Oxygenation conducted in low temperature clean water

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Abstract

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Aeration tests were conducted under non-standard conditions with clean tap water in various temperatures below 20 °C, with the aim of studying changes that may occur. An initial deoxygenation of 0.8 litre water was performed with sodium sulfite and a cobalt catalyst pre-dissolved in water, in order to bind already present dissolved oxygen. The resulting dissolved oxygen concentration after 20 minutes did not decrease below 2 mg/L, despite increasing the sodium sulfite concentrations. Thereafter, a reoxygenation with the same time interval was conducted by using an aeration system, which resulted in an increase of saturated oxygen concentration with lower temperatures. pH-measurements were carried out during the whole experiment in order to follow the conversion of sulfite to sulfate. The pH-data obtained confirmed that sulfite had been converted to sulfate, although, a few deviations could be observed for most of the experiments. The conductivity was also measured to ensure that the sulfite had been properly dissolved when added to the water tank. In general, the conductivity never deviated and held a constant trend throughout the tests. The collected data could not be made of use in order to properly determine how the aeration, for temperatures below 20 °C, could be evaluated. Further tests have to be performed in order for a definite conclusion to be drawn.
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1 Introduction

Wastewater treatment plants are facilities for purification of sewage and wastewater through a number of processes which use different methods for purification and are mainly comprised of mechanical-, biological- and chemical purification. This report will focus on the biological purification process which is based on supplying an activated sludge with oxygen by using an aeration system in order to collect organic material. The aeration system constitutes a crucial part of this process and hence requires a method to ensure its performance.

A method for measuring the performance of an aeration system during standard conditions has already been developed and industrially implemented. Testing relates to standard conditions, including clean water at 20 °C, under which different aeration systems can be compared. The problem with this method, however, is that at the wastewater treatment plants, there are not standard conditions. The water temperature in wastewater treatment plants are often below 10 °C depending on location, thus a temperature correction has to be applied both during tests and any operational unit during non-standard conditions. To save energy during the aeration there would be of interest to find a way to compensate for low temperatures. The tests of the aeration system is done in clean water and when performance efficiency has been properly evaluated, the device is to be used in wastewater with activated sludge.

1.1 Purpose

This thesis aims to prove and demonstrate the changes that occur for the standardized aeration test method conducted for temperatures below 20 °C.

2 Theory

2.1 Aeration

In wastewater plants aeration devices are used which ejects air into the contaminated water. The oxygen within the air bubbles diffuse into the water where it is dissolved [1]. There are various parameters that impact the amount of oxygen that is ultimately dissolved in the water, such as the barometric pressure and temperature of the water, as the dissolution of oxygen in water is correlated in such a way that lower temperatures yield more dissolved oxygen [1]. In order to give an estimate of how much mass of oxygen is transferred per unit time within the contaminated water, a standard oxygen transfer rate (SOTR) measurement is
conducted in clean water [1]. The definition of clean water is stated to be when standard conditions are met; ambient pressure of 1.00 atm and a water temperature of 20°C [1]. In a sense, this procedure allows for an estimate of the aeration performance. This gives a value for the SOTR, which can be used to calculate the actual oxygen transfer rate (OTR) under not standardized conditions and in waste water [1].

2.2 Deoxygenation

Before the aeration test curve can be recorded, a deoxygenation must be performed for the purpose of removing dissolved oxygen [1]. Thus, the definition of deoxygenation is the removal of dissolved oxygen in water. Sodium sulfite, Na₂SO₃, is a chemical compound that has been used primarily to extract oxygen from aqueous solutions [1]. In order to bind the dissolved oxygen, sodium sulfite has been used as binding agent with the presence of cobalt that catalyzes the chemical reaction [4]. Sodium sulfite has previously been used in order to de-oxygenate water by the means of chemistry, although several other chemicals has been used, such as potassium sulfite, K₂SO₃ and ammonium sulfite, (NH₄)SO₃ [4]. The oxidation rate for (NH₄)SO₃ is two times slower than for Na₂SO₃ when cobalt is used as a catalytic reagent [4]. The explanation for this can be deduced in terms of lower catalytic activity of the ammonia cobalt complex, Co(NH₃)₆³⁺, compared to the hydrated oxide Co³⁺ ions. Less stable Co³⁺ ions will be converted to less active Co(NH₃)₆³⁺ ions with ammonia present, while with absence of ammonia there will form more hydrated cobalt species.

In reaction kinetics, the order of the reaction rate is a determination of how the rate of a reaction is dictated by the concentration of a given species as well which species, within a chemical reaction, that affects the kinetics the most [4]. Furthermore, the rate order is derived from the rate law of a given chemical reaction and is determined through experimental methods.

In aqueous solutions, the sulfite anions are oxidized by the dissolved oxygen in the water according to the reaction formula 1 [4]. Although there is much uncertainty as to whether or not formula 1 describes exactly what happens, as the kinetics of the reaction varies considerably for lower temperatures [4].

$$\text{SO}_3^{2-} + 1/2\text{O}_2 \longrightarrow \text{SO}_4^{2-}$$  \hspace{1cm} (1)

Although, the aforementioned reaction is known to be rather slow, it can be accelerated in presence of certain metal ions such as Co²⁺, Cu²⁺, Fe²⁺, Mn²⁺ etc [4]. This, by lowering the activation energy required to form products from the
reactants. With cobalt as a catalyst the rate will be around twelve times faster than if copper would be used. Comparison with different cobalt catalysts gives that hydrated cobalt complex, \( \text{Co(H}_2\text{O)}_{6}^{3+} \), is faster than ammonia complex \([4]\).

There are differences in the reaction orders with respect to sulfite, oxygen and the used catalyst which complicates the understanding on how the volumetric mass coefficient, \( K_{L,a} \), is dependent on the concentration of these species in water \([4]\).

