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Removal of formaldehyde from industrial waste water

Master’s thesis within the Innovative and Sustainable Chemical Engineering

ALEXANDER NILSSON

Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
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ALEXANDER NILSSON

Supervisor: Oleg Pajalic, Perstorp
Examiner: Diana Bernin, Department of Chemistry and Chemical Engineering

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Department of Chemistry and Chemical Engineering
Division of Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

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ALEXANDER NILSSON
Department of Chemistry and Chemical Engineering
Chalmers University of Technology

Abstract

With increasing population comes increasing consumption of water. Water has historically been seen as an inexhaustible resource, but this is no longer the case. Both individuals and industries have started to make efforts to decrease the usage of water. One such effort is made by Perstorp, who are interested in internally recirculating waste water exiting their polyol plant instead of using fresh water. One of the streams leaving the production plant and feeding the water treatment plant contains 300 ppm of formaldehyde. This stream has to be purified before it can be recycled in order to prevent high concentration formaldehyde emission. In this thesis two different methods were investigated for degradation of the formaldehyde. Both of them are advanced oxidation processes using light with a wavelength below 400 nm. The first one uses titanium dioxide as a photocatalyst and the second one uses hydrogen peroxide. Both of the methods did successfully degrade formaldehyde with a conversion up to 40%. This is not high enough to fulfill the emission limits, possible reasons for this can be the temperature, the reaction time or the energy flux emitted from the UV-sources. Another likely factor was that the UV-sources used could not be submersed in the reactor, which meant that the light had to pass through either the glass of the reactor or a glass fibre before reaching the sample. The industrial scale version of this equipment has much higher capacity for emitting UV-flux and is able to irradiate the sample directly, so it is likely the conversion would increase when the equipment is sized up to industrial scale. The formaldehyde concentration was measured using spectrophotometric measurements and it was noted that the titanium oxide used for the photocatalytic experiments did absorb light. This led to results that are more unreliable the higher the photocatalyst concentration is. For this reason a low titanium dioxide concentration was used when evaluating this method. An economical evaluation of a industrial scale solution was made by contacting companies creating water cleaning equipment. When comparing the total cost of the two methods over 9 years it can be concluded that using these rough estimates is the method using hydrogen peroxide and UV-light is the most economically viable option of the two.

Keywords: Water purification, formaldehyde, advanced oxidation process, UV-light, photocatalytic reaction, hydrogen peroxide/UV-oxidation, techno economical validation.

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Alexander Nilsson, Gothenburg, August 2020

Contents

List of abbreviations

AOP	Advanced oxidation process
E_g	Band gap in the unit J
FA	Formaldehyde
H_2O_2	Hydrogen peroxide
$^\bullet OH$	Hydroxyl radicals
LED	Light emitting diode
RO	Reverse osmosis
TiO_2	Titanium dioxide
UV	Ultraviolet light
ppm	Parts per million on a mass basis, the same as mg/l
λ	Wavelength in the unit nm

List of Figures

List of Tables

1

Introduction

1.1 Background

Water is something that is often taken for granted. It is seen as a inexhaustible resource, but that is not the case. Only 2.5% of the earths water is fresh water and only around two fifths of that fraction can be used by humans. The human population is increasing fast and with it so does the water consumption [1]. Recently, more and more actions are being taken to counteract this rapid increase in fresh water usage. It can be that people buy a high-efficiency dishwasher or shorten the amount of time spent in the shower. All reduction helps to decrease the water usage, but it is not us individuals that are the largest consumers of water, it is the industries of the world. In this sector efforts has been and continue to be made to make the processes used more water efficient. A reduced water consumption is not only desirable from an environmental point, of view it is also a positive economical decision. This is because as the demand for water increases so does the price. 100 years ago water was viewed as a free resource and now it can be as expensive as any other resource that need to be purchased for use in the processes. This thesis will be looking at one such water usage reducing measure.

A water stream of around 10 cubic meters per hour that is leaving Perstorp´s polyol production process has a formaldehyde (FA) concentration of around 300 parts per million (ppm) on a mass basis. It also contains low concentrations of formic acid and methanol. A flow sheet of the water flow in the polyol plant is shown in Figure 1.1.

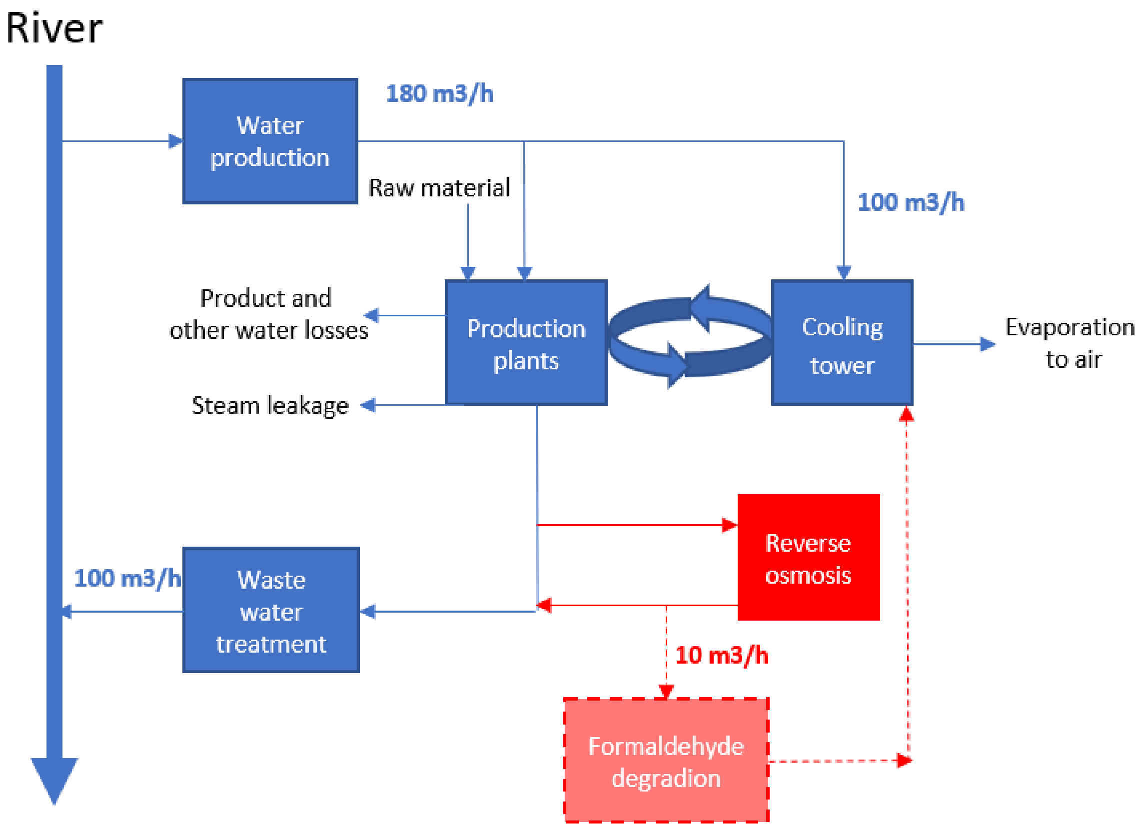

Figure 1.1: Flow sheet over the water flow at Perstorp´s polyol plant.

Raw water is taken from the nearby river Ypparpsån to supply the production plan with the water needed to produce the polyols. The water is also supplied to a cooling tower that provides the cooling needed in the production plants. The waste water leaving the production plants currently goes to a water treatment plant but Perstorp is at the moment working on setting up the reversed osmosis (RO), shown in red in Figure 1.1, process to reduce the amount of treatment needed.
The stream leaving the RO plant is currently sent to the biological water treatment plant off site. With the increasing demands for a reduced consumption of fresh water it is of interest to investigate if it is feasible to reuse a part of this waste stream. The recycled stream would then be entering the cooling tower and be cooled using air. This theoretical pathway is shown in dashed red in Figure 1.1. Then the water stream enters the cooling tower will part of the volatile formaldehyde evaporate into the air flow and follow the air out of the plant. It is not permitted by law to emit air with a FA concentration higher than 30 ppm. Therefore Perstorp wants to investigate if there is a feasible way to reduce the formaldehyde concentration in the water stream from around 300 ppm down to as far below the 30 ppm emission limit as possible. This means that at least 90% conversion is needed to reach this target. The removal of formaldehyde from industrial waste water is desirable from a ethical, ecological and economical point of view.

1.2 Aim

The aim of this project is to investigate the suitability of two methods for removing the pollutant formaldehyde from industrial waste water. These methods are a photocatalytic reactor and a process using hydrogen peroxide (H_2O_2) and ultraviolet light (UV). The stream has an initial concentration 300 ppm and is to be reduced to as low as possible. The emission limit for formaldehyde is 30 ppm, but limits can be lowered and therefore as low a formaldehyde concentration as possible should be strived for out of the reactor. The assessment will be done using experimental results and a techno-economical analysis.

