## Rapport SGC 166

# Preventing microbial growth on pall-rings when upgrading biogas using absorption with water wash

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## Preventing microbial growth on pall-rings when upgrading biogas using absorption with water wash

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## Abstract

For produced biogas to be usable as vehicle fuel it has to be upgraded to a higher energy content. This is accomplished by elevation of the methane concentration through removal of carbon dioxide. Absorption with water wash is the most common upgrading method used in Sweden today. The upgrading technique is based on the fact that carbon dioxide is more soluble in water than methane. Upgrading plants that utilises this method have problems with microbial growth in the system. This growth eventually leads to a stop in operation due to the gradually drop in upgrading capacity.

The aim of this thesis were to evaluate the possibility to through some kind of water treatment maintain an acceptable level of growth or altogether prevent it in order to maintain an acceptable process capacity and thereby avoid the need to clean. Through collection of literature the implementation possibilities were evaluated with regard to efficiency, economic sustainability and if there would be a release of any harmful substances.

In order to prevent the microbial growth in the columns the treatment should either focus on removing microorganisms or limit the accessible nutrients. For the single pass system it is concluded that the treatment should reduce the biofilm formation and be employed in an intermittent way. Among the evaluated treatments focusing on the reduction of microorganisms the addition of peracetic acid seems to be the most promising one. For the regenerating system the treatment method could focus on either one. As for the single pass system peracetic acid could be added to reduce the amount of microorganism. To reduce the amount of organic matter an advanced oxidation process could be deployed with the advantage that it also could remove the microorganisms.

## Sammanfattning

För att kunna använda den producerade biogasen som fordonsgas måste dess energiinnehåll höjas. Detta åstadkoms genom avskiljning av koldioxid så att metankoncentrationen ökar. Den vanligaste förekommande uppgraderingstekniken i Sveriges är absorption med vatten, som bygger på att koldioxid är mer lösligt än metan i vatten under tryck. Uppgraderingsanläggningarna har mikrobiell tillväxt på fyllkropparna i absorptionskolonnen, vilket ofrånkommligen orsakar en lägre uppgraderingskapacitet och slutligen är ett stopp i produktionen nödvändig för kunna tvätta fyllkropparna. Anläggningarna som recirkulerar processvattnet kan även ha tillväxt i kolonnen, där den lösta koldioxiden tas bort.

Syftet med detta arbete var att genom en litteraturstudie undersöka om det vore möjligt att undvika eller åtminstone hålla tillväxten under en acceptabel nivå genom någon typ av vattenrening. De olika reningsmetoderna utvärderades med avseende på möjlighet att implementeras i det befintliga uppgraderings systemet, effektivitet, möjliga utsläpp och ekonomisk hållbarhet.

För att begränsa tillväxt i kolonnerna ska vattenreningen antingen fokusera på att ta bort mikroorganismer eller begränsa tillgången på näringsämnen för bakterierna som når kolonnerna via biogasen, luften som används för att ta bort koldioxiden från vattnet, eller via vattnet. För uppgraderingsanläggningar där processvattnet bara passerar kolonnen en gång rekommenderas en reningsmetod som fokuserar på reducera bildandet av biofilmen. Av de utvärderade metoderna ter sig perättiksyra som det bästa alternativet. För system med recirkulerande processvatten skulle reningsmetoden fokusera på antingen reduktion av mikroorganismer, organiskt material eller både och. Som för anläggningar med ickecirkulerande vatten verkar perättiksyra vara det bästa alternativet för reduktion av mikroorganismer. En avancerad oxidationsprocess skulle kunna användas för att reducera mängden mikroorganismer och organiskt material.

