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Improved Chemical Dosing in Ryaverket's Post-Denitrification Process

Bachelor's thesis in Chemical engineering

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Abstract

This thesis was conducted at Gryaab AB's wastewater treatment plant, Ryaverket, in Gothenburg, Sweden. The project focused on improving the dosing control of methanol and phosphoric acid in the post-denitrification (ED) process. Methanol represents a significant operational cost and a large part of the plant's carbon footprint, while phosphoric acid is essential for maintaining effective denitrification. Previous investigations indicated uneven dosing between the six ED lines, resulting in suboptimal treatment efficiency.

To address this, a systematic sampling campaign was performed over several weeks. Samples were taken three times per week from each of the six ED lines and from the influent to the ED process. The samples were analysed for phosphate, nitrate, and chemical oxygen demand (COD). Based on these results, adjustments to methanol and phosphoric acid dosing were made through the DeltaV control system.

The results showed that phosphate concentrations varied significantly between lines, indicating inconsistencies in phosphoric acid dosing. Adjustments reduced some of these differences, but complete balance was not achieved, likely due to discrepancies between set and actual valve opening times. Similarly, variations in nitrate concentration suggested uneven methanol dosing, which was traced to unreliable flow measurements from oversized meters.

To ensure more stable and efficient chemical dosing, future work should focus on improving instrumentation reliability, including the replacement of flow meters and calibration of valve control. These improvements are expected to enhance process stability, reduce costs, and minimize environmental impact.

1. Introduction

Wastewater treatment is an essential process to maintain the health of our oceans by keeping pollution and sickness from spreading. Gryaab AB is the owner of the wastewater treatment plant Ryaverket, located in Gothenburg, Sweden and has the responsibility of treating the water of approximately 824 000 people [1]. The 13-mile-long underground tunnel network leads wastewater to Ryaverket from Ale, Gothenburg, Härryda, Kungälv, Lerum, Mölndal, and Partille. Ryaverket's wastewater treatment consists of mechanical, biological and chemical treatment [1]. The focus of this thesis will be on the biological treatment conducted in the denitrification process.

Methanol and phosphoric acid are added to the post-denitrification (ED) process. Primarily, methanol contributes to a significant annual cost, as well as a large portion of Ryaverket's carbon footprint [1]. Previous work has revealed that the dosing of methanol and phosphoric acid is uneven across the six lines that make up the ED process. The aim of this thesis will be to map the differences in the dosing of methanol and phosphoric acid across the six different lines and subsequently even out these discrepancies. The thesis will include tasks such as creating a test plan, collecting and preparing samples, and conducting analyses of phosphate, nitrate and chemical oxygen demand (COD). The results from these analyses will be used to adjust the existing control systems for methanol and phosphoric acid dosing. Afterward, further tests and analyses will be conducted to make additional adjustments, if necessary.

2. Background

2.2 Improved methanol dosing

It is important to optimize the methanol dosing as it represents a significant cost and has a large environmental impact. In previous work, Gryaab has observed that the dosing to the six different lines does not seem to be consistent across the various lines. The flow meters are oversized, which makes the flow measurement very uncertain for the flows dosing. A test was conducted to measure the flow using clamp-on meters, but this did not work as the pipes were not full. New meters are expensive as they need to be explosion-proof certified. Instead of purchasing new meters, the flow to the different lines will be indirectly controlled by measuring nitrate and/or COD concentrations in and out from each line. After that, the desired methanol dosing will be adjusted. Once adjusted, new measurements need to be carried out.

2.3 Improved phosphoric acid dosing

The phosphoric acid dosing is done one line at a time and is controlled by the opening time of the automatic valves for each line. During a previous thesis project at Gryaab, it was found that the phosphoric acid dosing to line 6 was lower than the average dosing. Since it was important not to have phosphate limitation in the line during the thesis, the valve opening time for that line was increased to thereby increase the dosing. The other lines were not checked, but it is likely that there is uneven dosing between all the lines. The phosphate concentration from all individual lines needs to be analysed and then adjusted by modifying the opening time for each line. Then, new phosphate concentration measurements need to be performed to further adjust the dosing if necessary.

3. Theory

3.1 History of wastewater treatment

Phosphorus and nitrogen are foundational nutrients to all living organisms [2]. But providing too many nutrients can have detrimental effects on our lakes, rivers and oceans. It can cause health risks in drinking water, oxygen deficiency and eutrophication in the recipient water [2, 3, 4]. These problems motivate us to remove phosphorus and nitrogen from our wastewater before it's released into the ocean.