This thesis will only use the methods presented above, even though there are other methods that can be used to degrade organic pollutants like formaldehyde. A method study were conducted before deciding which methods to move forward with and the result of this study can be found in Appendix A.

Below some important questions to be answered in this report are presented.

- Can the two investigated methods remove formaldehyde from a water solution? Which conversion can be achieved?
- Does reaction time, temperature and/or light flux influence the degree of degradation of the pollutant?
- Are these three methods scalable and if possible how this execution would look in an industrial scale? Are there any companies making this kind of equipment?
- Which of the two methods is the most economically viable?

2

Theory

In this chapter the theoretical background of this thesis is presented. It covers the theory behind compounds, techniques and processes used.

2.1 Formaldehyde

Formaldehyde contains one carbon atom and is the smallest aldehyde. The chemical structure of this molecule is shown in Figure 2.1. In Table 2.1 some chemical and physical properties are presented [2]. Formaldehyde is a very common molecule both in nature and industry. At room temperature it is a colourless gas that can be dissolved in water [3].

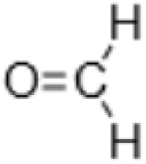

Figure 2.1: The atomic structure of pure formaldehyde.

Table 2.1: Physical and chemical properties of formaldehyde.

Chemical composition	HCHO
Synonym	Methanal
Molar weight	30.026 g/mol
Melting point	−92 °C
Boiling point	−19.1 °C
Density (at −20 °C)	0.815 g/cm^3

Formaldehyde is the most commonly occurring aldehyde in nature. It can can be created in natural phenomena, like erupting volcanoes and biodegadation of organic substances. The occurrence of FA in nature can also be caused by humans. It can be a product from combustion processes in for example cars and power plants [4]. A big part of the formaldehyde, that can be found in nature today, was also formed in photoreactions that occurred in the atmosphere in the time period before life existed on Earth [5]. There are theories that the FA created in the primitive atmosphere was the building blocks that made the first DNA and therefore linked to the creation of life on Earth [6].

The first synthesising of formaldehyde was done by Butlerov in 1859. It was created when methylene acetate was hydrolysed. Although Butlerov found a way to make formaldehyde it would take 8 years before it was identified by a German scientist named von Hoffmann. During the remaining part of the 19th century the production process was improved using different noble metal catalysts [6]. In the century that followed FA would become an important commodity used for many different applications.

Some of the most prominent cases were as a raw material in the making of plastics and for medical purposes. In medicine, formaldehyde dissolved in water has been most widely used in embalming fluids used in chemical embalming of human cadavers. This method for preservation of corpses has been less common in more recent times but does still occur in some cases [7]. Formaldehyde has not only been used to preserve humans, it has also been used as a food preservative. This is not allowed anymore since it has been found out that formaldehyde is toxic to humans.

The symptoms from FA poisoning can be both acute and chronic [8]. Acute symptoms occur when exposed to high concentration of FA during a time frame shorter than 24 hours. Oral consumption of formaldehyde can give acute symptoms like dizziness and vomiting. If exposed to FA during a long time the effect can be chronic instead. What these chronic effects are can vary. It has carcinogenic properties which means that it can promote the creation of cancerous tumours [9]. The country with the biggest problem with FA poisoning is China. This is due to the continued existence of a widespread usage of formaldehyde as a preservative, despite it being illegal [8].

In today´s industries the most common use case for FA is as a building block in production of other compounds. Examples of such compounds are urea-formaldehyde, different kinds of resins and a wide variety of organic compounds [9]. Perstorp is using FA to make polyhydric alcohols, or polyols, that can be used for many different things. Examples of usages is as solvent and building block in further synthesis. Formaldehyde is most commonly sold as formalin, which is an aqueous solution of FA. Formalin can have varying composition, but commonly it contains around 40% of FA and contains small amounts of formic acid and methanol.

2.2 Advanced oxidation processes

In advanced oxidation processes (AOPs) hydroxyl radicals ($^{\bullet}$OH) are used to initiate degradation of a pollutant. They can be performed at ambient temperature and pressure [10]. AOPs are effective reactions of high conversions and fast reaction times. The biggest drawback with using this kind of reactions are that they are non selective. This means that it is very hard to control which compound in the sample will and which will not be degraded. AOPs also are not suitable when chemical complexities are to be preserved. It is not possible to control how far the reaction will proceed with other means than the reaction time. If the process is not stopped the oxidation process will continue until the oxidation chain has reached its smallest components. In the case with aqueous solutions containing organic compounds these components are carbon dioxide and water.

The first AOP was developed as early as the 19th century [11]. The first method used is called the Fenton process, named after its creator, and is using ferrous ions (Fe^{2+}) and hydrogen peroxide to create $^{\bullet}$OH. The hydroxyl radicals oxidised organic pollutants present in a water solution. The Fenton process is still used today, but during the years more methods to create the radicals have been developed. There are methods using light, electricity and catalysts to name a few. There are also combinations of these different processes, for example electro-Fenton, photo-Fenton and photocatalysis.

Formaldehyde can, with an AOP, be reduced into carbon dioxide and water. With an AOP this is done in two steps and initialised by hydroxyl radicals [4]. In the first step the FA reacts with two $^{\bullet}$OH and forms formic acid and water. The formic acid will then react with two more hydroxyl radicals to create the final product carbon dioxide and water. The oxidation path of the degradation from formaldehyde to carbon dioxide and water is described in Equations 2.1 and 2.2. The oxidation that occurs in AOPs is highly effective but not selective. For this reason advanced oxidation processes are appropriate to use when a complete degradation is wanted and none of the complexity of the reagents are to be preserved.

$$\mathrm{HCHO} + 2\,^{\bullet}\mathrm{OH} \rightarrow \mathrm{HCOOH} + \mathrm{H_2O} \tag{2.1}$$

$$\mathrm{HCOOH} + 2\,^{\bullet}\mathrm{OH} \rightarrow 2\,\mathrm{H_2O} + \mathrm{CO_2} \tag{2.2}$$

2.3 UV-light

Light consists of electromagnetic radiation. The energy content of the light varies with the wavelength, the lower the wavelength the more energy the light contains. Ultraviolet radiation is divided into three different categories depending on its wavelength, the different intervals is presented in Table 2.2.

Table 2.2: The different categories of ultraviolet radiation and their wavelength intervals [12].

Type	Wavelength [nm]
UVA	400-315
UVB	315-280
UVC	280-100

The majority of the UV-radiation on earth is emitted from the sun. The sunlight contains UV-light of all three kinds, with UVA being the most prevalent at ground level. This comes from the fact that most of the other two kinds of UV-light is absorbed in the earths atmosphere[12]. All of the UVC is absorbed on its way to the earth´s surface and around 10% of the UVB is passing through the atmosphere. It is UV-radiation of type B and C that causes the human skin to get sun burnt if exposed to sun light for extended amounts of time. The colour change in the skin´s pigment is caused by exposure to UVA. Being irradiated by UV-light, of any type, can increase the risk of developing skin cancer [13].

2.4 Photocatalysis using a semiconductor catalyst

One way to initialise an AOP is by using a photocatalytic process. This technique utilises semiconductors ability to absorb energy from photons in order to excite an electron. The band gap is the energy difference between the highest band containing electrons, the valence band, and the lowest unoccupied band, the conductor band. If the energy of the light is equal or higher than the band gap (E_g) an electron in the photocatalyst´s valence band will be excited into the conductor band [14]. The electron stays in the excited state for femtoseconds before returning to the valence band and releasing the energy, which can be used create radicals [15]. A visual depiction of the excitation process is shown in Figure 2.2.

