40s 60s



Slow mixing time test



Sedimentation time test



Correlation between zeta potential and others

Test	Sample	Zeta potential (mV)		Correlation coefficient
		After rapid mixing	After sedimentation	
Chemical-1	Blank4	-16	-13	0,86
	Trial2,2 (100 μ mol)	-14	-11	
	Trial1,2 (150 μ mol)	-10	-10	
	Trial3,2 (200 μ mol)	-11	-8,3	
	Trial4,2 (300 μ mol)	-8,6	-5,6	
Chemical-2	Blank	-13	-12	0,98
	Trial1 (200 μ mol)	-10	-7,2	
	Trial2 (300 μ mol)	-8,6	-6,2	
	Trial3 (400 μ mol)	-7,3	-5,5	
pH adjustment with chemical-1	Blank3	-14	-13	0,98
	Trial1pH (150 μ mol)	-10	-8,3	
	Trial4pH (300 μ mol)	-6,9	-6,1	
	Trial5pH (400 μ mol)	-7,4	-4,9	
pH adjustment with chemical-2	Blank	-13	-12	0,85
	Trial1pH (200 μ mol)	-10	-7,4	
	Trial2pH (300 μ mol)	-6,0	-7,2	
	Trial3pH (400 μ mol)	-6,8	-6,1	
Rapid mixing rate	Blank	-18	-14	0,99
	200 rpm	-7,9	-6,8	
	300 rpm	-8,6	-7,3	
	400 rpm	-7,5	-7,6	
Rapid mixing time	Blank	-14	-14	0,84
	10 s	-6,4	-5,4	
	20 s	-6,6	-6,2	
	40 s	-7,6	-7,1	
	60 s	-4,5	-8,3	
Slow mixing time	Blank	-18	-14	0,97
	10 min	-7,7	-7,0	
	20 min	-6,2	-6,0	
	30 min	-5,6	-6,0	
	40 min	-5,5	-5,9	
	Blank2	-15	-14	
	10 min2	-6,7	-8,4	
	20 min2	-7,9	-7,8	
Sedimentation time	Blank	-14	-13	0,97
	10 min	-5,6	-5,3	
	20 min	-8,1	-8,5	
	30 min	-6,8	-8,2	
	40 min	-8,1	-7,8	

Test	Sample	Zeta potential (mV)	2nd phase	Correlation coefficient
		After rapid mixing	RMS/DC average	
Chemical-1	Trial2,2 (100 μmol)	-14	76	0,95
	Trial1,2 (150 μmol)	-10	268	
	Trial3,2 (200 μmol)	-11	280	
	Trial4,2 (300 μmol)	-8,6	345	
Chemical-2	Trial1 (200 μmol)	-10	47	1,0
	Trial2 (300 μmol)	-8,6	55	
	Trial3 (400 μmol)	-7,3	59	
pH adjustment with chemical-1	Trial1pH (150 μmol)	-10	242	-0,76
	Trial4pH (300 μmol)	-6,9	139	
	Trial5pH (400 μmol)	-7,4	221	
pH adjustment with chemical-2	Trial1pH (200 μmol)	-10	53	0,86
	Trial2pH (300 μmol)	-6,0	62	
	Trial3pH (400 μmol)	-6,8	56	
Rapid mixing rate	200 rpm	-7,9	380	-0,13
	300 rpm	-8,6	312	
	400 rpm	-7,5	287	
Rapid mixing time	10 s	-6,4	283	-0,64
	20 s	-6,6	347	
	40 s	-7,6	260	
	60 s	-4,5	185	
Slow mixing time	10 min	-7,7	265	0,68
	30 min	-5,6	327	
	40 min	-5,5	299	
	10 min ²	-6,7	235	
	20 min ²	-7,9	264	
Sedimentation time	10 min	-5,6	342	-0,82
	20 min	-8,1	371	
	30 min	-6,8	352	
	40 min	-8,1	354	