Health risks in drinking water can be caused by high levels of nitrate. That is because nitrate becomes nitrite which, when consumed, affects haemoglobin in the red blood cells, damaging the oxygen intake [2]. Studies also suggest that there is a correlation between high amounts of nitrate in drinking water and stomach cancer [2].

3.2 Biological nitrogen removal

According to Fredriksson [2], nitrogen can be found in the form of nitrogen gas, organically bound nitrogen, ammonia, ammonium, laughing gas, nitrogen monoxide, nitrite, nitrogen dioxide and nitrate. The main supply of nitrogen to water treatment plants is through the population's consumption of protein-rich food. Protein-rich food breaks down via ammonium in the body and becomes urine, which contains ammonia. Some ammonium is also excreted out of the body in the form of faeces. Nitrogen that must go through a long network often arrives at the treatment plant in the form of ammonium or organically bound nitrogen. This means that because of the 13-mile tunnel network that leads to Ryaverket, most of the nitrogen arriving is in those forms [1, 2].

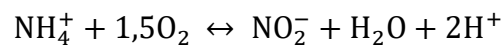
Furthermore, nitrogen found in nature naturally transforms between different oxidation states. These transformations may also occur during the water treatment process. This can be used to achieve controlled biological nitrogen removal. But even without biological nitrogen removal, some of the nitrogen is naturally assimilated into biowaste entering the process. That is because the bacteria require nitrogen for growth. This accounts for 10-30% of nitrogen being removed. To reach a higher degree of nitrogen removal, different methods need to be used, such as the process's nitrification and denitrification. Nitrification and denitrification are methods utilized in biological nitrogen removal and work by combining the two microbiological processes to transform nitrogen into nitrogen gas [2].

3.1.1 Nitrification

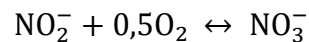
In the nitrification process nitrogen, arriving in the form of ammonium, is turned into nitrate by bacteria. It starts with ammonium oxidizing bacteria turning ammonium ions into nitrite ions. Which in turn is turned into nitrate ions by nitrite oxidizing bacteria. This is what's called nitrification. The nitrifying bacteria gain energy by oxidizing ammonium or nitrite.

Schematic description with reaction formula [2]:

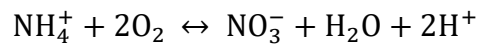
Bacteria turn ammonium ions into nitrite ions through oxidation:



Bacteria turn nitrite ions into nitrate ions through oxidation:



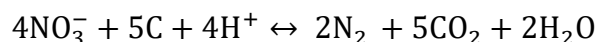
The total reaction can be written as:



3.1.2 Denitrification

The denitrification process in water treatment comes after the nitrification process. It is dependent on the nitrification process providing nitrate for the bacteria to consume [4,5]. When bacteria are found in an environment that lacks oxygen they will conduct nitrate respiration, which is when the bacteria reduce nitrogen in nitrate [5]. This is an essential step in denitrification. The bacteria also need energy and a carbon source to perform this process which is provided from the breakdown of organic material [5].

Schematic description with reaction formula [2]:



Denitrification is dependent on four things: the access to nitrate, the absence of oxygen, the availability of carbon and the temperature [2,5]. The speed of denitrification also depends on how fast the bacteria respire. The speed of respiration is dependent on temperature and the carbon source. Higher temperature and more abundance of carbon mean faster respiration.

Continuously dosing methanol in the denitrification will speed up the process as it is a more reliable carbon source than wastewater [2,5]. The result of denitrification is nitrogen gas which is emitted into the atmosphere where it's already abundant [2,5].

3.1.3 Phosphoric acid dosing

Phosphoric acid is dosed because phosphorous is a limiter for the reaction. There is often too little phosphate left in the water when it arrives to ED [6].

If phosphorus is excessively removed in upstream processes, it may hinder the bacteria's ability to perform denitrification effectively. Therefore, ensuring an adequate phosphorus supply is crucial for maintaining optimal denitrification performance [6].

To mitigate phosphorus limitation, phosphoric acid is added to the wastewater. This provides a readily available form of phosphate, which is essential for the growth and activity of denitrifying bacteria. By supplementing phosphorus, the microbial communities can maintain their metabolic functions, leading to enhanced denitrification efficiency [6].