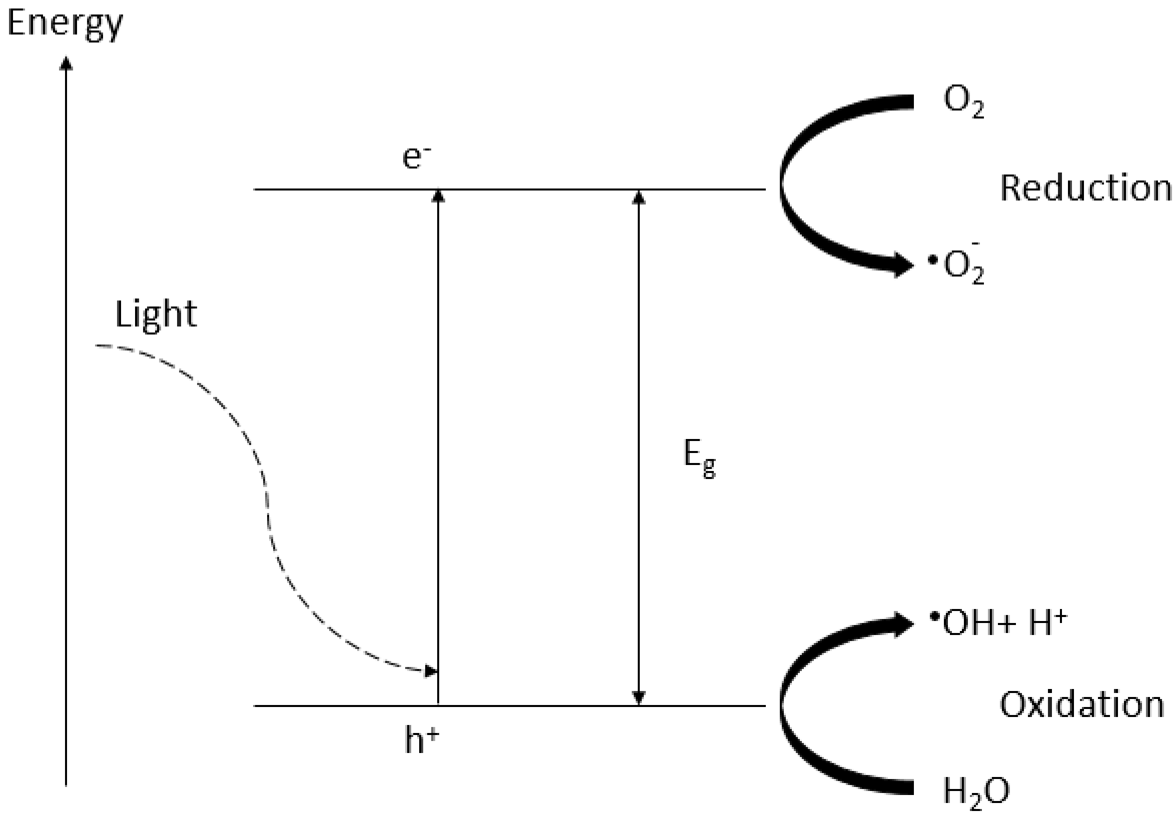

Figure 2.2: The mechanism of electron excitation in a semiconductor photocatalyst.

The most commonly used semiconductor photocatalyst is titanium dioxide (TiO_2). It also has other use cases such as cosmetic products and paint where it is mainly used as a pigment. This semiconductor can have a variety of different crystalline forms, the most common variants being anatase and rutile [16]. The anatase crystals have a spherical shape while the rutile crystals have a more elongated shape [17].

TiO_2 is widely used as a photocatalyst because of it has a lot of beneficial properties. For example it is mechanically strong, cheap compaired to other semiconductors, chemically inert and not toxic. The biggest draw back with using TiO_2 is that its band gap is to wide for electrons to be excited by the energy of visible light [18]. Light with a wavelength of 400 nm or below is needed for the excitation to happen, this means that light in in the UV-range is needed. One very important factor for why TiO_2 is chosen as a photocatalyst is that after the excitation the structure returns to its original state. This means that the catalyst can be reused for many experiments as long as it can be separated from the other contents of the reactor.

2.5 Oxidation using hydrogen peroxide and ultraviolet light

The AOP that is the most implemented in the industry uses H_2O_2 and UV to create hydroxyl radicals [10]. When irradiated with UV-light, the hydrogen peroxide is split into two $^{\bullet}OH$ that can start an AOP to degrade the pollutant. H_2O_2 has a weak absorption of light in the UV spectrum, which leads to a low degree of conversion to $^{\bullet}OH$. For this reason the concentration of H_2O_2 that is added at the start of the experiment is important. To split a hydrogen peroxide molecule UV-light of type C is needed.

3

Methods

In this chapter the experimental and theoretical methods used in this thesis to study and evaluate the methods of formaldehyde degradation is presented.

3.1 LED UV reactor

For the experimental proceedings using UV-light so called light emitting diodes (LEDs) were used. Three different wavelengths in the ultra violet spectra were used in the experiments, but all of them has an energy consumption of 600 mA. Four LEDs, with the same wave length, were soldered to a circuit board and the board was then mounted on heat sinks. An air flow is applied to the heat sinks during the experiment to prevent overheating of the LEDs. The circuit board was connected to a power source with 2 A and 6.1 V. A picture of the mounted 310 nm LEDs can be found in Figure 3.1. The experiments were conducted with a sample volume of 5 ml for all of the experiments. Most of the experiments had a reaction time of one hour but to evaluate the impact of the reaction time some five hour experiments were conducted.

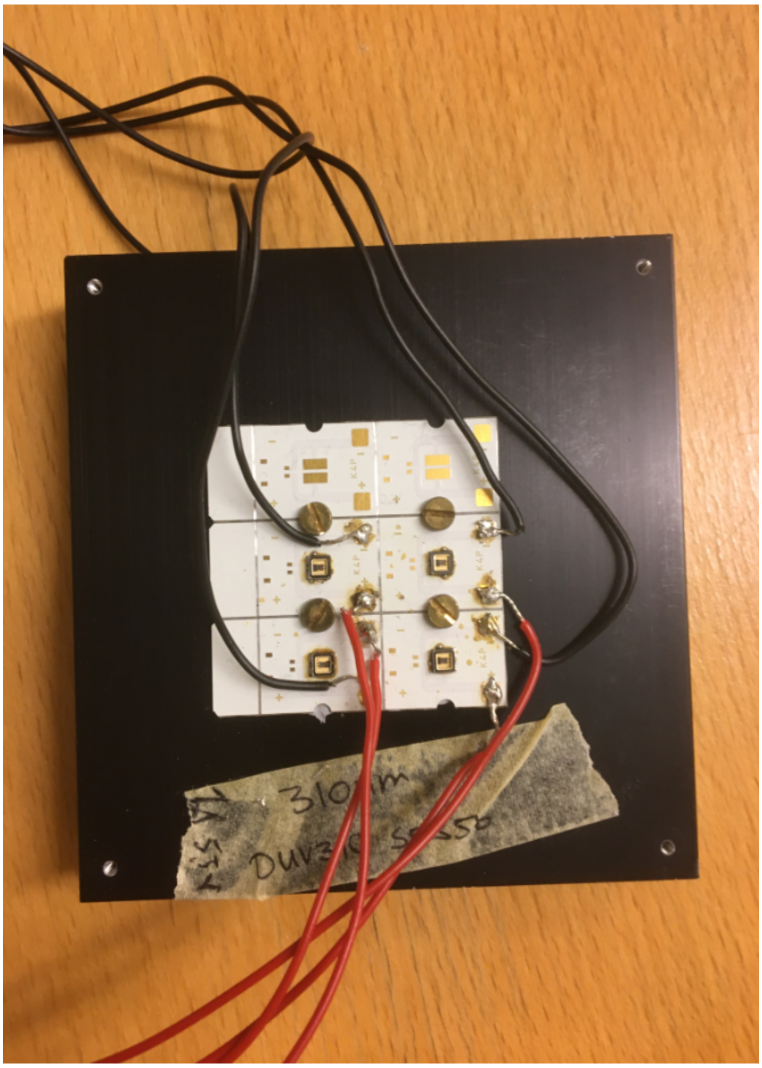

Figure 3.1: Picture of the LED setup.

3.2 Formaldehyde solution

To simulate the process water that is supposed to be recycled a formaldehyde solution with a similar composition was used in the experiment. The components in this solution and their respective concentrations are presented in Table 3.1. One aspect of the process stream that was not able to be simulated was the temperature. The equipment for stable and precise heating to temperatures around 50 °C was not available.

Table 3.1: Composition of the aquatic formaldehyde solution used for the experiments.

Component	Concentration [ppm]
Formaldehyde	300
Methanol	25
Formic acid	250

3.2.1 Irradiation methods

Two different methods were used to irradiate the reactor vessel with UV-light. One using glass fibres to transfers the light from the LEDs to the reactor and one where the LEDs were directly placed against the reactor wall.

3.2.1.1 Glass fibre irradiation method

In the glass fibre case a protective plastic plate was mounted above the LEDs. The plate had four holes were glass fibres were placed so that each fibre rested upon a LED. The other end of the fibre was placed in a glass vial containing the sample. The vial is equipped with a lid where a plastic pipe has been put through a hole in the top so that the fibres can be placed into the sample inside the vial. During the experiment the sample and reference was stirred. The sides of the reactor vessel are covered with aluminium foil. In Figure 3.2 a schematic depiction of this experimental setup is shown and a picture of the equipment can be found in Figure 3.3.

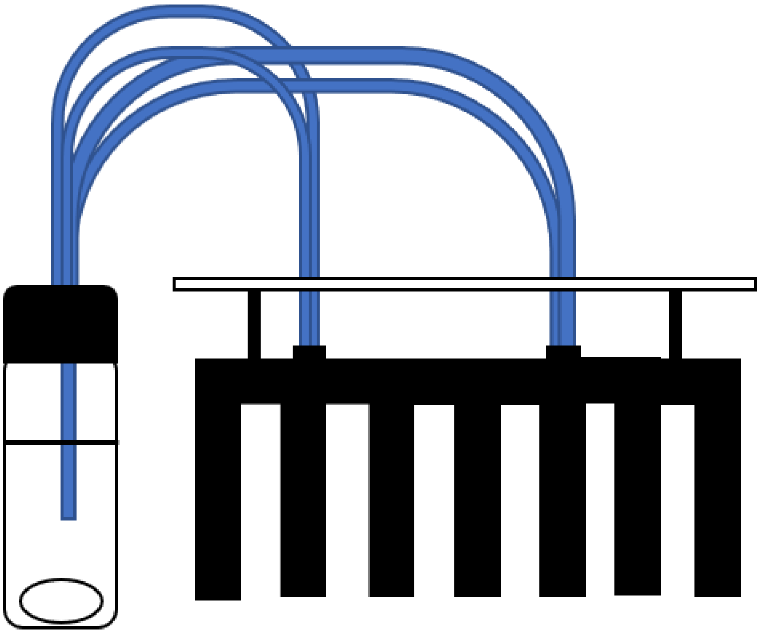

Figure 3.2: Schematic layout of the glass fibre setup.