The senior application specialist at Xylem, Lars Uby, explained during a meeting the relationship between oxygen solubility and temperature. For higher temperatures, the oxygen solubility decreases while for lower temperatures it increases. Uby also explained the definition of dissolved oxygen in a body of water is the presence of free oxygen molecules that are not bound to the water molecules. By aeration, the air bubbles will contain oxygen that can diffuse through the gas-liquid interface, formed by the walls of the air bubble and the water outside, by diffusion into the water.

In order to maintain accuracy in the measurements, it is recommended from previous studies that the initial deoxygenation test should not be used, as it is known that the chemistry behind the oxidation of sodium sulfite is rather unknown, especially for temperatures well below \( 20^\circ\text{C} \) \([6]\). The water should instead be reused for the compliance procedure \([2]\). The initial test can also be used to verify the system \([1]\).

The concentration of sodium sulfite to be used is recommended to be 7.88 mg/L per 1 mg/L dissolved oxygen concentration\([1]\), plus some extra to compensate for the oxygen transfer still occurring during the reoxygenation \([6]\). The concentration of cobalt to catalyze reaction 1 should be between 0.1 mg/L to 0.5 mg/L \([1]\).

### 2.3 Model

As of today, there are varieties of the one and the same model at hand that can be used to fit an equation to the data obtained from the dissolved oxygen measurements, in order to visualize and interpret the data\([7]\). The model mentioned is known as the exponential model, which can be applied to the given data in two different ways: either by the logarithm deficit method or as it is, exponentially \([1]\). The reason as to why there are two ways of applying the model is because of the fact that in many aeration systems, \( c_\infty [\text{kg/m}^3] \), is not constant and can vary over time and depending on the depth of the water tank used during analysis, thus the behaviour can be expressed using one of these applied methods\([2]\). In previous studies, the main issues when implementing a mathematical model to a given data
set have been whether or not the used equation can accurately describe the system which is studied and the accuracy of the calculated parameters using the specified method of the model [7].

The equation to obtain values for the concentration of the dissolved oxygen content at a given time in the water volume, can be described in equation 2 [7].

\[ c(t) = c_\infty - (c_\infty - c_0) \cdot e^{-K_{La}t} \]  

(2)

Where \( c_\infty \) is the saturation concentration of the dissolved oxygen, \( c_0 \) is the concentration of the dissolved oxygen at time zero and \( K_{La} \) being the volumetric mass transfer coefficient [1]. By applying this model to the data, approximate values for the volumetric mass transfer coefficient, \( K_{La} \), and the saturated dissolved oxygen concentration at time infinity, \( c_\infty \) can be obtained to estimate the performance of the aeration device used during wastewater treatment [1].

The standard exponential method which uses this model to represent the change in dissolved concentration over time, mentioned above, is based on non-linear regression in order to yield accurate values for \( c_\infty \) and \( K_{La} \) [1]. As the data does not follow a linear trend, the applied regression minimizes deviations between measured data and the calculated data in order to generate an accurate trend line [1]. The non-linear regression of the obtained data set can be performed using spreadsheet software such as Microsoft Excel [6].

The advantage and necessity of using non-linear regression is the fact that the mathematical regression is based off on a method of least squares summation [7]. During the model implementation, the aim is to be able to fit the calculated data to the obtained data of the dissolved oxygen with as small deviation as possible. The minimization of deviations is the consequence of the least square summation, which assures that the sum of the squares between the calculated values and the obtained ones are as small as possible [7]. Ultimately, the errors that might be observed during the correct fitting of the model should be a consequence of uncontrollable factors during the experimentation process and not from the applied regression [7]. These kind of errors show up arbitrarily and do not follow a trend. If, however, the errors do show up and follow a trend that can be followed, the errors are most likely due to the implemented model or a faulty non-linear regression [7].

The values calculated from the exponential method using logarithm deficit fitting, has to be truncated in order to avoid negative values as these cannot be handled logarithmic as the dissolved oxygen concentration approaches \( c_\infty \) [7]. The advantage of using the exponential method is that truncation of data is not
necessary, because of the fact that logarithmic values will not be considered as the saturation concentration of the dissolved oxygen is reached [2]. This states that the model mentioned can yield values for the estimation of the parameters with higher precision than e.g. the logarithm deficit model without the need of truncating the obtained values [2]. Two important deviations that arise when using this model, which need to be considered, is that it does not solely take into consideration that the oxygen transfer is occurring both via the air bubbles and the water surface, furthermore that the saturated dissolved oxygen concentration varies with the depth.

2.4 Parameters

There are several parameters of importance to consider during wastewater treatment processing [1]. There are two parameters in the exponential model, mentioned above, that needs to be calculated, in order to give an estimation for the performance of the aeration system in question.

The volumetric mass transfer coefficient of oxygen, $K_{L,a}$ [min$^{-1}$], is a measure of oxygen transferred from air bubbles into the open water. Thus, it is a parameter that corresponds to a diffusion process of the oxygen. The oxygen molecules diffuse through the interface of the air bubble wall into the open water and by using the given model, $K_{L,a}$, can thus be experimentally determined.

The saturated dissolved oxygen concentration, $c_\infty$[kg/m$^3$], is the amount of dissolved oxygen after re-oxygenation of the water at time infinity, while $c_0$ is the amount of dissolved oxygen at time zero [1]. During reoxygenation of the water in question, the obtained oxygenation curve can be used to estimate $c_\infty$ and $K_{L,a}$ by observing different parts of it [1]. The rising part of the curve, up to 85% of dissolved oxygen concentration, will be sensitive for the estimation of the volumetric mass transfer coefficient while the mostly static part, over 90% dissolved oxygen concentration, will be sensitive for the estimation of the saturated dissolved oxygen concentration [1].