Phosphoric acid supplementation in denitrification processes addresses phosphorus limitation, ensuring that denitrifying bacteria have the necessary nutrients to function efficiently. This practice enhances nitrogen removal in wastewater treatment systems, contributing to improved water quality and compliance with environmental standards [6].

4. Methodology

4.1 Sampling

Sampling and analysis were carried out at least three times per week. Samples were collected from the control station for the ED system. Before sampling could begin, the valves for all six ED lines had to be opened, followed by a 30-minute waiting period. This delay allowed the ventilation of accumulated hydrogen sulphide gas in the pipes, which builds up over time due to the presence of wastewater, ensuring a safe working environment [7].

Samples were collected in 250 mL plastic flasks, one for each of the six lines, plus one for incoming water to ED, resulting in a total of seven samples per session.

4.2 Filtering the sample

The samples were filtered using two distinct methods, one for phosphate analysis and another for nitrate analysis. Both procedures employed vacuum filtration using a filtering funnel, filter holder, filter membrane, clamp, and filtering flask [8]. The difference between the two methods was the type of filter material used. For phosphate analysis, both glass fibre filters, with a pore size of 1,6 μm , and membrane filters, with a pore size of 0,45 μm , were utilized to ensure higher purity. For nitrate analysis, only a membrane filter was required.

The filtration began with the assembly of the filtration apparatus and activation of the vacuum [8]. For nitrate filtration, a membrane filter was placed directly onto the plastic filter support. In contrast, for phosphate filtration, a glass fibre filter was first placed on the plastic support, followed by a membrane filter layered on top [8]. With the filter in place, the suction tube was connected to the apparatus while the valve remained closed [8]. The sample was then poured into the filtering funnel up to the 100 mL mark. Once ready, the valve was opened to initiate vacuum filtration. Upon completion, the filtered sample was collected in a 100 mL flask.

4.3 Nitrate analysis

LCK339 and LCK340 Nitrate cuvette tests from Hach were used to measure the amount of nitrate in the wastewater samples. LCK339 Nitrate cuvette test has a measuring range of 0.23-13.5 mg/L and was used on water samples taken from line 1-6 [9]. The LCK340 Nitrate cuvette test has a measuring range of 5-35 mg/L and was used on samples taken from water just before entering the denitrification process [9]. The higher measuring range was used

because the wastewater has not yet been completely cleaned of nitrate before entering the post-denitrification. The lower measuring range is used on wastewater coming out of the post-denitrification since nitrate there is low, always below 13.5 mg/l.

LCK339 cuvette packages come with 25 cuvettes filled with pre-dose reagent [9]. 1 ml of already filtered sample is extracted using a 100 – 1000 µl automatic pipette and dispensed in the cuvette. 0,2 ml of the provided reagent marked “A” is extracted, also using a 100 – 1000 µl automatic pipette and dispensed in the same cuvette. The cuvette is then mixed by turning it up and down 2-3 times. After waiting 15 minutes for the reaction to complete the results can be analysed using a spectrophotometer [9]. It is important to wipe the cuvette clean before placing it for analysis. If the sample has a high amount of nitrate the cuvette will have a pink colour. The results are analysed using a DR6000 spectrophotometer and are read as mg/L.



Figure 1: LCK339 nitrate testing kit [9]

4.4 Phosphate analysis

Phosphate was measured using PhosVer accuvac ampule test, from Hach, with a measuring range of 0,02-2,50 mg/L PO₄ [10]. The ampules contain an exact amount of reagent for ease of use. The test is performed by following a few simple steps. First you need to pour at least 40ml of filtered sample into a beaker and at least 10ml of filtered sample into a cuvette. Then the ampule is removed from the box and the tip is pressed into the beaker filled with sample.

The tip is pressed hard enough to break so that the vacuum inside causes the ampule to suck in the sample [10]. Once the ampule is filled it is stirred for 30 seconds. After 30 seconds the reaction needs another 2 minutes to complete, a total reaction time of 2 minutes and 30 seconds [10]. Once the reaction has completed, and if the amount phosphate is high, the contents of the ampule should have a dark blue colour [10]. Analysing the results with a spectrophotometer will give an exact mg/L count of phosphate.