Test	Sample	Zeta potential (mV)	Turbidity (NTU)	Correlation coefficient
		After sedimentation		
Chemical-1	Blank4	-13	1,4	-0,71
	Trial2,2 (100 μ mol)	-11	0,18	
	Trial1,2 (150 μ mol)	-10	0,15	
	Trial3,2 (200 μ mol)	-8,3	0,14	
	Trial4,2 (300 μ mol)	-5,6	0,12	
Chemical-2	Blank	-12	1,4	-0,86
	Trial1 (200 μ mol)	-7,2	0,93	
	Trial2 (300 μ mol)	-6,2	0,74	
	Trial3 (400 μ mol)	-5,5	1,0	
pH adjustment with chemical-1	Blank3	-13	1,2	0,73
	Trial1pH (150 μ mol)	-8,3	1,1	
	Trial4pH (300 μ mol)	-6,1	1,6	
	Trial5pH (400 μ mol)	-4,9	1,4	
pH adjustment with chemical-2	Blank	-12	1,4	0,52
	Trial1pH (200 μ mol)	-7,4	1,2	
	Trial2pH (300 μ mol)	-7,2	1,7	
	Trial3pH (400 μ mol)	-6,1	2,5	
Rapid mixing rate	Blank	-14	1,1	0,20
	200 rpm	-6,8	1,1	
	300 rpm	-7,3	1,0	
	400 rpm	-7,6	1,4	
Rapid mixing time	Blank	-14	1,3	-0,30
	10 s	-5,4	1,0	
	20 s	-6,2	1,5	
	40 s	-7,1	1,0	
	60 s	-8,3	0,89	
Slow mixing time	Blank	-14	1,3	-0,15
	10 min	-7,0	2,2	
	20 min	-6,0	1,9	
	30 min	-6,0	0,5	
	40 min	-5,9	0,41	
	Blank2	-14	1,3	
	10 min2	-8,4	1,2	
	20 min2	-7,8	1,0	
Sedimentation time	Blank	-13	1,5	-0,33
	10 min	-5,3	1,3	
	20 min	-8,5	1,6	
	30 min	-8,2	1,6	
	40 min	-7,8	0,83	

Test	Sample	Zeta potential (mV)	UV 254 absorbance	Correlation coefficient
		After sedimentation		
Chemical-1	Blank4	-13	0,21	-0,034
	Trial2,2 (100 μ mol)	-11	3,4	
	Trial1,2 (150 μ mol)	-10	1,7	
	Trial3,2 (200 μ mol)	-8,3	1,5	
	Trial4,2 (300 μ mol)	-5,6	0,97	
Chemical-2	Blank	-12	0,21	-0,99
	Trial1 (200 μ mol)	-7,2	0,15	
	Trial2 (300 μ mol)	-6,2	0,14	
	Trial3 (400 μ mol)	-5,5	0,14	
pH adjustment with chemical-1	Blank3	-13	0,18	-0,98
	Trial1pH (150 μ mol)	-8,3	0,10	
	Trial4pH (300 μ mol)	-6,1	0,079	
	Trial5pH (400 μ mol)	-4,9	0,076	
pH adjustment with chemical-2	Blank	-12	0,21	-0,99
	Trial1pH (200 μ mol)	-7,4	0,15	
	Trial2pH (300 μ mol)	-7,2	0,15	
	Trial3pH (400 μ mol)	-6,1	0,14	
Rapid mixing rate	Blank	-14	0,18	-1,0
	200 rpm	-6,8	0,080	
	300 rpm	-7,3	0,084	
	400 rpm	-7,6	0,090	
Rapid mixing time	Blank	-14	0,18	-0,95
	10 s	-5,4	0,077	
	20 s	-6,2	0,077	
	40 s	-7,1	0,077	
	60 s	-8,3	0,078	
Slow mixing time	Blank	-14	0,18	-0,98
	10 min	-7,0	0,084	
	20 min	-6,0	0,078	
	30 min	-6,0	0,076	
	40 min	-5,9	0,075	
	Blank2	-14	0,18	
	10 min2	-8,4	0,082	
	20 min2	-7,8	0,08	
Sedimentation time	Blank	-13	0,18	-0,91
	10 min	-5,3	0,083	
	20 min	-8,5	0,084	
	30 min	-8,2	0,083	
	40 min	-7,8	0,082	