The concentration of the sodium sulfite, sodium sulfate and cobalt are parameters that affect the reaction kinetics and, thus, the obtained results [1]. Sodium sulfate is a product that is formed during the oxidation of sulfite [6]. During the oxidation of sulfite, the pH is observed to slightly increase and then drop back as sulfate is formed, thus, the consequence is that one obtains a variation of the pH in the water, which can be measured in order to observe the relation between the sodium sulfite and sulfate, respectively [6]. This relation can be used in order to see if there is an incomplete oxidation taking place [6]. By measuring the conduc-
tivity in the water, the dissolution of the sulfite can be followed as a complementary measurement in order to monitor the oxidation process. Although, the study that was performed on the conductivity and the pH did not necessarily yield accurate quantification of the oxidation reaction [6]. The knowledge of the oxygen transfer rate could be used in order to set up a mass balance of the sulfite, but would not explicitly tell the accuracy of the measurements [6].

For aeration systems that process wastewater, the oxygen transfer rate (OTR) is the parameter of interest, which is obtained by performing reoxygenation tests [1]. The oxygen transfer rate is the mass of oxygen per unit time dissolved in a volume of water [kgO₂/h]. The standard oxygen transfer rate (SOTR) is a measurement that is conducted in order to obtain the OTR for aeration devices working under standard conditions, i.e 20 °C, and is calculated according to equation 3 [1].

\[ SOTR = K_L a \cdot c_\infty \cdot V \]  

where \( K_L a \) [min⁻¹] is the rate of mass transfer, \( c_\infty \) [kg/m³] is the determination point value of the steady-state dissolved oxygen concentration as time approaches infinity and \( V \) is the volume of the water. Thus, the difference between these two definitions is that SOTR is the oxygen transfer rate in water during standard conditions, while the OTR is the oxygen transfer rate in process water when the barometric pressure, temperature varies and are at different levels of dissolved oxygen than for standard conditions [1].

In order to calculate SOTR for non standard conditions, temperature corrections have to be applied to the involved parameters[1]. An empirical temperature correction factor \( \Theta \) should be used when calculating \( K_L a \). This correction factor has been proven to be equal to 1,024, although could vary depending on the aeration system and test tank used. In order to calculate the correct value for the saturation concentration of dissolved oxygen, a separate temperature correction factor, \( \tau \), has to be used. For standard conditions a value for \( K_L a \) is calculated, \( K_L a_{20} \), which is then used for experiments that are conducted under non standard conditions to obtain the \( K_L a \) that corresponds to the given temperature. The saturation value of the dissolved oxygen under standard conditions, \( c_\infty_{20} \), is used to obtain a correct value for \( c_\infty \) under non standard conditions. The equations below describe the aforementioned temperature corrections under non standard conditions[1].

\[ K_L a_{20} = K_L a \cdot \Theta^{(20-T)} \]  

\[ c_\infty_{20} = c_\infty (1/\tau) \]  

\[ SOTR = K_L a_{20} \cdot c_\infty_{20} \cdot V \]
2.5 Assembly

The devices used for wastewater treatment differs from user to user, depending on the conditions that are demanded by customers. The devices used also depend on the performance scale, i.e. for laboratory purposes, smaller reactors are optimal [7]. Although the designated environments during the experimental phase, and the results obtained, should relate to the end-design and be applicable to larger scale purposes [7].

The main device that is used during wastewater treatment by biological means is an aerator, which ejects air bubbles into the water through a nozzle with a specific rate. The airflow from the aerator is measured in a volume of air per unit time and the flow may be adjusted if the aerator allows the possibility [1]. As stated in [7] there are two ways of supplying oxygen to the water and allowing the mass transfer of oxygen to take place. Either by assigning an aeration device by the surface of the water or submerging it and allowing bubbles to be ejected directly into the bulk of the water, thus allowing oxygen mass transfer to take place during the ascension of the bubbles from the depth of the tank. For surface aeration, the mass transfer will take place at the surface of the water tank that is exposed to the air either through hydraulic pumps or sprays that mixes the air with water at the surface, thus introducing oxygen into the water [3]. According to [5] the usage of submerged aeration in order to oxygenate a deeper water body exceeding six feet, is more beneficial than surface aeration as the oxygen is introduced at the depth of the water and allows for oxygen transfer to take place over a greater volume than surface aeration. Surface aeration is often used as a mean to transfer oxygen when water depth is shallow [5].

For the purpose of homogeneity of the chemicals used within the water, Lars Uby recommended the usage of magnetic mixers, in addition to the mixing that comes with the emission of air bubbles from the aerator device. This creates a flow and allows the chemicals to distribute evenly throughout the reactor. The necessity of acquiring a homogeneous solution of chemicals during the aeration test is to ensure that the deoxygenation process takes place evenly throughout the tank [1]. If accumulation of chemicals begin to take place, there will be uneven deoxygenation within the tank at particular zones which impacts the results and consequently impacts the evaluation of an aerators performance during wastewater treatment [7]. The same condition of homogeneity should be applied for the dissolved oxygen. By having an even amount of dissolved oxygen within the water tank that can react with the sodium sulfite, the less will the probability be of finding zones within the tank where deoxygenation happens unevenly. According to [1] during standard procedures, multiple dissolved oxygen probes were placed within
the tank, with an equal distance away from each other and be able to detect an equal portion of the tank, in order to ensure that different zones in the tank have had an equal amount of dissolved oxygen [1]. The amount and placement of the dissolved oxygen probes depend on the tank size, aerator device placement and mixing pattern within the tank.

3 Method

3.1 Preparations

Before the experiments were conducted, batches of 4 litres of the sodium sulfite and hydrated cobalt chloride were produced in order to save time when the tests were conducted. The concentration that was used in the tests for sodium sulfite was 90 mg/L and 120 mg/L and for cobalt it was 0.5 mg/L. When the chemicals were weighed it did not exactly match the concentrations and to compensate for that water was added. To know what the actual concentration was in the batch equation 7 was used.

\[ c = \frac{m}{V} \] (7)

where \( c \) is the concentration of the solution in unit g per litre, \( m \) is the mass of the chemical in unit gram, and \( V \) is the volume of the solution in unit litre.