Figure 2: Phosphate accuvac ampules [10]

4.5 COD (Chemical Oxygen Demand) analysis

The organic compounds in the sample are oxidized with potassium dichromate in a sulfuric acid solution using silver sulphate as a catalyst at 148°C for two hours [11]. The organic carbon is oxidized to carbon dioxide and water. The oxidizable material reduces the amount of potassium dichromate, converting Cr^{6+} to Cr^{3+} [11]. As this reduction occurs, the solution changes colour from yellow-orange to green [11]. The remaining amount of potassium dichromate in the sample is measured with a photometer. The COD_{Cr} value is calculated based on the amount of dichromate consumed [11]. Mercuric sulphate binds the chloride ions because chloride interferes with the analysis and gives inaccurate results.

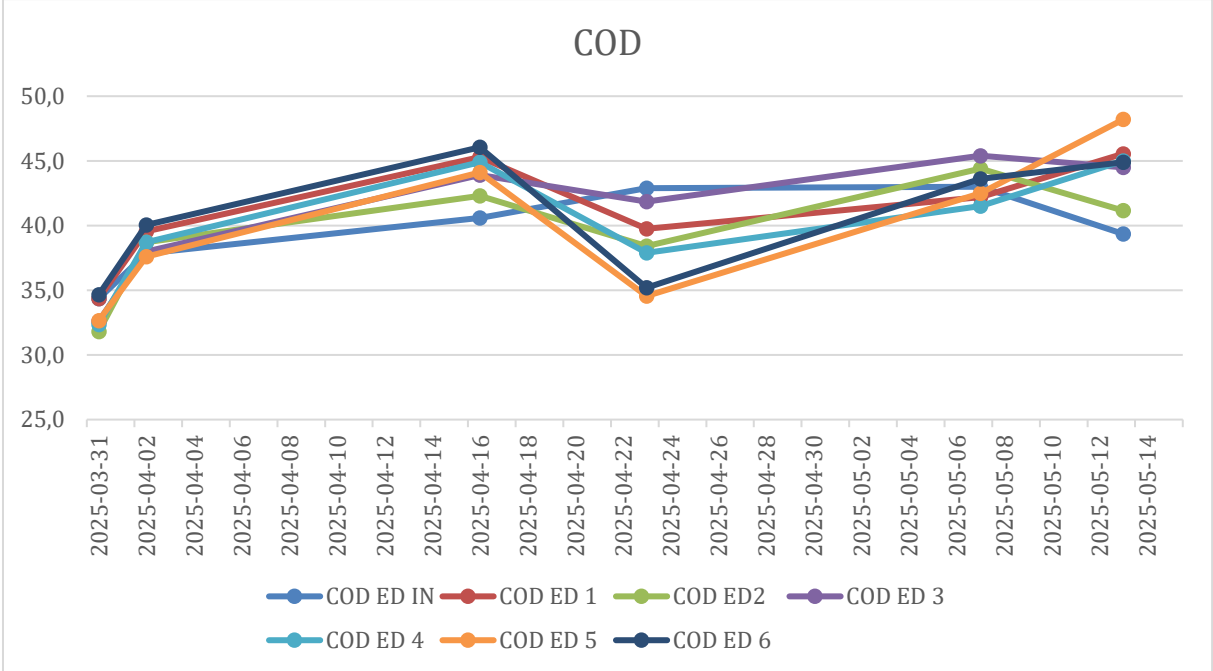
4.6 Dosing adjustments

At the end of the week, dosing for the chemicals were adjusted based on the results of the weeks analysis. Phosphoric acid dosing was lowered if results indicated a high amount of phosphate in the water and raised if results indicated low amounts of phosphate. Dosing was controlled through the SCADA DeltaV, and adjustments were made by engineers at the facility.

COD helps identify potential overdosing of methanol. If the COD concentration is significantly higher out from a line compared to the incoming to the ED process, it indicates overdosing. The COD in the incoming water to ED is considered non-biodegradable, since it otherwise would have been consumed in the preceding treatment steps. Phosphate is directly influenced by increasing or decreasing the phosphoric acid dosage. Nitrate is removed in ED, so it should be low, and about the same concentration out from every line. Higher nitrate out from a zone could indicate too low dosing of either methanol or phosphoric acid.