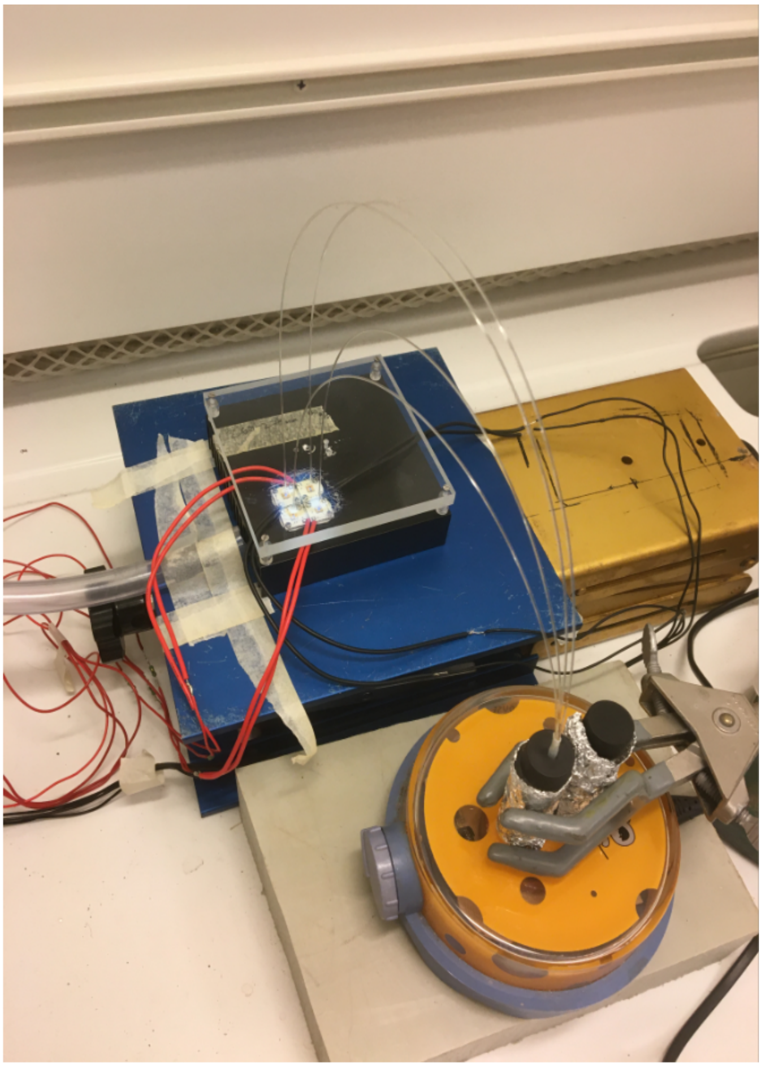

Figure 3.3: Picture of the glass fibre setup.

3.2.1.2 Direct irradiation method

The other irradiation method uses a different kind of reactor vessel. Instead of a cylindrical vial a glass flask with square sides is used. The plastic plate is removed so that the LEDs can be placed directly against the reactor wall. A stirring bar was added to the reactor to ensure that the solution was mixed throughout the experiment. A schematic depiction of the direct irradiation setup is shown in Figure 3.4 and a picture of the setup can be found in Figure 3.5.

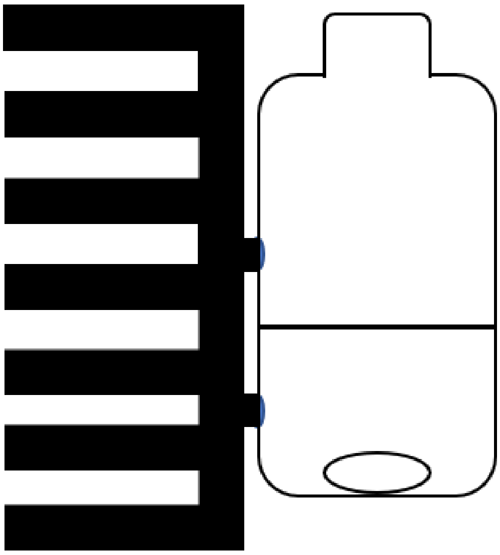

Figure 3.4: Schematic layout of the direct irradiation setup.

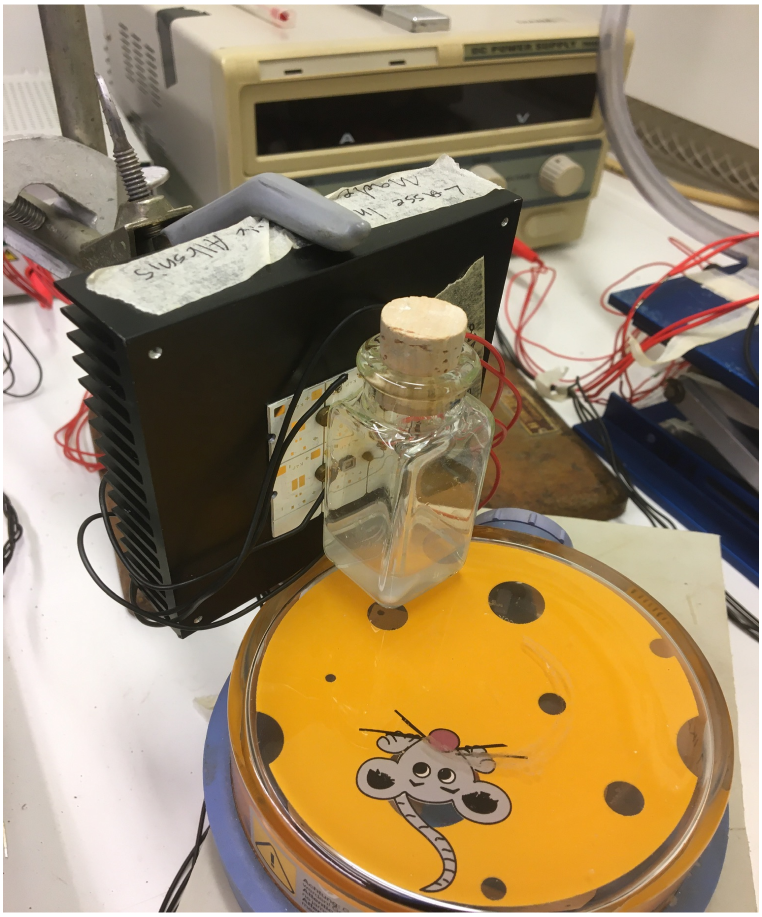

Figure 3.5: Picture of the direct irradiation setup before the reactor is covered with aluminium foil.

3.3 Titanium dioxide photocatalytic reaction

In the photocatalytic reaction TiO_2 is added to the formaldehyde solution in the reactor vessel. Three different concentration levels of titanium oxide were used in the experiments; 0.4, 0.8, 3.2 g/l. Since the photocatalytic reaction is activated by UV-light with wavelength below 400 nm both irradiation methods can be used. This means that the LEDs with a wavelength of 310 nm can be used. 310 nm was also chosen for a practical reason since it was used less often by others.

For the experiments four different kinds of titanium dioxide was used. They were denoted A to D and information about the different variants can be found in Table 3.2. For two of the TiO_2 kinds additional information about the specific surface area was obtained which is presented in Table 3.3. To investigate whether the TiO_2 samples were interfering with the results, spectrophotometric measurements were conducted on water mixed with the different kinds of TiO_2.

Table 3.2: Information about the four different variants of TiO_2. The particle sizes that is presented are average values as provided by the the TiO_2 manufacturer.

Abbreviation	Manufacturer	LOT number	Mineral form	Particle size [nm]
A	Alfa Aesar	B07X024	Anatase	15
B	Aldrich	MKBP2332V	Anatase	<25
C	Aldrich	MKBF7443V	Anatase	44000
D	Acros Organics	A0266752	Anatase	4230

Table 3.3: Information about the specific surface area for two of the kinds of TiO_2.

Abbreviation	Specific surface area [m^2/g]
A	240
C	10

3.4 Hydrogen peroxide and ultra violet light reaction

As presented in Section 2.5, an AOP can be used to degrade organic pollutants can be performed using H_2O_2 an UV-light. To do this, a wavelength of below 280 nm is needed to create hydroxyl radicals from the hydrogen peroxide. The glass reactor does not let through light with a wavelength shorter than 300 nm and therefore the direct irradiation method can not be used.