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## Contents

1	Intr	roduction	1
<b>2</b>	Bac	kground	<b>2</b>
	2.1	Biogas production	2
	2.2	Upgrading the Biogas	3
	2.3	Absorption with water wash	4
		2.3.1 Regenerating plants	5
		2.3.2 Single pass plants	6
	2.4	Problems with absorption by water wash	7
		2.4.1 Growth in the absorption column	8
		2.4.2 Growth in the desorption column	8
		2.4.3 The solution at present date	8
	2.5	Water quality	9
		2.5.1 Water from sewage treatment plant	9
		2.5.2 Drinking water	10
3	Me	thod	11
4	$\mathbf{Res}$	ults	12
	4.1	Chemical methods	14
		4.1.1 Chlorination, $Cl_2$	14
		4.1.2 Chlorine dioxide, $ClO_2$	17
		4.1.3 Hydrogen peroxide, $H_2O_2$	19
		4.1.4 Peracetic acid, $CH_3COOOH$	20
		4.1.5 Ozone, $O_3$	22
	4.2	UV radiation	24
	4.3	Advanced oxidation processes	27
		4.3.1 $UV/H_2O_2$	28
		$4.3.2  O_3/H_2O_2  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  $	29
		4.3.3 $UV/O_3$	29
		4.3.4 $O_3/H_2O_2/UV$	30
		4.3.5 UV/CH <sub>3</sub> COOOH	31
		4.3.6 $Fe^{2+}/H_2O_2$	31
	4.4	Filtration	32
		4.4.1 Water filtration	32
		4.4.2 Air filtration	32
	4.5	Summary	33
5	Dis	russion	₹1
0	5 1	Single pass	95 95
	0.1	511 Treatment method	36
	59	Begenerating	38
	0.2	5.2.1 Treatment method	39
			50
6	Cor	iclusions 4	41
	6.1	Single pass	41
	6.2	Regenerating	41
	6.3	What to do next? $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	41

References		42
A	Flowchart of the regenerating process	46
в	Flowchart of the single pass process	47

## 1 Introduction

In order to use biogas as vehicle fuel the gas has to be upgraded to a higher methane content. This is accomplished by removing carbon dioxide from the gas, thus elevating the methane concentration. There are four different upgrading techniques in use in Sweden today; pressure swing adsorption, absorption with water wash, absorption with Selexol and absorption with chemical reaction. Upgrading by absorption with water wash, water scrubbing, is the most common in Sweden. Absorption with water wash can be divided into to two processes with regard to the process water, which could either be single pass or regenerating.

This technique is based on the principle that carbon dioxide is more soluble in water than methane. Carbon dioxide is removed from the gas in an absorption column, where raw biogas gas enters from the bottom and the water from the top. The gas is pressurised before entering the column because the higher the pressure the more soluble is carbon dioxide. The absorption column is filled with plastic packings called pall-rings, to provide more surfaces between the gas and the water in order to elevate the exchange.

Upgrading plants that utilises this method has problems with microbial growth in the system, which inevitable causes clogging and as a consequence a loss in upgrading capacity. Eventually the capacity is so low that it is necessary to stop the production in order to clean the pall-rings and the absorption column. The cleaning is a time consuming job and any stop in the production has economical implications. All upgrading plants with single pass experience microbial growth on the pall-rings in the absorption column. One of the regenerating plants also experiences growth on the pall-rings in the desorption column where the carbon dioxide is removed.

The aim of this investigation was to assess the possibility to prevent microbial growth in the absorption column when upgrading biogas to vehicle fuel using absorption with water wash. More specifically if some kind of water treatment could hinder the establishment of a bacterial community in the absorption column or maintaining the growth under an acceptable level. The purpose is also to address the problem with microbial growth in the desorption column. It is evaluated if this could be handled either by treatment of the water or with some kind of filter for the incoming raw gas and air.

### 2 Background

#### 2.1 Biogas production

**Anaerobic digestion** Biogas is produced through anaerobic digestion of organic material. The degradation of organic matter to its most reduced form methane requires a versatile group of microorganisms, since different microorganisms perform different steps in the degradation process. The degradation process is divided into four steps.

1. Hydrolysis

complex organic matter  $\rightarrow$  soluble organic molecules

- 2. Fermentation soluble organic molecules→ fermentation products
- 3. Acetogenesis

fermentation products — acetic acid (CH\_3CO\_2H), hydrogen (H\_2) and carbon dioxide (CO\_2)

4. Methanogenesis products of the acetogenesis  $\rightarrow$  methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>)

**Biogas content** The produced gas consist of 45-85% methane and 15-45% carbon dioxide [1]. It may also contain small amounts of hydrogen sulphide  $(H_2S)$ , ammonia  $(NH_3)$  and nitrogen gas  $(N_2)$ . The raw gas also contains water and sometimes particles.

**Biogas plants** There are about 200 plants in Sweden that produces or collects biogas, 120 treats sewage water sludge, 20 treats organic waste and 60 collects gas from landfills [2]. The upgrading plants are located close to the plants that produces biogas, since its not energetically favourable to transport the raw gas very long. There could be piplines of a couple of kilometre.

**Applications of the biogas process** Biogas has many different applications depending on the methane content of the gas. The refined raw gas can be used for heat and electricity production. Upgraded gas be used as vehicle fuel or distributed in the natural gas grid. The fermented sludge can be used as fertilisers, and the overall process is a way to handle organic waste.