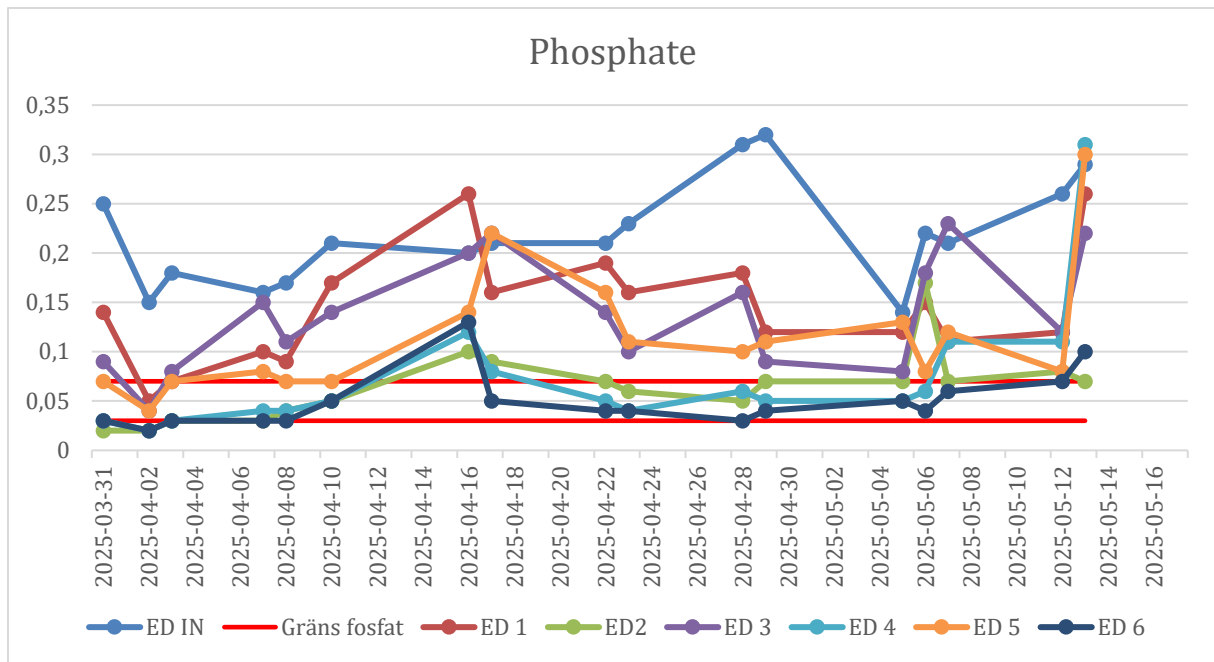
The dosing of phosphoric acid was changed first, to see if it would also affect the nitrate results, since the treatment process is phosphorus limited. The first weeks were focused on increasing the dosing for ED 2, 4, and 6, since analysis showed low phosphate concentration. Then the focus was on reducing the dosing in ED 1 and 3, which had higher concentrations. After checking in DeltaV to see whether the actual dosing matched the set dosing it found that the actual dosing was slightly longer than what was entered, which explains why it was difficult to reduce the phosphate levels. Methanol dosing was also lowered for ED 2, from 10% to 5%, since the nitrate levels there were too high even after phosphate adjustments.