The test volume was 0.8 litre and to calculate how much volume of sodium sulfite solution, hydrated cobalt chloride solution and water that needed to be added, the following mathematical relations were thought through.

\[
\text{proportion of solution} = \frac{\text{wanted concentration}}{\text{actual concentration}}
\]

\[
\text{volume of solution} = 0.8 \cdot \text{proportion of solution}
\]

\[
\text{volume of water} = 0.8 - V_{Co} - V_{NaSO_3}
\]

As is mentioned in section 2.2, there have been numerous observations of insufficient deoxygenation during the first sulfite batch aeration test, thus, this information had to be taken into consideration before recording any measurements of the first official test at the given temperature if for any reason the water had to be changed.

To know how much of the solution to be kept in the tank after the initial test and how much to add of the sodium sulfite solution and the hydrate cobalt chloride solution, the following mathematical model, given by Lars Uby, senior application specialist at Xylem, was used.
\[ V_{NaSO_3} = \frac{V_{tot} \cdot c_{DS}}{c_{NaSO_3}} \] (8)

\[(V_{tot} - V_{Co} - V_{NaSO_3}) \cdot c_{DC} + V_{Co} \cdot c_{Co} = V_{tot} \cdot c_{DC} \]

\[ \Rightarrow V_{Co} = \frac{V_{NaSO_3} \cdot c_{DC}}{c_{Co} - c_{DC}} \] (9)

\[ V_0 = V - (V_{Co} + V_{NaSO_3}) \] (10)

where

- \( V_{NaSO_3} \) = volume of sodium sulfite solution needed to be added for next test,
- \( V_{Co} \) = volume of hydrated cobalt chloride needed to be added for next test,
- \( V_{tot} \) = total volume in the tank
- \( V_0 \) = volume of test water kept for next test,
- \( c_{NaSO_3} \) = concentration of sodium sulfite solution in the batch,
- \( c_{Co} \) = concentration of cobalt in the batch of hydrated cobalt chloride solution,
- \( c_{DS} \) = desired concentration of sodium sulfite,
- \( c_{DC} \) = desired concentration of cobalt.

### 3.2 Experiment

The aeration tests were performed in a facility at Hammarby Sjöstadsverk located in Henriksdal, Stockholm.

The volumes of water and hydrated cobalt solution that was calculated for the first test was placed in a tank with a magnetic mixer, two aerators, a pH-meter, a conductivity meter and a DO-probe. The arrangement is shown in figure 1. The aerators was on for ten minutes and then sodium sulfite solution was added to start the deoxygenation. To start the reoxygenation the aerators was turned on again. The data was recorded throughout the whole experiment using a camera, and thereafter manually inserted into Excel.
Figure 1: Arrangement of the devices in the water tank.

The water temperature in the tank was controlled by water bath in a cooling bag, see figure 2, where the water temperature was controlled by adding either ice or hot water.

Figure 2: The water tank in the cooling bag.
3.3 Measurements

Different process parameters was measured, listed in table 1, the most important being the dissolved oxygen concentrations for classifying the performance of the aeration system. DO concentrations was measured using a WTW Oxi 3315 DO–probe which was placed in the water tank, which measures the concentration of dissolved oxygen per unit of time.

In order to successfully obtain results, the various environmental parameters was measured so that conditions for the experiments were controlled. The barometric pressure was determined by collecting meteorological information from SMHI. The pH of the solution was monitored using a WTW pH 3110 pH-meter. An electrical conductivity meter, WTW Cond 3210, was used to measure the conductivity.

The aeration process was conducted at 20°C and at temperatures below 20°C, thus required constant temperature measurements of the water tank. Every measurement device had a thermometer and data was collected from each device every five second during both the deoxygenation and reoxygenation process for 20 minutes each.

<table>
<thead>
<tr>
<th>Dissolved oxygen concentration</th>
<th>Conductivity</th>
<th>pH</th>
</tr>
</thead>
</table>

Table 1: Parameters that was measured during the aeration.

3.4 Calculations

For every test the value of $K_L \alpha$, $c_\infty$ and SOTR was calculated. $c_\infty$ was found by looking at what dissolved oxygen concentration the reoxygenation ended at. $K_L \alpha$ was calculated by finding the slope in the reoxygenation curve where the dissolved oxygen concentration begins to increase until it has reached 98% of $c_\infty$. The SOTR for 20°C was calculated by using equation 3 with the values of $K_L \alpha$ and $c_\infty$ founded, while the SOTR for temperatures below 20°C was calculated using equation 4-6.
4 Results

4.1 Oxygenation measurements

In figure 3-6 the result of the dissolved oxygen concentration measurements with 90 mg/L sodium sulfite is shown. Figure 3 is used as a standard test because it is the test that most closely resembles standard conditions. The standard test was performed with the pressure 0.9958 atm and the tests shown in figure 4-6 were performed with the pressure 0.9968 atm.

![Graph of Oxygenation between 19.2 °C and 20.1 °C](image)

Figure 3: Deoxygenation and reoxygenation curve for 90 mg/L of sodium sulfite at temperatures between 19.2 °C and 20.1 °C.

![Graph of Oxygenation between 8.5 °C and 9.2 °C](image)

Figure 4: Deoxygenation and reoxygenation curve for 90 mg/L of sodium sulfite between 8.5 °C and 9.2 °C.
Figure 5: Deoxygenation and reoxygenation curve for 90 mg/L of sodium sulfite between 6.0 °C and 6.1 °C.

Figure 6: Deoxygenation and reoxygenation curve for 90 mg/L of sodium sulfite at temperatures between 2.6 °C and 3.6 °C.