3.5 Determination of the formaldehyde concentration in water samples

To determine the formaldehyde concentration spectrophotometry was used. Formaldehyde is colourless so to make it detectable it is reacted with Hantzsch reagent. This reaction results in the creation of 3,5-diacetyl-1,4-dihydrolutidine. The reaction path of the colouring reaction is shown in Figure 3.6. The yellow colour of this compound can be detected by spectrophotometry and through this the colourless formaldehyde can now be detected. This is the method for measurement of formaldehyde concentration in aqueous samples that Perstorp uses.

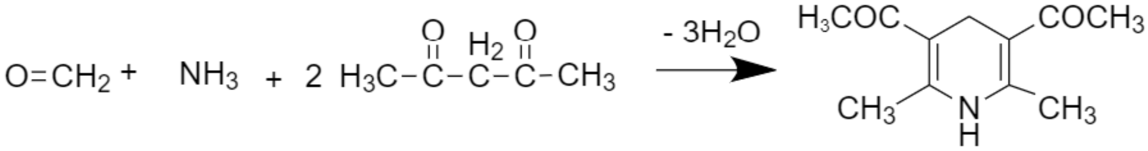

Figure 3.6: The creation path of 3,5-diacetyl-1,4-dihydrolutidine, a compound detectable by spectrophotometry.

3.5.1 Preperation of Hantzsch reagent

The Hantzsch reagent is made by dissolving 75 g of ammonium acetate in 300 ml of distilled water. To this solution 1.5 ml acetic acid and 1 ml acetylacetone is added. Lastly the solution is mixed thoroughly and the Hantzsch reagent can be stored up to three months in refrigeration. The Hantzsch reagent used in these experiments was provided by Perstorp.

3.5.2 Measurement of formaldehyde concentration

In a vial 1 ml of the sample is mixed with 1 ml of the Hantzsch reagent. The vial is heated for 10 minutes at a temperature of 60 °C. After that the vial is cooled for an equal amount of time. The solution was then diluted to one tenth of the original concentration. 2.5 ml of the diluted solution is put in a quarts cuvette in spectrophotometer and measured at a wavelength of 412 nm. This is done for both the sample and a reference that goes through the same process as the sample with the exception for the irradiation with UV-light. The conversion is calculated by comparing the sample to the reference sample.

3.6 Techno economical evaluation

To evaluate the economical viability of the two methods of formaldehyde degradation investigated, contact was made with companies producing equipment to perform this task at an industrial scale. An investigation was made to find suitable fits for providers of the equipment. Informational material and patterns from different providers for both the methods was studied. When suitable companies where found they were contacted was made and was pro approximate process configurations needed to accomplish the task. Economical information was also provided that gave rough estimates for the size of the capital and operating costs if their equipment would be implemented for the task.

4

Results and discussion

In this chapter the result from the investigation of the degradation of formaldehyde will be presented and discussed. The result and discussion from the method comparison conducted before deciding which methods to focus on can be found in Appendix A.

4.1 Photocatalysis using a semiconductor catalyst

The complete raw data from the photocatalytic experiments can be found in Appendix B in Tables B.1 to B.7. Firstly a titanium dioxide concentration of 0.8 g/liter was used in the experiments. Studying these results, that can be found in Appendix B, a trend could be seen. The ones using TiO_2 A had a higher conversion compared to the other types. When C was used the conversion was consistently lower than 3% and B gave a consistent negative conversion. The conversions for both A and D did vary more between the different tests but since A had higher peaks this type of TiO_2 was chosen to focus on in further repetitions. The results from these initial experiments, using TiO_2 of type A, can be found in Table 4.1. Increasing the TiO2 concentration to double the initial amount while using TiO2 D was also tested. The result from this test can be found in Table B.6. This experiment gave no conversion and thus increasing the concentration was not investigated further.

Table 4.1: The experiments having a concentration of 0.8 g/l of TiO_2 type A. All of these experiments have a reactor volume of 5 ml.

Exp nr	Irr method	λ [nm]	Time [h]	Ref Abs	Sample Abs	Conversion [%]
1	Direct	310	1	0.471	0.363	22.9
2	Direct	310	1	0.541	0.418	22.7
3	Direct	310	1	0.389	0.366	5.69
4	Direct	310	1	0.265	0.249	5.83
5	Direct	310	5	0.379	0.350	7.72
6	Glass fibre	310	1	0.523	0.476	9.09
7	Glass fibre	310	5	0.45	0.437	4.49
8	Glass fibre	310	5	0.404	0.396	1.91
9	Direct	280	1	0.686	0.387	43.6
10	Direct	280	5	0.528	0.392	25.8

In the values of the reference absorbance a variation was found. A possible reason for this variation is that the TiO_2 is absorbing light and gives unstable values. To investigate if this is the case the absorbance of pure water with dissolved TiO_2 was tested, using the same concentration as the diluted samples had. Since these samples did not contain any formaldehyde that needed to be coloured no Hantzsch reagens was added. The experiments was repeated four times for each kind of TiO_2 and the measurement values are presented in Table 4.2.

Table 4.2: Spectrophotometric analys of 0.08 g/l TiO_2 of all different types.

Exp nr	TiO_2 type	Absorption at 412 nm
1	A	0.786
2	A	0.656
3	A	1.245
4	A	1.169
5	B	1.316
6	B	1.338
7	B	2.196
8	B	1.300
9	C	0.155
10	C	0.139
11	C	0.116
12	C	0.113
13	D	0.813
14	D	0.808
15	D	0.813
16	D	0.841

From these results it can be noted that TiO_2 does absorb light at the wavelength of 412 nm. This means that the formaldehyde absorbance will be affected by this phenomena but since the reference has the same TiO_2 concentration the impact of this should be reduced. But still random variations in the mixing between the reference and the sample will occur and this will affect the result. Another possible way to decrease this effect is to filter the sample and reference before the measurement, but this was not tested in these experiments. This in combination with that TiO_2 of type B have the highest interference from the TiO_2 is a likely reason for the the negative conversion received in the experiments using this TiO_2 type. In order to decrease this effect the TiO_2 concentration was decreased to half of the original concentration. The results from repeated experiments using 0.4 g/l of TiO_2 A can be found in Table 4.3. The TiO_2 concentration using TiO_2 of type B and C was also decreased in some of the experiments. Using these gave a similar result as they did using the higher concentration and therefore A was used for repeats that could be compared to the ones made using 0.8 g/l.

Table 4.3: The experiments having a concentration of 0.4 g/l of TiO_2 type A. All of these experiments have a reactor volume of 5 ml, a wavelength of 310 nm and uses the direct irradiation method.

Exp nr	Reaction time [h]	Reference Abs	Sample Abs	Conversion [%]
1	1	0.245	0.173	29.5
2	1	0.286	0.242	15.3
3	1	0.240	0.166	30.8
4	1	0.237	0.249	-5.25
5	1	0.262	0.197	24.7
6	1	0.210	0.192	8.37
7	1	0.148	0.120	18.9
8	1	0.163	0.116	28.7
9	1	0.212	0.146	31.2
10	5	0.253	0.192	16.6
11	5	0.272	0.158	41.9

To assess if the reference values of the experiment using the lower TiO_2 concentration were less varied, the standard deviation was calculated for both the 0.4 g/l and the 0.8 g/l data sets presented in Table 4.3 and 4.1. The standard deviations and the mean values of the reference absorbance values are presented in Table 4.4.

Table 4.4: The mean value and standard deviation of the photocatalytic experiments using both 0.4 and 0.8 g/l TiO_2.

TiO_2 conc [g/l]	Mean reference absorbance	Standard deviation
0.4	0.230	0.0412
0.8	0.464	0.109

It can be seen that the mean and the standard deviation was decreased by about half when the amount TiO_2 added was decreased. That the mean was decreased was expected since it was already observed that the TiO_2 concentration is affecting the absorbance value. More of note is that the standard deviation decreased. This indicates that the random mixing differences that is suspected to lead to the fluctuations in the reference values has also decreased. This means that more reliable results were obtained when the lower TiO_2 concentration were used.

From the conversion results presented in Table 4.3 it can be seen that the photocatalytic experiments do degrade formaldehyde. The degree of conversion does vary but except for one outlier, experiment number 4, the experiments did consistently degrade 8-40% of the pollutants. The negative conversion in experiment number 4 does most likely has its explanation in human error, either in the execution of the reaction or the measurement. The conversion is not as high as the 90% goal, so it was attempted to find an explanation to was what limited the conversion from reaching a higher value. One thing that was tested was to extend the reaction time.

To investigate this 5-hours experiments were conducted and the results from these can be found as experiment 10 and 11 in Table 4.3. The conversion does not increase significantly so it is most likely not the reaction time that is the limiting factor. Even though the reaction time was five times as long as the shorter experiments, number 10 was in the same range as the shorter ones and 11 was only slightly higher than the other ones.