**Environmental aspects** Upgraded biogas is an environmentally friendly vehicle fuel, where carbon dioxide and water are the main products of the combustion of methane. Although carbon dioxide is a strong greenhouse gas the combustion does not contribute to the increased greenhouse effect, since it is already in the fast circulation of the carbon, and not in the circulation in which fossil fuel is created. The fermented sludge is a good fertiliser that contains a lot of nutrients that are available for the crop. By using this fertiliser the nutrients are recycled back to the land.

#### 2.2 Upgrading the Biogas

The energy content of the biogas has to be elevated for the gas to be usable as vehicle fuel. This is accomplished by removal of the carbon dioxide. The energy content of the raw gas varies between 4.5 and 8.5 kWh/Nm<sup>3</sup> depending on the methane content [1]. The N stand for normal cubic meter, which is  $1m^3$  gas at 1.01 bar and 0 °C. The energy content is defined by the concentration of methane, 10% of CH<sub>4</sub> in the dry gas correspond to approximative 1 kWh/Nm<sup>3</sup> [3]. For example, biogas with 97% methane has an energy content of 9.67kWh/Nm<sup>3</sup>. In Sweden the raw gas is upgraded to this methane concentration so that the vehicles can be driven on both biogas and natural gas. If the the gas is to be distributed in the natural gas grid propane is added to elevate the energy content to match the natural gas that has an energy content of 11kWh/Nm<sup>3</sup> [4]. In gas stations this is not done, the vehicles can handle this difference in energy content.



Figure 1: Biogas buss [2].

Corrosive and harmful substances such as hydrogen sulphide  $(H_2S)$  and particles have to be removed, otherwise they could cause damage to the engine. These substances could cause damage to the upgrading system so they are preferably removed early. However, this is not the case with water absorption methodology. Here the hydrogen sulphide is removed in the absorption column along with the carbon dioxide [5].

Since the gas has relatively low density, it has to be pressurised before it can be used as vehicle fuel or be distributed in the natural gas grid. There are twentythree upgrading plants in Sweden that are either in use or being constructed (2006) [2]. Of the four upgrading techniques that are in use in Sweden today, absorption with water wash is the most commonly used method [1].

#### 2.3 Absorption with water wash

Absorption with water wash, or water scrubbing, is used to remove carbon dioxide and also hydrogen sulphide from the raw gas. The method is based on the fact that  $H_2S$  and  $CO_2$  are more soluble in water than methane. Carbon dioxide dissolves in water and thereby lowers the pH of the process water from neutral or slightly above to acidic conditions. According to Henry's law the higher the carbon dioxide partial pressure the more soluble is the carbon dioxide, that is reaction (2.1) is driven to the right.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
 (2.1)

Condensed water and particles are removed prior to the compressor. After being pressurised to 9-12 bars, the gas is led to the absorption column, where it enters from the bottom. Water is flushed from the top and in order to create more surfaces for the gas and the water to interact the column is packed with pallrings. Upgraded gas will exit the absorption column at the top. Since the gas is saturated with water it has to be dried. The dried gas is then pressurised to about 200 bars [1]. The gas is also odourised to make it possible to detect a leak, since methane is odourless.





Figure 2: Absorption column to the left [5], and pall-rings to the right [6].

Methane is partially soluble in pressurised water. So after the absorption column the methane that has dissolved in the water is removed by returning it to gas by lowering the pressure to an intermediate pressure of about 2-4 bars in a flash tank. The gas containing high levels of methane is returned to the raw gas before it enters the compressor. This is done to minimise the methane losses. There are two types of plants that use this method to upgrade the gas: regenerating where the process water is recirculated and single pass, where the water passe the absorption column only once [5]. The absorption technique described above is the same for both types.

#### 2.3.1 Regenerating plants

To be able to recirculate the water, the dissolved carbon dioxide has to be removed. The carbon dioxide is removed in a desorption column, where the water enters from the top and air is blown from the bottom. Just like the absorption column the desorption column is packed with pall-rings to increase surfaces for the water and the air to interact [5]. A low carbon dioxide partial pressure removes dissolved carbon dioxide from the water by returning it to its gaseous form (driving reaction (2.1) to the left). This raises the pH up to around neutral and the water temperature increases. A heat exchanger is used to lower the temperature to an absorption temperature of  $15 \,^{\circ}$ C.