The result of the dissolved oxygen concentration measurements with 120 mg/L sodium sulfite is shown in figure 7 and figure 8. Figure 7 is the result of the initial test that was mentioned in section 2.2 and figure 8 is the result between 4.5 °C and 4.6 °C. Both test were performed with the pressure 0.9859 atm.
Figure 7: Deoxygenation and reoxygenation curve for the initial test run with 120 mg/L sodium sulfite at temperatures between 4.6 °C and 8.5 °C.

Figure 8: Deoxygenation and reoxygenation curve for 120 mg/L of sodium sulfite at temperatures between 4.5 °C and 4.6 °C.

4.2 Conductivity measurements

The result of the conductivity measurements with 90 mg/L sodium sulfite is shown in figure 9-12.
Figure 9: Conductivity curve with 90 mg/L sodium sulfite at temperatures between 19.2 °C and 20.1 °C.

Figure 10: Conductivity curve with 90 mg/L sodium sulfite at temperatures between 8.5 °C and 9.2 °C.

Figure 11: Conductivity curve with 90 mg/L sodium sulfite at temperatures between 6.0 °C and 6.1 °C.
Figure 12: Conductivity curve with 90 mg/L sodium sulfite at temperatures between 2.6 °C and 3.6 °C.

The result of the conductivity measurements with 120 mg/L sodium sulfite is shown in figure 13 and figure 14.

Figure 13: Conductivity curve for the initial test run with 120 mg/L of sodium sulfite at temperatures between 4.6 °C and 8.5 °C.
Figure 14: Conductivity curve with 120 mg/L sodium sulfite at temperatures between 4.5 °C and 4.6 °C.

4.3 pH measurements

The result of the pH measurements with 90 mg/L sodium sulfite is shown in figure 15-18.

Figure 15: pH curve with 90 mg/L sodium sulfite at temperatures between 19.2 °C and 20.1 °C.
Figure 16: pH curve with 90 mg/L sodium sulfite at temperatures between 8.5 °C and 9.2 °C.

Figure 17: pH curve with 90 mg/L sodium sulfite at temperatures between 6.0 °C and 6.1 °C.

Figure 18: pH curve with 90 mg/L sodium sulfite at temperatures between 2.6 °C and 3.6 °C.
The result of the pH measurements with 120 mg/L sodium sulfite is shown in figure 19 and figure 20.

Figure 19: pH curve with 120 mg/L sodium sulfite at temperatures between 4.6 °C and 8.5 °C.

Figure 20: pH curve with 120 mg/L sodium sulfite at temperatures between 4.5 °C and 4.6 °C.

4.4 $K_{L,a}$, $c_\infty$ and SOTR

In table 2 and 3 the value of $K_{L,a}$, $c_\infty$ and SOTR is shown for the different concentrations of sodium sulfite. The appendix contains every calculation used in order to obtain the values seen in table 2 and table 3.
Table 2: $K_La$, $c_\infty$ and SOTR for tests with 90 mg/L of sodium sulfite.

<table>
<thead>
<tr>
<th>Test</th>
<th>$K_La$ [s$^{-1}$]</th>
<th>$c_\infty$ [mg/L]</th>
<th>SOTR [mg/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6-3.6 $^\circ$C</td>
<td>0.0143</td>
<td>13.7</td>
<td>0.153598</td>
</tr>
<tr>
<td>6.0-6.1 $^\circ$C</td>
<td>0.0152</td>
<td>12.4</td>
<td>0.153867</td>
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<tr>
<td>8.5-9.2 $^\circ$C</td>
<td>0.0164</td>
<td>11.5</td>
<td>0.154246</td>
</tr>
<tr>
<td>19.2-20.1 $^\circ$C</td>
<td>0.0156</td>
<td>9.1</td>
<td>0.113568</td>
</tr>
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</table>

Table 3: $K_La$ and $c_\infty$ for tests with 120 mg/L of sodium sulfite.

<table>
<thead>
<tr>
<th>Test</th>
<th>$K_La$ [s$^{-1}$]</th>
<th>$c_\infty$ [mg/L]</th>
<th>SOTR [mg/s]</th>
</tr>
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<tbody>
<tr>
<td>4.6-8.5 $^\circ$C</td>
<td>0.0140</td>
<td>12.7</td>
<td>0.1472</td>
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<tr>
<td>4.5-4.6 $^\circ$C</td>
<td>0.0152</td>
<td>12.7</td>
<td>0.159439</td>
</tr>
</tbody>
</table>

5 Discussion

5.1 Obtained results

The focus of this report was to show that the reaction kinetics of the oxidation of sodium sulfite for temperatures below 20 $^\circ$C varied.

5.1.1 Sodium sulfite concentration of 90 mg/L

Figure 3 shows the oxygenation of the water at a temperature interval of 19.2 $^\circ$C to 20.1 $^\circ$C. The lowest amount of dissolved oxygen, after the deoxygenation, is approximately 4 mg/L which is too high according to literature. The conductivity, which is shown in figure 9 for the given temperature interval, follows a constant trend which implies good dissolution of the sodium sulfite within the water. Observing the pH measurement that corresponds to this test run, which is shown in figure 15, it can be deduced that the sodium sulfite steadily converts into sodium sulfate as the pH drops in a linear fashion almost immediately after the sulfite is added to the water. However, just after 1500 seconds, there is a small increase in pH that never drops back to the original trend it followed previously. This could suggest that some of the sulfate has converted back into sulfite. The time interval in which the changes occur correspond to the plateaued region of the reoxygenation curve. At this point, the dissolved oxygen concentration had reached its maximum value of saturation after which no changes in the concentration could be observed. This emphasizes that no sulfate had been converted back to sulfite, but no definite
conclusions can be drawn since the aeration system was continuously feeding the water with oxygen, which most likely would result in the sulfite reconverting back into sulfate.