Another factor that might impact the degree of conversion is the temperature. When studying excising research done on photocatalytic reactions it was noticed that most of the were conducted at room temperature, but it was still relevant to study since the process water at Perstorp has a temperature around 50 °C. Unfortunately was it not practically possible to have continuous heating that could keep a steady and controllable temperature throughout the experiments using the setup that was available. Another method that was tested to simulate the elevated temperatures of the process stream was to preheat the sample in the vial used as reactor vessel. Before the reaction was started the vial was therefore heated so that it kept 50 °C when the heating was stopped. Even though an effort was made to start the reaction as fast as possible it was found that the vial with the sample returned room temperature just minutes after the heating stopped. For this reason it was decided to conduct the experiments at constant room temperature. It was preferred to keep the temperature constant, even if it was not the same as the reference process stream. The temperature gradient that occurs in the preheated experiment might introduce additional uncertainty and since already performed research was performed at room temperature keeping it constantly at this temperature level seemed like the best course of action.

It is also possible that the TiO_2 concentration was a factor that limits the conversion from reaching higher levels. Especially when the concentration of the photocatalyst was decreased to 0.4 g/l is this a possibility. With the method available for these experiments was this not able to be tested since the increased content of TiO_2 leads to more uncertainty introduced in the results.

The most likely factor, that can hinder the conversion to be higher left, is the efficiency of the UV-LEDs. The ultraviolet sources used for these experiments has a very low energy usage and this means low conversion of electric energy to UV-light compared to other UV-sources. In all of the experiments the maximal voltage safe for the LEDs was applied to give a as high as possible energy output from the UV-LEDs. Industrial grade UV-sources are based on different technology and this makes comparing the two cases difficult. It is likely that in the industrial case it is possible to provide a higher UV-flux. This increased flux may increase the rate of formaldehyde degradation and through that increase the conversion. The flux is a difficult parameter to measure since it will decrease the further away from the UV-source. A way to reduce the impact this flux decrease is to install multiple UV-lamps, which is done in most industrial UV-reactors.

The LEDs used for these experiments can not be immersed into the solution that is to be purified, which is a possibility with UV-sources used on an industrial scale. This introduces more potential efficiency losses because the UV-light has be transported to the sample instead of irradiating it directly. To do this two different pathways were used, direct and glass fibre. Both the irradiation methods have their positives and negatives. In both cases the flux of UV-light can be assumed to be decreased before reaching the sample in the rector vessel. In the glass fibre case a portion of the light will be emitted to the surroundings while being lead through the glass fibre. In the direct method the reduction in light flux comes from the reactor vessel itself. The glass in the wall absorbs part of the UV-light from the LEDs. The amount of the light that passes through is decreasing with decreasing wavelength, to a degree that the glass walls stops any light with a wavelength lower than 300 nm. A possible solution to this problem is to use a rector vessel of another material. For example a quartz reactor would let a much higher degree of the lower wavelengths of UV-light pass through. Unfortunately the time to get a quartz flask delivered was too long for it be testable.

4.2 Hydrogen peroxide and UV-light reaction

The other method for formaldehyde degradation that was investigated was the H_2O_2 and UV-light initiated advanced oxidation process, that is described in Section 2.5. There have been studies to determine what concentration of hydrogen peroxide the sample should have at the start of the experiment: one such investigation has been done by Perstorp and in this paper it was concluded that for degrading 300 ppm of formaldehyde in a water solution, 500 ppm is a suitable starting concentration for H_2O_2 [19]. For this reason this concentration was chosen as the starting concentration of hydrogen peroxide for these experiments. The experiment was also conducted without adding any H_2O_2 to see if this made any difference. All of these results can be found in Table 4.5.

Table 4.5: The experiments having a concentration of 500 of H_2O_2 type A. All of these experiments have a reactor volume of 5 ml, a wavelength of 260 nm and a reaction time of 1 hour. They are all using the optic fibre irradiation method.

Exp nr	**H_2O_2 [ppm]**	**Reference Abs**	**Sample Abs**	**Conversion [%]**
1	0	0.165	0.163	1.66
2	0	0.170	0.162	4.62
3	500	0.172	0.117	32.0
4	500	0.184	0.147	20.1
5	500	0.169	0.106	37.4
6	500	0.158	0.0985	37.8
7	500	0.191	0.129	32.7
8	500	0.175	0.128	27.0

The two first experiments were done without any addition of hydrogen peroxide. From these it can be observed that the degradation still occurred, to a small degree, when irradiated with ultra violet light of wavelength 260 nm for one hour, even though no additional reagent was added. This indicates that it can be expected that that an even higher conversion when the H_2O_2 is added to the solution.

The absorbance values from Table 4.5 has a low spread, which can be seen from the standard deviation value presented in Table 4.6. The standard deviation for these experiments is smaller than the standard deviations for the photocatalytic experiments presented in Table 4.4. This is most likely due the fact that the H_2O_2 does not contain any TiO_2 that absorbs light in the spectrophotometric measurement and interfere with the measured reference values.

Table 4.6: The mean value and standard deviation of the reference absorbances from the hydrogen peroxide and UV-light experiments.

H_2O_2 conc [ppm]	**Mean reference absorbance**	**Standard deviation**
500	0.173	0.00955

Experiments number 3 to 8 presented in Table 4.5 is all repetition of the same experimental conditions. To the same water solution containing formaldehyde used for all other experiment was H_2O_2 added until a 500 ppm concentration was reached. After one hour of irradiation of 260 nm wavelength UV-light using the glass fibre irradiation method it can be concluded that this approach does degrade formaldehyde. The conversions are between 20-40 %, which is approximately the same range as the experiments using TiO_2 instead of hydrogen peroxide. Possible reasons for the conversion not reaching higher levels is temperature and reaction time, which was not tested for these experiments. They can be assumed to have a small impact because of the same reasons discussed for the TiO_2 experiments in Section 4.1 and the same can be said about the UV-flux emitted from the UV-sourses. The primary goal for these experiments, of both kinds, was to investigate the methods and see if the could degrade formaldehyde from a water solution. This primary goal has been successfully accomplished.

4.3 Techno economical evaluation

To evaluate the economical viability of the investigated degradation methods, companies creating solutions for water purification were contacted. What was asked of them was if they have the possibility to produce a plant, using either a photocatalytic reaction or hydrogen peroxide and UV-light, to handle 10 cubic meters per hour of process water and reduce the formaldehyde concentration from 300 ppm to below 30 ppm. They was also asked to make an estimate capital and operational costs for their solution to the task.

4.3.1 Purifics

For the reaction using TiO_2 as a photocatalyst the Canadian company Purifics was contacted. Purifics makes photocatalytic cleaning supplies for mainly drinking water but does also do some industrial pollution degradation solutions. They claim to be able to accomplish the task but to determine the exact configuration and effect of the UV-source they need to be sent water samples to run bench tests. They use ceramic filters to recycle the TiO_2 and claims to be able to recirculate 100% of the photocatalyst, no make up is needed. They recommend switching the UV-source every three years and to replacing the TiO_2 at the same time. Purifics provide 20 liters of photocatalyst which they say should last 25 years. An approximation of the capital cost of this equipment is between 3.4 and 5.1 million SEK. The UV-lamp that needs to be changed once every three years costs 170 000 SEK and for the switch the cleaning process needs to be stopped for approximately 8 hours. To be able to compare this cost with the other method the total cost for this method over nine years was calculated. Purifics process solution would cost between 3,9 and 4,6 million SEK.

4.3.2 Ultraaqua

The company that was contacted about the hydrogen peroxide and UV-light reaction is called Ultraaqua. They are based in Denmark and make water cleaning solutions using ultraviolet light. The system Ultraaqua suggested for the degradation of formaldehyde consists of a cylindrical steel tank reactor. In the reactor 7 UV-sources made of quartz would be placed. Each of the UV-lamps would be able to emit ultraviolet radiation with an effect of 6 kW, which gives the reactor a total UV-capacity of 42 kW. Ultraaqua also recommended that in addition to the pumps attached to the reactor, an extra circulation system to further increase the rate the system can degrade formaldehyde should be installed. A rough estimate of the installation cost for this system would be 564 thousand SEK and the recirculation system would add an additional 162 thousand to this cost. To estimate the operating cost the cost for H_2O_2 needs to be calculated. Hydrogen peroxide with 50% purity can be purchased for 6,6 SEK per liter and if the process stream of 10 cubic meters water per hour should contain 500 ppm of H_2O_2 it is needed to add 2,5 liters per hour. With an estimated process run time of 8000 hours per year it results in a yearly cost of 132 thousand SEK. Using this it was calculated that Ultraaqua´s solution would cost 1,92 million SEK with reticulation and 1,75 million without after 9 years of run time.

4.4 Comparison

Comparing the total cost of the process solutions from Purifics and Ultraaqua after nine years it can be seen that the method using hydrogen peroxide is less expensive. The reason only the cost after nine years is compared, and not other values like the payback time or net present value, is that it is difficult to estimate the profit from a cleaning operation like this one. The main reason for this price difference is the more complex design of the photocatalytic system. However, one advantage this method has is that it does not have any need for continuous addition of chemicals. It should also be noted that all cost values given are rough estimates and not exact figures. However, since the cost for the TiO_2 system is more than twice as expensive than the H_2O_2 method, it can be concluded that the solution from Ultraaqua is preferable from a economical point of view.