5. Results



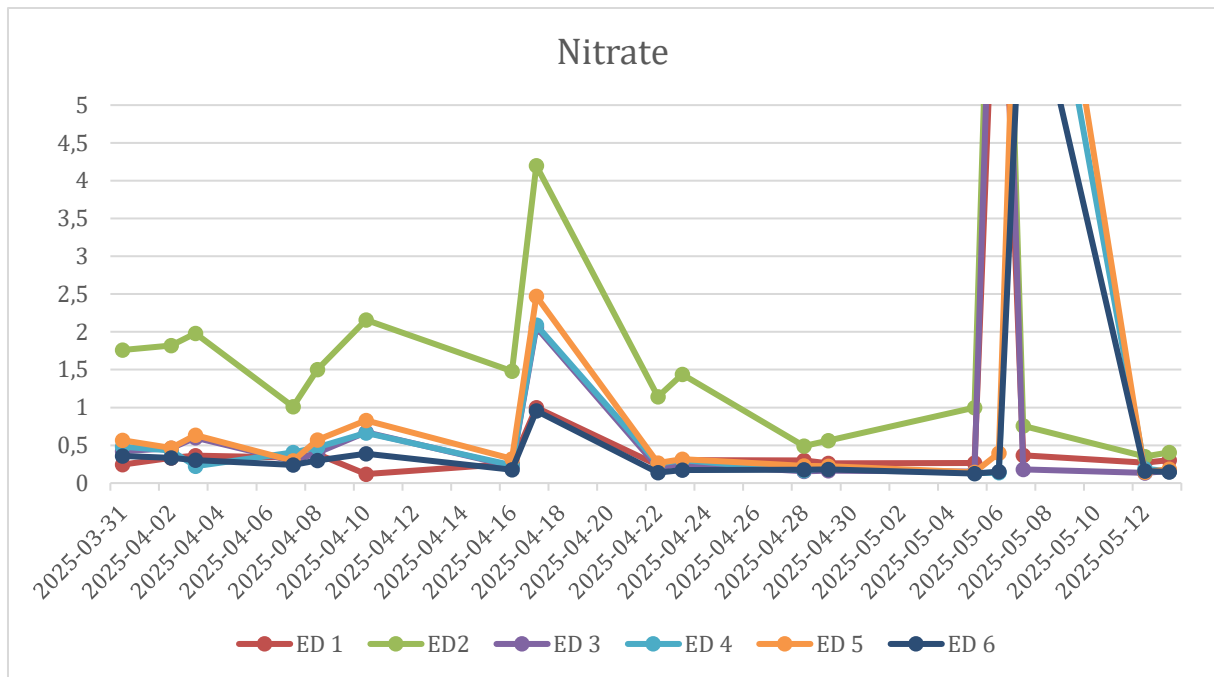
Graph 1: COD concentration results over the entire thesis period presented in a line graph.

The graph shows that COD has continuously increased at the plant. COD should be inert, so all lines should have a similar number of COD passing through. If the COD is too high, it may indicate that methanol is being overdosed. For the most part, the values have been very similar, except for the last day.



Graph 2: Phosphate concentration results over the entire thesis period presented in a line graph.

Here you can see how the phosphate levels in the ED lines have varied throughout the thesis project. The red lines at the bottom indicate the threshold for an acceptable phosphate concentration. The dates when changes were made to phosphoric acid dosing have also been marked. The graph shows that in the beginning, only half of the values were within the acceptable range for phosphate, while the rest were either too high or too low. The reason phosphate levels increase so much toward the end of the project is that methanol was turned off in certain lines, so the best representation is before April 6th. The adjustments to dosing managed to raise the lines with a low concentration of phosphate, while the lines with higher concentration remained above the threshold, even after adjustments.



Graph 3: Nitrate results throughout the entire thesis period presented in a linear diagram

This graph shows that line 2 has always had slightly higher nitrate levels, but we managed to lower it to match the other lines by reducing the methanol dosage. In general, the nitrate level is a bit low, but it's consistent. The points that deviate are due to interruptions in methanol dosing or other tests conducted on the ED lines.

6. Discussion

One of the key challenges observed during the project is the daily fluctuation in phosphorus levels in the incoming wastewater to Ryaverket. This variability makes constant dosing problematic. While the current system attempts to adjust dosing automatically, inconsistencies still occur.

6.1 Methanol dosing discussion

A likely explanation for inconsistent methanol dosing is the inaccuracy of the existing flow meters, which struggle to measure low flow rates reliably. These meters play a central role in the automated dosing calculations via the DeltaV control system. If the flow readings are incorrect, the dosing becomes unreliable. Replacing the current flow meters could be a solution, but new units must be EX-classified due to safety regulations in the treatment environment, which significantly increases the cost.

Phosphate concentrations are typically measured once per week for both the water entering and leaving the ED process, using samples collected after the flows from the different lines have been mixed. The laboratory result of the incoming phosphate concentration is used to calibrate and adjust the online phosphate analyser, which serves as the basis for calculating the required phosphoric acid dosage. However, due to issues with flow measurements in the individual lines and potential valve malfunctions, the automatic dosing system appears to not function perfectly.

6.2 Phosphoric acid dosing discussion

A possible issue with the phosphoric acid dosing lies in the valve control. Observations in DeltaV revealed that the actual valve opening times differ from the set values, leading to further dosing inconsistencies. For example, if the dosing timer was set to 80 seconds the actual dosing would be 90 seconds or more.