Test	Sample	Zeta potential (mV)	COD (mg/l) Unfiltered	Correlation coefficient
		After sedimentation		
Chemical-1	Blank4	-13	35	-0,94
	Trial2,2 (100 μ mol)	-11	30	
	Trial1,2 (150 μ mol)	-10	24	
	Trial3,2 (200 μ mol)	-8,3	23	
	Trial4,2 (300 μ mol)	-5,6	20	
Chemical-2	Blank	-12	32	-0,98
	Trial1 (200 μ mol)	-7,2	27	
	Trial2 (300 μ mol)	-6,2	24	
	Trial3 (400 μ mol)	-5,5	24	
pH adjustment with chemical-1	Blank3	-13	26	-0,99
	Trial1pH (150 μ mol)	-8,3	18	
	Trial4pH (300 μ mol)	-6,1	14	
	Trial5pH (400 μ mol)	-4,9	14	
pH adjustment with chemical-2	Blank	-12	32	-0,98
	Trial1pH (200 μ mol)	-7,4	25	
	Trial2pH (300 μ mol)	-7,2	27	
	Trial3pH (400 μ mol)	-6,1	24	
Rapid mixing rate	Blank	-14	27	-0,99
	200 rpm	-6,8	14	
	300 rpm	-7,3	14	
	400 rpm	-7,6	17	
Rapid mixing time	Blank	-14	28	-0,96
	10 s	-5,4	14	
	20 s	-6,2	14	
	40 s	-7,1	14	
	60 s	-8,3	15	
Slow mixing time	Blank	-14	26	-0,93
	10 min	-7,0	16	
	20 min	-6,0	16	
	30 min	-6,0	14	
	40 min	-5,9	13	
	Blank2	-14	25	
	10 min2	-8,4	13	
	20 min2	-7,8	15	
Sedimentation time	Blank	-13	27	-0,96
	10 min	-5,3	14	
	20 min	-8,5	18	
	30 min	-8,2	16	
	40 min	-7,8	15	

Test	Sample	Zeta potential (mV)	COD (mg/l) Filtered	Correlation coefficient
		After sedimentation		
Chemical-1	Blank4	-13	31	-0,95
	Trial2,2 (100 µmol)	-11	27	
	Trial1,2 (150 µmol)	-10	23	
	Trial3,2 (200 µmol)	-8,3	23	
	Trial4,2 (300 µmol)	-5,6	20	
Chemical-2	Blank	-12	30	-1,0
	Trial1 (200 µmol)	-7,2	23	
	Trial2 (300 µmol)	-6,2	22	
	Trial3 (400 µmol)	-5,5	22	
pH adjustment with chemical-1	Blank3	-13	25	-0,97
	Trial1pH (150 µmol)	-8,3	15	
	Trial4pH (300 µmol)	-6,1	13	
	Trial5pH (400 µmol)	-4,9	13	
pH adjustment with chemical-2	Blank	-12	30	-1,0
	Trial1pH (200 µmol)	-7,4	23	
	Trial2pH (300 µmol)	-7,2	23	
	Trial3pH (400 µmol)	-6,1	21	
Rapid mixing rate	Blank	-14	25	-1,0
	200 rpm	-6,8	13	
	300 rpm	-7,3	15	
	400 rpm	-7,6	16	
Rapid mixing time	Blank	-14	25	-0,96
	10 s	-5,4	13	
	20 s	-6,2	13	
	40 s	-7,1	13	
	60 s	-8,3	14	
Slow mixing time	Blank	-14	24	-0,97
	10 min	-7,0	15	
	20 min	-6,0	14	
	30 min	-6,0	12	
	40 min	-5,9	12	
	Blank2	-14	24	
	10 min2	-8,4	14	
	20 min2	-7,8	13	
Sedimentation time	Blank	-13	25	-0,88
	10 min	-5,3	14	
	20 min	-8,5	13	
	30 min	-8,2	14	
	40 min	-7,8	16	