5

Conclusion

The findings of this study shows that both of the photocatalyic and the hydrogen peroxide/UV reactions successfully degrades formaldehyde in a water solution. The photocatalyst TiO_2 does however absorb light which leads to uncertainties in the spectrophotometric formaldehyde measurements. The standard deviation did decrease when the TiO_2 concentration was decreased from 0.8 to 0.4 g/l which means that decreasing the amount of added TiO_2 gives more reliable results. Therefore the experiments using the lower concentration level was used when evaluating the degree of conversion. The experiments using both of the methods gave conversion results below 40%, which is lower than the 90% conversion goal set in order to achieve the emission limit for formaldehyde. Possible reasons for this can be reaction time, reaction temperature and the energy output of the UV-sources. According to the results of this study does increasing the reaction time not give any significant increase in the conversion. The temperature influence was not able to be tested, but excising research suggest that the influence of this parameter is small. The UV-sources used for these experiment output light with low energy so increasing the energy flux emitted from the UV-sources would likely increase the conversion. Another way to increase the energy content of the UV-radiation is to decrease the losses the environment. In the experimental setup used for these experiments it was not possible to illuminate the sample directly which increases the energy losses. Using rough economical estimates, received from Purifics and Ultraaqua, it was concluded that using hydrogen peroxide was the most economically viable option of the two.

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A

Appendix 1

A.1 Possible methods

Here the different methods will be briefly presented and discussed. The focus will be on efficiency of formaldehyde removal, stage in the development of the process and implementation possibilities. A simple cost estimation will also be preformed to assess the economical feasibility of each of the methods. The descriptions and cost estimations will not include pumps, for the bulk flow, since the real stream already needs to be pumped for transportation to the water treatment plant. This comparison will focus on on removal of formaldehyde from aqueous solutions. Gaseous methods is only discussed briefly in Section A.1.10. If not otherwise stated the reactions are carried out at atmospheric pressure and room temperature. A conversion summary between different methods can be found in Table A.1.

A.1.1 Hydrogen peroxide/UV process

When a water solution containing hydrogen peroxide is exposed to UV-light the hydrogen peroxide can split into two hydroxyl radicals that can reduce formaldehyde into carbon dioxide and water [20], This is called an Advanced Oxidation Process (AOP) and most of the reactions presented in this report are AOPs, although the mechanism for creating the radicals does vary between methods. The starting components and end products in all AOPs are shown in Equation A.1. A pseudo-first order kinetic model can be fitted to experimental data from degradation of formaldehyde using all types of AOPs [21]. A solution with 400 ppm formaldehyde had 1% of the original formaldehyde left after one hour of reaction [22]. Another experiment made by Kajitvichyanukul et al. using this method with a start concentration of 10 ppm had about 48% degradation after 1 hour [20].

$$CH_2O + 2H_2O_2 \rightarrow CO_2 + 3H_2O \tag{A.1}$$

Investments needed for this process are a reactor and a UV-source. Operating cost consists mostly of cost for purchasing hydrogen peroxide.

A.1.2 Fenton process

In the Fenton process ferrous ion (Fe^{2+}) are used to react with another compound, most often hydrogen peroxide, to create radicals that can start an AOP with formaldehyde according to Equation A.1 [23]. In a study the concentration started at 400

ppm and rather quickly reached a conversion of 90% and then it seemed like the reaction stopped since the concentration of formaldehyde was constant after the initial drop.
This method needs a reactor and two kinds of chemicals; hydrogen peroxide and ferrous ions. This is a well explored and used reaction.

A.1.3 Fenton-like catalytic process

In this Fenton-like process the iron, here in the form of ferric chloride, is used an catalyst to initiate the reaction described in Equation A.1. What is added to this reaction is hydrogen peroxide, ferric chloride and methanol, for stopping polymerisation of formaldehyde, and the reaction can occur at room temperature [23]. In this experiment the formaldehyde concentration was 500 ppm and after around two hours 5% of the original formaldehyde was remaining.
This process have a low capital cost since an atmospheric, room temperature capable reactor is used. The big operating costs comes from purchase of hydrogen peroxide, methanol and ferric chloride. It can be explored if it is possible to separate and reuse the ferric chloride, since these are unaffected by the reaction.

A.1.4 Photo-Fenton process

The Fenton process can be catalysed using UV-light, in whats called the photo-Fenton process. The ferrous ion reacts with hydrogen peroxide and creates hydroxyl radicals that starts an AOP, which results in the decomposition of formaldehyde into carbon dioxide and water [24]. This mean that this is a combination between a H_2O_2/UV process and an Fenton process. In one experiment the starting concentration was 400 ppm and after two hour 99% of the original concentration was remaining but already after one hour the remaining formaldehyde was less than 10% of the original amount. Another experiment was starting with 10 ppm and ended up with a 90% conversion after 1 hour [20]. One study found a 93% conversion after just 10 minutes [24]. A possible reason for this much shorter reaction time is that this experiment was conducted at acidic conditions whereas the other two were conducted at neutral pH. But after this level of degradation was reached the reaction stopped and no further concentration decrease was detected.
This method has a similar cost to to the H_2O_2/UV process with the additional cost of the purchase of the ferrous ions. It may be advantageous for the reaction rate to add acid to lower the pH, but this adds another cost and may decrease the lowest possible.

A.1.5 Electro-Fenton process

Another way of doing the Fenton process is using electricity to further drive the reaction forward [25]. This can be done in two ways; either directly or indirectly. In the direct method hydrogen peroxide is generated at the negatively charged anode and Fe^{2+}-ions at the positively charged cathode. The indirect method regulates the H_2O_2-concentration by manual addition of hydrogen peroxide. This gives a better control of the production of hydroxyl radicals. This is good when the stream to be purified have a high formaldehyde concentration. This method was used in combination with a bioreactor to purify a water stream containing approximately 7500 ppm of formaldehyde [25]. A 51% degradation of formaldehyde was achieved in the reactor after 6 minutes of reaction and a H_2O_2 addition rate of 10 millimoles per minute.

For the case covered in this report it may be possible to use the direct method since the staring concentration is an order of magnitude lower than the study where the indirect is used [25]. But it seems like direct electro-Fenton is not used that often, since no experiments with this technique to remove formaldehyde could be found.

A.1.6 Chemical-free UVC/VUV process

This method uses vacuum UV (VUV) and UV-C radiation to initiate the oxidation of formaldehyde into carbon dioxide and water [21]. Both of these types of ultra violet radiation have short wave lengths, in this case the UVC had a wave length of 254 nm and the VUV had 185 nm. It is called vacuum UV because the radiation energy can be absorbed by oxygen. This is used in this method to break the covalent bonds in water and create radicals that can oxidize formaldehyde into water and carbon dioxide. This method has been preformed at concentrations around 300 ppm which is the range of interest in this study. A formaldehyde removal of around 99% was achieved [21]. The experiment was conducted in a semi-continuous reactor there the water was circulated through the reactor for one hour. The formaldehyde removal is reduced if anions are introduced into the system. The degradation is especially sensitive to the presence of nitrate ions.

This method is only described in a report from 2019 and there is no documentation of any pilot or full scale plants using this method. The semi-continuous nature of this method can cause some difficulties when the water need to be recycled for one hour. This means that if there should not be any accumulation of water, the process needs to be large enough to treat one hour´s worth of water at the same time. This method does not use any chemicals so the operation costs can be expected to be low. The equipment needed is reactor equipped with a VUV and UVC capable ultra violent light source with capacity of at least one hours worth of water.

A.1.7 Catalytic oxidation using nickel-oxide

Another method of removing formaldehyde is to use a nickel-oxide catalyst to oxidize it to water and carbon dioxide via an intermediate state of formic acid [26]. The catalyst can at room temperature create radicals that react with the formaldehyde in a batch reactor. The starting concentration were 30 ppm and after one and a half hour a 90% conversion was reached using a catalyst density of 2 kilograms per cubic meter [26]. After the experiment the catalyst can be regenerated using NaOCl.

This method has a relatively low capital cost with only a batch reactor and catalyst needed. The only chemical needed for operation of the process is the NaOCl to regenerate the catalyst. This reactor may be promising but no reports of any experiment done at concentrations close to the one relevant for this report. The reaction time for this method is also one of the longer ones but this may be possible to shorten with changed operating conditions.