Figure 4 shows the oxygenation curve for the temperature interval 8.5 °C and 9.2 °C. As can be seen, the maximum value for the dissolved oxygen concentration, prior to the deoxygenation, lies at 11.7 mg/L whilst after the process, the concentration drops to 2.6 mg/L. At the beginning of figure 10, which shows the conductivity, there is a slight increase of the conductivity for about 20 seconds. This suggests that the sodium sulfite had not been properly mixed after adding it to the tank, until approximately 20 seconds had passed. Looking at figure 16, the sulfite is converted to sulfate as time passes, although, there are two distinct points that can be discerned which tells that the sulfite has converted back to sulfate. Just after the deoxygenation, around 130 seconds, some of the sulfite seems to convert back into sulfite. However, the pH seems to decrease to the same value it had before, albeit, after 1300 seconds when the reoxygenation is initiated, the sulfate is once again converted to sulfite. As mentioned above, this behaviour was also observed for the oxygenation test taking place under 20 °C, with the exception of this experiment resulting in multiple deviations which could be due to errors stemming from the equipment used.

Figure 5 shows the oxygenation curve for 6 °C. The maximum dissolved concentration prior to the deoxygenation is 12.5 mg/L. After deoxygenation, the value is 2 mg/L. Figure 11 shows the conductivity of this test. The trend shown suggests a good dissolution of the sulfite throughout the experiment, while figure 17 shows the pH. From this measurement it can be concluded that the sodium sulfite successfully converts to sulfate, although at a lower rate since the conversion continuously occurs during the reoxygenation stage.

Figure 6 shows the oxygenation curve for the temperature interval 2.6 °C to 3.6 °C. The maximum value of the dissolved oxygen concentration, before the deoxygenation, lies at a value of 13.8 mg/L, while it drops to 4 mg/L after the deoxygenation. From figure 12, which shows the corresponding conductivity measurement, there seems to be certain deviations during the reoxygenation. All the deviating points have the same value of conductivity. The time interval of this behaviour can be observed to correspond to the increase in pH from figure 18, which implies that sulfate has been formed.

In order to see how a further decrease in temperature would affect the outcome of the oxygenation at 90 mg/L sulfite, the following test was conducted at a temperature between 6.0 °C and 6.1 °C. The lowest value of the dissolved oxygen,
after deoxygenation is at 2 mg/L, whilst for the subsequent test, which was conducted at a temperature interval of 2.6 ℃ to 3.6 ℃, the lowest value is 4 mg/L. The sodium sulfite concentration remains the same for both tests, the only varying parameter being the temperature. The difference in lowest amount of dissolved oxygen might be due to the temperatures under which the experiments were conducted. As mentioned in section 2.2, the solubility of dissolved oxygen in water tends to increase with lower temperatures, which is observed in the graphs by the maximum concentration of dissolved oxygen for respective temperature. For the experiment conducted at 2.6 ℃ to 3.6 ℃, the maximum dissolved oxygen concentration reached a value of 13.7 mg/L while for a temperature of 6.0 ℃ to 6.1 ℃ the maximum value is 12.5 mg/L. Since the concentration of the sodium sulfite was constant for these temperature intervals, the resulting oxygen concentration after the deoxygenation reached a higher value for the experiment conducted at 2.6 ℃. Taking a look at figure 3, which was conducted at a temperature of approximately 20 ℃, the same relation should be observed. Although, this is not the case. The oxygen concentration prior to the deoxygenation was at a maximum value of 9 mg/L and decreased to a value of 4 mg/L, after the process.

5.1.2 Sodium sulfite concentration of 120 mg/L

The sulfite concentration was increased in order to obtain lower values of the dissolved oxygen concentration after the deoxygenation. According to [1] and [4], the amount of the desired sodium sulfite to be added is proportional to the amount of dissolved oxygen there is in the water before deoxygenation is initiated. Thus, as can be seen in figure 7, the dissolved oxygen concentration is at approximately 14 mg/L and this correlates to a sodium sulfite concentration of 110 mg/L. Although, an excess of sodium sulfite has to be added, which was calculated with the equations in section 3.1. The final concentration was 120 mg/L.

Figure 7 depicts the initial test run for the oxygenation of the water at a temperature interval of 4.6 ℃ and 8.5 ℃. For a sodium sulfite concentration of 120 mg/L, after conducting the deoxygenation process, the dissolved oxygen concentration lies at approximately 2 mg/L.

Reading the oxygenation curve in figure 8, which is the official test at 4.5 ℃ to 4.6 ℃, shows a value for the dissolved oxygen concentration, which lies approximately at 4.9 mg/L. Although, the sodium sulfite concentration is identical to the initial test run, there is a clear difference to be noticed.

The conductivity for the initial test run can be found in figure 13. The constant behaviour suggests a complete dissolution of the sodium sulfite and pH
measurements, figure 19, show a trend which implies that sodium sulfite has been converted to sodium sulfate. Thus, why the lowest values of the dissolved oxygen concentration, after deoxygenation, differ may be due to the fact that the initial test run was executed over a clear temperature interval, whilst the temperature for the official run was more or less static.

5.1.3 Parameters

Table 2 presents the calculated parameters for each conducted oxygenation test with a sodium sulfite concentration of 90mg/L. The value for $K_{La}$ is similar for the temperature interval $2.6\, ^\circ C$ to $9.2\, ^\circ C$. According to Lars Uby, the value for $K_{La}$ should increase with higher temperatures, which it does until $9.2\, ^\circ C$. For $20\, ^\circ C$, $K_{La}$ is seen drastically dropping down to $0.0385 \, s^{-1}$. The value for $c_{\infty}$ should drop with increased temperature, which it clearly does according to table 2. The calculation of SOTR, using equation 6, should yield a minimum value for a temperature of approximately $15\, ^\circ C$ and the values obtained behave accordingly. However, this cannot be completely determined, as the experiments conducted do not cover the temperature interval between $10\, ^\circ C$ and $20\, ^\circ C$.