Test	Sample	Zeta potential (mV)	TOC (mg/l)	Correlation coefficient
		After sedimentation		
Chemical-1	Blank4	-13	12	-0,93
	Trial2,2 (100 µmol)	-11	10	
	Trial1,2 (150 µmol)	-10	8,2	
	Trial3,2 (200 µmol)	-8,3	8,2	
	Trial4,2 (300 µmol)	-5,6	6,9	
Chemical-2	Blank	-12	12	-0,99
	Trial1 (200 µmol)	-7,2	9,4	
	Trial2 (300 µmol)	-6,2	9,3	
	Trial3 (400 µmol)	-5,5	8,9	
pH adjustment with chemical-1	Blank3	-13	9,9	-0,99
	Trial1pH (150 µmol)	-8,3	6,6	
	Trial4pH (300 µmol)	-6,1	5,0	
	Trial5pH (400 µmol)	-4,9	5,0	
pH adjustment with chemical-2	Blank	-12	12	-0,99
	Trial1pH (200 µmol)	-7,4	8,8	
	Trial2pH (300 µmol)	-7,2	8,3	
	Trial3pH (400 µmol)	-6,1	8,0	
Rapid mixing rate	Blank	-14	10	-1,0
	200 rpm	-6,8	5,4	
	300 rpm	-7,3	5,5	
	400 rpm	-7,6	5,7	
Rapid mixing time	Blank	-14	9,5	-0,93
	10 s	-5,4	5,3	
	20 s	-6,2	5,0	
	40 s	-7,1	5,1	
	60 s	-8,3	5,0	
Slow mixing time	Blank	-14	9,4	-0,98
	10 min	-7,0	5,5	
	20 min	-6,0	4,9	
	30 min	-6,0	4,8	
	40 min	-5,9	4,9	
	Blank2	-14	9,6	
	10 min2	-8,4	5,3	
	20 min2	-7,8	5,2	
Sedimentation time	Blank	-13	10	-0,90
	10 min	-5,3	5,5	
	20 min	-8,5	5,4	
	30 min	-8,2	5,5	
	40 min	-7,8	5,4	

Test	Sample	Zeta potential (mV)	DOC (mg/l)	Correlation coefficient
		After sedimentation		
Chemical-1	Blank4	-13	12	-0,94
	Trial2,2 (100 µmol)	-11	9,6	
	Trial1,2 (150 µmol)	-10	8,2	
	Trial3,2 (200 µmol)	-8,3	8,0	
	Trial4,2 (300 µmol)	-5,6	6,6	
Chemical-2	Blank	-12	12	-0,99
	Trial1 (200 µmol)	-7,2	9,9	
	Trial2 (300 µmol)	-6,2	8,8	
	Trial3 (400 µmol)	-5,5	8,9	
pH adjustment with chemical-1	Blank3	-13	9,6	-0,99
	Trial1pH (150 µmol)	-8,3	6,5	
	Trial4pH (300 µmol)	-6,1	4,9	
	Trial5pH (400 µmol)	-4,9	4,9	
pH adjustment with chemical-2	Blank	-12	12	-0,99
	Trial1pH (200 µmol)	-7,4	8,6	
	Trial2pH (300 µmol)	-7,2	8,1	
	Trial3pH (400 µmol)	-6,1	7,8	
Rapid mixing rate	Blank	-14	9,1	-1,0
	200 rpm	-6,8	5,2	
	300 rpm	-7,3	5,6	
	400 rpm	-7,6	5,9	
Rapid mixing time	Blank	-14	9,4	-0,93
	10 s	-5,4	5,1	
	20 s	-6,2	5,0	
	40 s	-7,1	5,0	
	60 s	-8,3	4,8	
Slow mixing time	Blank	-14	9,0	-0,98
	10 min	-7,0	5,5	
	20 min	-6,0	5,1	
	30 min	-6,0	4,9	
	40 min	-5,9	4,7	
	Blank2	-14	9,4	
	10 min2	-8,4	5,3	
	20 min2	-7,8	5,1	
Sedimentation time	Blank	-13	10	-0,90
	10 min	-5,3	5,4	
	20 min	-8,5	5,3	
	30 min	-8,2	5,4	
	40 min	-7,8	5,3	