A.1.8 Photocatalytic reactor

Formaldehyde can be removed using a catalyst and UV-light. The most commonly used catalyst for this kind of process is titanium oxide (TiO_2). It functions as a semi conductor excited by the UV-radiation and can crate free radicals that can degrade formaldehyde into carbon dioxide and water. Below two methods using this catalyst are presented.
The first one is a fixed bed photocatalytic reactor. The water enters a reactor that is filled with Raching rings, made of glass, coated with TiO_2 and is then illuminated with UVA-radiation [27]. The reactor was surrounded by six UVA sources. The experiment was conducted in both a closed-loop setup and a continuous open-loop setup. The experimental result was compared with two types of models, a dispersion model and a tank-in-series model. The concentration tested that was the closes to the concentration relevant in this case was was 16 milimole per cubic meter which is 480 ppm on mass basis. After one hour in the reactor around 60% of the formaldehyde was removed [27]. The models fitted to the reactor did both do an adequate job to describe the process and it is a possibility to use them to further optimise the process.
The fixed bed photocatalytic reactor did not achieve a high enough removal percentage during the one hour long test [27]. The starting concentration was higher than the actual case and the trend was that a bigger fraction was removed when the starting concentration was decreased. This means that it is likely that the removal will approach the wanted degree but most likely the residence time in the reactor will need to be longer than one hour. The material needed for this process is a reactor, Raching rings in glass that need to be coated in TiO_2 and six UVA lamps. Since no addition of chemicals is needed the method should have low operational cost. This means that the overall cost can be expected to be rather low, with the most expensive parts being the catalyst and the reactor.
The second kind of reactor uses nanoparticles of TiO_2 that are doped with nitrogen [28]. The doping was done using a sol-gel technique and the size of the catalyst particles ended up around 20 nm. After one hour of reaction time 64% of the initial concentration of 400 ppm was removed [28]. This was using a batch reactor with a UV-source in the middle and a temperatures between 25 and 30 °C.
This reactor did not reach a high enough conversion but photocatalytic reactors are still very interesting, but using a different kind of TiO_2 catalyst.

A.1.9 Removal of formaldehyde through pervaporation using a composite membrane

There are methods of removing formaldehyde without destroying the structure, one way to do this is using a membrane. Different kinds of membranes can be used. One type of membrane is made of a composite consisting of polymethylsiloxane (PDMS) and polyvinylidene flouride (PVDF) [29]. To increase the hydrophobicity the PDMS is mixed with TiO_2 before being coated on top of a PVDF-membrane. This membrane will allow selective permeation of formaldehyde, because of its hydrophobicity. The water and formaldehyde mixture is pervaporated, at around 50 °C, and passes by the membrane that has a pressure gradient to promote the passage of formaldehyde.

Membrane methods are interesting since a pure formaldehyde stream can be recovered from the water stream. It it can be interesting to investigate the economical feasibility of this or other membrane methods to access if it can be beneficial to separate out the formaldehyde instead of oxidize it.

A.1.10 Gaseous methods

There are many different way of removing formaldehyde from air. For example it can be adsorbed, in materials like boron nitride nanotubes [30] or chemically modified active carbon [31]. It is also possible to catalytically oxidize formaldehyde in the gas phase. For these methods a higher temperature is needed than for corresponding aqueous reaction [32, 33, 34]. None of these methods seem to be more effective than the aqueous ones. Especially considering that using a gas phase reaction introduces a additional process step there the formaldehyde is removed from the water stream.

A.2 Comparison

In Table A.1 the degrees of formaldehyde removal for the different methods. The ones that will be further investigated is the photo-catalytic reactor, H_2O_2/UV and the pervaporation through a membrane. All of these methods are used in industry applications already and deemed to be most suitable for this application.

Method	Start conc. [ppm]	Conversion [%]	Reaction time [h]
H_2O_2/UV [22]	400	99	1
H_2O_2/UV [20]	10	48	1.3
Fenton [22]	400	90	1
Fenton-like [23]	500	95	2
Photo-Fenton [22]	400	99	2
Photo-Fenton [20]	10	94	1.2
Photo-Fenton [24]	50	93	0.17
Electro-Fenton [25]	7500	51	0.1
Chemical-less UVC/VUV [21]	300	99	1
Nickel-oxide catalyst [26]	30	90	1.5
Photocatalytic fixed bed [27]	480	60	1
Nano photocatalyst [28]	400	62	1

Table A.1: Conversion comparison for formaldehyde between the different methods.

B

Appendix 2

In this appendix the raw data from the experiments will be presented.

B.1 Titanium dioxide photocatalytic reaction

Table B.1: The experiments having a concentration of 0.4 g/l of TiO_2 type A. All of these experiments have a reactor volume of 5 ml, a wavelength of 310 nm and using the direct irradiation method.

Exp nr	**Reaction time [h]**	**Reference Abs**	**Sample Abs**	**Conversion [%]**
1	1	0.245	0.173	29.5
2	1	0.286	0.242	15.3
3	1	0.240	0.166	30.8
4	1	0.237	0.249	-5.25
5	1	0.262	0.197	24.7
6	1	0.210	0.192	8.37
7	1	0.148	0.120	18.9
8	1	0.163	0.116	28.7
9	1	0.212	0.146	31.2
10	5	0.253	0.192	16.6
11	5	0.272	0.158	41.9

Table B.2: The experiments having a concentration of 0.8 g/l of TiO_2 type A. All of these experiments have a reactor volume of 5 ml.

Exp nr	**Irr method**	λ **[nm]**	**Time [h]**	**Ref Abs**	**Sample Abs**	**Conversion [%]**
1	Direct	310	1	0.471	0.363	22.9
2	Direct	310	1	0.541	0.418	22.7
3	Direct	310	1	0.389	0.366	5.69
4	Direct	310	1	0.265	0.249	5.83
5	Direct	310	5	0.379	0.350	7.72
6	Glass fibre	310	1	0.523	0.476	9.09
7	Glass fibre	310	5	0.45	0.437	4.49
8	Glass fibre	310	5	0.404	0.396	1.91
9	Direct	280	1	0.686	0.387	43.6
10	Direct	280	5	0.528	0.392	25.8

Table B.3: The experiments using TiO_2 type B. All of these experiments have a reactor volume of 5 ml and had a reaction time of one hour.

Exp nr	**TiO_2 conc [g/l]**	**Irr method**	λ **[nm]**	**Ref Abs**	**Sample Abs**	**Conversion [%**
1	0.4	Direct	310	0.147	0.159	-7.89
2	0.4	Direct	310	0.145	0.156	-7.65
3	0.8	Direct	280	0.381	0.404	-5.89
4	0.8	Direct	310	0.292	0.291	-0.546
5	0.8	Direct	310	0.246	0.298	-21.2

Table B.4: The experiments using TiO_2 type C. All of these experiments have a reactor volume of 5 ml and had a reaction time of one hour.

Exp nr	**TiO_2 conc [g/l]**	**Irr method**	λ **[nm]**	**Ref Abs**	**Sample Abs**	**Conversion [%**
1	0.4	Direct	310	0.153	0.114	25.3
2	0.4	Direct	310	0.136	0.133	1.96
3	0.8	Direct	280	0.396	0.383	3.25
4	0.8	Direct	310	0.261	0.256	1.58
5	0.8	Direct	310	0.248	0.248	2.34

Table B.5: The experiments using TiO_2 type D using the glass fibre irradiation method. All of these experiments have a reactor volume of 5 ml.

Exp nr	**TiO_2 conc [g/l]**	**Time [h]**	λ **[nm]**	**Ref Abs**	**Sample Abs**	**Conversion [%]**
1	0.8	1	310	0.305	0.270	11.2
2	0.8	1	310	0.388	0.338	13.1
3	0.8	5	310	0.484	0.439	9.89
4	3.2	1	310	0.500	0.501	-0.206

Table B.6: The experiments using TiO_2 type D using the direct irradiation method. All of these experiments have a reactor volume of 5 ml.

Exp nr	TiO_2 conc [g/l]	Time [h]	λ [nm]	Ref Abs	Sample Abs	Conversion [%]
1	0.8	1	280	0.404	0.389	3.74
2	0.8	1	310	0.250	0.211	18.2
3	0.8	1	310	0.232	0.210	9.54

Table B.7: Spectro photo metric analys of 0.08 g/l TiO_2 of all different types.

Exp nr	TiO_2 conc [g/l]	Absorption at 412 nm
1	A	0.786
2	A	0.656
3	A	1.245
4	A	1.169
5	B	1.316
6	B	1.338
7	B	2.196
8	B	1.300
9	C	0.155
10	C	0.139
11	C	0.116
12	C	0.113
13	D	0.813
14	D	0.808
15	D	0.813
16	D	0.841

B.2 Titanium dioxide photocatalytic reaction

Table B.8: The experiments having a concentration of 500 of TiO_2 type A. All of these experiments have a reactor volume of 5 ml, a wavelength of 260 nm and a reaction time of 1 hour. They are all using the direct irradiation method.

Exp nr	H_2O_2 [h]	Reference Abs	Sample Abs	Conversion [%]
1	0	0.165	0.163	1.66
2	0	0.170	0.162	4.62
3	500	0.172	0.117	32.0
4	500	0.184	0.147	20.1
5	500	0.169	0.106	37.4
6	500	0.158	0.0985	37.8
7	500	0.191	0.129	32.7
8	500	0.175	0.128	27.0