Table 3 shows the calculated values of the parameters for a sodium sulfite concentration of $120mg/L$. The initial test run had a clear temperature interval, whilst the official test had a temperature that stayed rather static, still their $K_{La}$ values were similar. $c_{\infty}$ were identical. The value for SOTR is seen to be higher at $4.6\, ^\circ C$. No experiment was conducted at $15\, ^\circ C$, thus, the minimum value for SOTR was never calculated, as for the case described above.

5.1.4 Other observations

When observing the oxygenation curves for respective temperature, a common trend can be found during the deoxygenation stage. The oxygen concentration can be seen to increase steadily, although with a small magnitude, until reoxygenation is initiated. This occurrence is most likely due to transfer of oxygen from the open air through the surface of the water, since the vessel was not sealed.

The increase of sodium sulfite, from $90 \, mg/L$ to $120 \, mg/L$ did not seem to yield the presumed results, which was to decrease the dissolved oxygen concentration, after deoxygenation. As can be seen in figure 6 and 8, the two experiments resulted in different maximum and minimum values for the dissolved oxygen concentration during the deoxygenation stage. This is most likely due to the temperature difference. Comparing the fraction of extracted oxygen from the water for respective experiment, it can be concluded that a higher concentration of sodium sulfite,
unexpectedly, resulted in a lower fraction of extracted oxygen.

5.2 Comparing to literature

All the articles at hand mention using at least two dissolved oxygen measurement probes, whilst during the tests only one was used due to limited resources. This means that the detection of dissolved oxygen was only constricted to a particular zone within the water. Relative to literature, which made use of multiple measuring probes, the dissolved oxygen concentration could be obtained from various areas in the water, thus, yielding more representative values for the concentration relative to the entire water tank. Furthermore, the volume used during the aeration tests, compared to the volumes used in previous experiments, was much smaller. This implies that the detection zone of the oxygen probe, relative to the whole volume of water, could be compared to the measurements carried out in larger volumes. The main reason as to why multiple probes have been used during prior experiments is due to the fact that the dissolved oxygen concentration varies for different zones. Although, in this case perfect mixing conditions were assumed.

5.3 Limitations

The lab equipment at hand had been used for previous, unknown, experiments and sterilizing them was not an option. Thus, remaining chemicals, even after thorough wash with deterring agents, could have been present in the vessel during the tests. How these might have affected the results is hard to determine as there was no knowledge of which chemicals had been used. Occasionally, employees at Hammarby Sjöstadsverk had to use vessels which were intended to be used as means of transferring sodium sulfite and cobalt solutions.

In order to lower the temperature below 20°C, cooling bags was used as economic reasons did not allow for the investment of a proper cooling system. In other words, the temperature was regulated manually. Difficulties maintaining a certain set temperature may have affected the outcome as the intended temperature interval could not be withheld since the only type of thermal isolation stemmed from the cooling box. Often times, the temperature swayed incrementally during the de- and reoxygenation processes. Thus, instead of measuring for one specific temperature, the measurement took place for a temperature interval. As mentioned in sections 2.1 and 2.2, both the solubility of the dissolved oxygen and kinetics of the sodium sulfite oxidation are affected by temperatures overall. Therefore, having the de- and reoxygenation process taking place over a temperature interval, instead of at a specific temperature, may affect the interpretation of the data. Although, the impact of this relation cannot be entirely defined.
The deoxygenation was performed using sodium sulfite, although another method using nitrogen could also have been used as stated in literature. According to [6], either sodium sulfite or nitrogen gas could be used to extract the dissolved oxygen from the water volume. Compared to sodium sulfite, nitrogen is an environmentally friendly gas, generates more reliable data and is mainly used in bench-scale laboratory. The cons of using nitrogen gas is that it affects the assembly, investment in a separate pressure vessel or tank in order to eject it into the water is necessary. Another aspect as to why nitrogen was not used is the fact that the equipment given was not fit for the usage of nitrogen as an oxygen binding agent.

5.4 Possible improvements

Human errors have to be regarded. The choice of using a camera to record obtained data and then manually inserting the data every five seconds was as accurate as a method available at the time. Instead, by using, e.g., a software that could automatically tabulate the data obtained from the various measuring devices, the errors arising from manually recording and inserting the data could be minimized significantly. The time between the addition of sodium sulfite just before the deoxygenation, pressing the record button and starting the stopwatch had to be precise. This type of execution obstructs tabulation of the data which is of great concern, since the parameters change abruptly at the beginning of the respective processes, thus, requiring a more precise method for recording the data.

When measuring the volumes of each solution, before they were put into the final vessel, a graduated cylinder was used which depicted the volume in millilitres and the solutions were manually transferred into the cylinder. The transfer was made sure to be accurate, albeit, with an accuracy of the human eye. Another factor that would complicate the addition of the solutions, especially the sodium sulfite, was that it had to be measured exactly before the transfer to the final tank. This is due to the fact that some of the sodium sulfite that is near the surface may oxidize from the open air. If possible, an automated device could be used with sufficient accuracy to neglect the errors arising from the manual measurements.

5.5 Time frame

The time frame available was also a limiting factor. If more time had been allowed, further tests could have been conducted to either confirm whether or not certain deviations had a specific cause, such as those that might have stemmed from the given equipment, or if they showed up arbitrarily. This could have had crucial impact because of the aforementioned cooling system that was used, in order to
decide whether or not the results from the varying temperatures during the de- and reoxygenation were a constant occurrence or actually varied.

6 Conclusion

The oxygenation curves, pH- and conductivity measurements show patterns that are difficult to relate with each other in order to determine an accurate and concise conclusion. In order to determine the performance of aeration systems during non-standard conditions, the science behind the reactions occurring between the sulfite and dissolved oxygen has to be evaluated. The kinetic behaviour of the oxidation of sulfite is difficult to follow using the obtained data and further experiments have to be conducted. The fact that the dissolved oxygen concentration reaches values above 0 mg/L after deoxygenation shows that not enough oxygen has been extracted from the water or that more time may be needed for the process to complete, thus an evaluation of the aeration performance for these tests cannot be deducted.