During the work with this thesis an extended sampling campaign was conducted. Sampling was done on each ED line multiple times per week, and the dosing was adjusted based on measured concentrations of phosphate, nitrate, and COD. The data from the sampling shows

that even after major adjustments of the valve opening time, resulting in large variations in valve opening time between the lines, there are still significant differences in phosphate concentrations in the water from the lines. Line 1, 3 and 5 have higher phosphate concentration than line 2, 4 and 6, even though the valve opening time is a lot shorter. However, there seems to be a decrease in phosphate from line 1, 3 and 5 throughout the test, even though it is not as clear as it was expected to be.

6.3 Future work

For sustainable and efficient dosing control, the root causes must be addressed. This includes replacing flow meters and investigating the discrepancies in valve opening time. Resolving these technical issues is essential to enable reliable automatic dosing and improve overall process stability.

7. References

- [1] Gryaab AB. *Kort om Gryaab* [Internet]. Gothenburg: Gryaab AB; [cited 2025 Aug 4]. Available from: <https://www.gryaab.se/om-gryaab/kort-om-gryaab/>
- [2] Fredriksson O. *Avloppsteknik 2 – Reningsprocessen* [Sewage Technology 2 – The Treatment Process]. 3rd ed. Stockholm: Svenskt Vatten AB; 2013.
- [3] Swedish Agency for Marine and Water Management (Havs- och vattenmyndigheten). *Varför behöver avloppsvatten renas och vilka huvudregler finns om rening?* [Internet]. Gothenburg: HaV; 2019 Oct 15 [cited 2025 Aug 4]. Available from: <https://www.havochvatten.se/avlopp-och-dricksvatten/sma-avloppsanlaggningar/fragor-och-svar-om-sma-avlopp/ovriga-fragor/2019-10-15-varfor-behover-avloppsvatten-renas-och-vilka-huvudregler-finns-om-rening.html>
- [4] Swedish Environmental Protection Agency (Naturvårdsverket). *Avlopp* [Internet]. Stockholm: Naturvårdsverket; [cited 2025 Aug 4]. Available from: <https://www.naturvardsverket.se/amnesomraden/avlopp/>
- [5] In-Situ. *Tertiary denitrification and very low phosphorus limits* [Internet]. Loveland (CO): In-Situ Inc.; [cited 2025 Aug 4]. Available from: <https://in-situ.com/uk/pub/media/support/documents/tertiary-denitrification-and-very-low-phosphorus-limits.pdf>
- [6] Stanek R, Záborská J. *The impact of the phosphorus limitation on denitrification efficiency and specific sludge production in industrial wastewater treatment* [Internet]. Water Sci Technol. 2024 Sep 16; wst2024312. [cited 2025 Aug 4]. Available from: <https://iwaponline.com/wst/article/90/7/2146/104751/The-impact-of-the-phosphorus-limitation-on>
- [7] Yara. *Luktproblem och H₂S-bekämpning* [Internet]. Sweden: Yara Sverige; [cited 2025 Aug 4]. Available from: <https://www.yara.se/miljoframjande-losningar-och-kemikalier/luktproblem-och-h2s-bekampning/>
- [8] SciTek Global. *About vacuum filtration apparatus* [Internet]. UK: SciTek Global Ltd.; [cited 2025 Aug 4]. Available from: <https://www.scitexglobal.com/about-vacuum-filtration-apparatus.html>

[9] Hach. *Nitrate cuvette test 0.23–13.5 mg/L NO₃-N, 25 tests (LCK339)* [Internet]. Loveland (CO): Hach Company; [cited 2026 Jun 1]. Available from: <https://uk.hach.com/p-nitrate-cuvette-test-023-135-mgl-no-n-25-tests/LCK339>

[10] Hach. *PhosVer® 3 Phosphate Reagent AccuVac® Ampules, pk/25* [Internet]. Loveland (CO): Hach Company; [cited 2026 Jun 1]. Available from: <https://www.hach.com/p-phosver-3-phosphate-reagent-accuvac-ampules-pk25/2508025>

[11] Hach UK. *COD cuvette test, 150–1000 mg/L, for AP3900 Laboratory Robot* [Internet]. Loveland (CO): Hach Company; [cited 2025 Aug 4]. Available from: https://uk.hach.com/p-cod-cuvette-test-150-1000-mgl-for-ap3900-laboratory-robot/APC114?srsId=AfmBOoq-ZQrGbHdxYqcNHJ_0nnsSRddMWvGQPHozFyP-klTidBpp7Kkj

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