References


A Calculations of SOTR

A.1 20.1 °C

\[ c_\infty = 9.1 \text{ mg/L} \]
\[ K_L a = 0.0156 \text{ s}^{-1} \]
\[ SOTR = K_L a \cdot c_\infty \cdot V = 0.0156 \cdot 9.1 \cdot 0.8 = 0.113568 \text{ mg/L} \]

A.2 3.6 °C

\[ c_\infty = 13.7 \text{ mg/L} \]
\[ K_L a = 0.0143 \text{ s}^{-1} \]
\[ K_{La_{20}} = K_L a \cdot \Theta^{(20-T)} = 0.0143 \cdot 1.024^{(20-3.6)} = 0.021099 \text{ s}^{-1} \]
\[ \tau = \frac{c_\infty}{9.1} = 1.50549451 \]
\[ c_{\infty_{20}} = c_\infty (1/\tau) = 13.7 \cdot (1/1.50549451) = 9.1 \text{ mg/L} \]
\[ SOTR = K_{La_{20}} \cdot c_{\infty_{20}} \cdot V = 0.021099 \cdot 9.1 \cdot 0.8 = 0.153598 \text{ mg/L} \]

A.3 6.1 °C

\[ c_\infty = 12.4 \text{ mg/L} \]
\[ K_L a = 0.0152 \text{ s}^{-1} \]
\[ K_{La_{20}} = K_L a \cdot \Theta^{(20-T)} = 0.0152 \cdot 1.024^{(20-6.1)} = 0.021136 \text{ s}^{-1} \]
\[ \tau = \frac{c_\infty}{9.1} = 1.362637 \]
\[ c_{\infty_{20}} = c_\infty (1/\tau) = 12.4 \cdot (1/1.362637) = 9.1 \text{ mg/L} \]
\[ SOTR = K_{La_{20}} \cdot c_{\infty_{20}} \cdot V = 0.021136 \cdot 9.1 \cdot 0.8 = 0.153867 \text{ mg/L} \]

A.4 9.2 °C

\[ c_\infty = 11.5 \text{ mg/L} \]
\[ K_L a = 0.0164 \text{ s}^{-1} \]
\[ K_{La_{20}} = K_L a \cdot \Theta^{(20-T)} = 0.0164 \cdot 1.024^{(20-9.2)} = 0.021188 \text{ s}^{-1} \]
\[ \tau = \frac{c_\infty}{9.1} = 1.263736 \]
\[ c_{\infty_{20}} = c_\infty (1/\tau) = 11.5 \cdot (1/1.263736) = 9.1 \text{ mg/L} \]
\[ SOTR = K_{La_{20}} \cdot c_{\infty_{20}} \cdot V = 0.021188 \cdot 9.1 \cdot 0.8 = 0.154246 \text{ mg/L} \]
A.5 4.6 °C

\[ c_\infty = 12.7 \text{ mg/L} \]
\[ K_{La} = 0.0140 \text{ s}^{-1} \]
\[ K_{La20} = K_{La} \cdot \Theta^{(20-T)} = 0.014 \cdot 1.024^{(20-4.6)} = 0.02022 \text{ s}^{-1} \]
\[ \tau = \frac{c_\infty}{9.1} = \frac{12.7}{9.1} = 1.395604 \]
\[ c_{\infty20} = c_\infty(1/\tau) = 12.7 \cdot (1/1.395604) = 9.1 \text{ mg/L} \]
\[ SOTR = K_{La20} \cdot c_{\infty20} \cdot V = 0.02022 \cdot 9.1 \cdot 0.8 = 0.1472 \text{ mg/L} \]

A.6 Initial test at 4.6 °C

\[ c_\infty = 12.7 \text{ mg/L} \]
\[ K_{La} = 0.0152 \text{ s}^{-1} \]
\[ K_{La20} = K_{La} \cdot \Theta^{(20-T)} = 0.0152 \cdot 1.024^{(20-4.6)} = 0.021901 \text{ s}^{-1} \]
\[ \tau = \frac{c_\infty}{9.1} = \frac{12.7}{9.1} = 1.395604 \]
\[ c_{\infty20} = c_\infty(1/\tau) = 12.7 \cdot (1/1.395604) = 9.1 \text{ mg/L} \]
\[ SOTR = K_{La20} \cdot c_{\infty20} \cdot V = 0.021901 \cdot 9.1 \cdot 0.8 = 0.159439 \text{ mg/L} \]
1. Genomförde ni test med proben i dött vatten och observerade att den visade ända ner till 0 mg/l syre?
Ja när vi testade att blanda lösningen av natriumsulfit till den volymen som skulle användas till ett enskilt försök och inte en stor batch gick DO-koncentrationen ner väldigt snabbt till noll.

2. Var bubblaren avstängd under deoxygeneringen under alla försök?
Ja bubblaren stängdes av och sedan tillsattes natriumsulfit.

3. Kan man använda konduktiviteten som ett mått på total iblandad sulfit?
   Vilka försök startade från ca noll sulfit? (First-batch-problemet?)
Det skulle kunna gå att avgöra hur mycket sulfit som finns iblandat med hjälp av konduktivitet, men att tester med nytt vatten måste göras för att avgöra detta. Det försök som startade med noll sulfat var testet med temperatur mellan 4,6 grader och 8,6 grader med 120 mg/l sulfit.

4. Kan det ha varit problem med att proben varit något isolerad från omrörningen?
Detta bör inte ha uppstått då proben var placerad i mitten av tanken och hyfsat långt ner i tanken.

5. Borde mer Na2SO3 ha använts – hade det gett lägre DO?
Förmodligen hade mer natriumsulfit behövts användas. Tester med högre koncentrationer hade behövts göras för att tydligt kunna svara på detta.