The gas that leaves the desorption column at the top, consisting of carbon dioxide and other gases such as hydrogen sulphide, is deodourised through a gas filter and then released to the atmosphere [4]. A simplified discribition of the process is given in Figure 3. The complete process is described in Figure 6 in appendix A on page 46.



Figure 3: Absorption with water wash with regeneration.

 $\rm H_2S$  is absorbed together with CO<sub>2</sub> in the absorption column. Hydrogen sulphide is highly soluble in water and all cannot be removed in the desorption column. Some of the hydrogen sulphide is also oxidised with air to elementary

sulphur in the desorption column. This sulphur accumulates and may cause operational problems after a while. This is a reason to make sure that as much as possible of the hydrogen sulphide is removed prior to the absorption column. Water wash with regeneration is not recommended when the raw gas contains high levels of hydrogen sulphide [3].

This method is not the most cost effective alternative, if non-expensive water is available. That is if the upgrading plant can use water from a sewage treatment plant.

#### 2.3.2 Single pass plants

To keep the costs for process water down single pass upgrading plants uses cleaned water from the sewage water treatment plants. This means that this type of upgrading plant needs to be in the close proximity of a sewage treatment plant.

The principle of the absorption and the flash tank is the same as for the regenerating plants. After the flash tank, where the methane that has dissolved in the water is removed, the water is depressurised and returned to the sewage water treatment plant [6]. Since the upgrading plants use water from the sewage treatment plant the temperature of the process water follows the seasonal variations ranging from about 4 to  $21 \,^{\circ}$ C [6]. A simplified discribition of the process is given in Figure 4. The complete process is described in Figure 7 in appendix B on page 47.



Figure 4: Absorption with water wash without regeneration.

#### 2.4 Problems with absorption by water wash

Many of the single pass upgrading plants in Sweden reports growth in the absorption column, but only one regenerating plant reports growth in the desorption column [6]. However some of the regenerating plants that do not report growth clean their pall-rings and absorptions column as a preventative measure. So regenerating plants can experience growth, although it is more rare than for single pass upgrading plants.



Figure 5: Microbial growth on pall-rings [6].

A student thesis at the department for water and environmental studies at Linköping Universitet analysed the clogging material and determined the type of bacteria it contained. The appearance and the content of the growth varied at the upgrading plants, as can be seen in Table 1. Fungi and actinomycetes are contaminants in wastewater, but can survive as spores in the raw gas, and thereby enter the absorption column via the raw gas [6].

Table 1: Bacterias detected in the absorption column at different upgrading plants [6].

Microorganism	Jönköping	Linköping	Kristianstad	Uppsala
	$(s.p.)^1$	$(r.)^2$	(s.p.)	(s.p.)
Methanotroph type I		x		X
Methanotroph type II		x		
Gram-negative bacteria		x		X
Gram-positive bacteria	x	x	x	X
Actinomycetes	x			
Fungi	x	X		X

There are different factors affecting the growth. For example the problem seems to be temperature dependent, since the growth is more extensive in the summer [7]. According to a supplier the extent of the problem with growth also seems to be dependent of the material being degrading [5]. Where organic matter from the slaughter house or the food industry seems to cause more

<sup>&</sup>lt;sup>1</sup>single pass

<sup>&</sup>lt;sup>2</sup>regenerating

problems. An explanation to this is, that the produced biogas contains more nutrients and thus promotes growth. However, not all plants that upgrade biogas from digesters that digest slaughter house waste experience growth.

#### 2.4.1 Growth in the absorption column

All the upgrading plants that are single pass experience extensive growth in the absorption column. Plants with regeneration of the water also experiences growth but not to the same degree. This leads to the assumption that it is the water that is the main cause of the extensive growth in the absorption column. High level of nutrients promote growth of biofilms [8]. This is probably why the microbial growth is more severe in the upgrading plants with single pass, due to the higher level of nutrients in the water.

Upgrading plants with single pass uses water from sewage treatment plants that contains biological material that can get caught in the pall-rings or cause growth. Recirculating systems use drinking water that is much cleaner. Effectively disinfected drinking water does not contain actinomycetes, fungi or methanotrophs and the allowed colony count in drinking water is low. This means that the growth in this kind of system is mainly caused by the addition of bacteria and organic matter from the incoming air in the desorption column and or the incoming raw gas.

#### 2.4.2 Growth in the desorption column

An upgrading plant with recirculating water experiences bacterial growth in the desorption column. They reported even more growth in the desorption column than in the absorption column [6]. The main cause for the growth in the desorption column could be the air that is used to transform the carbon dioxide from the dissolved state back to the gaseous state. This air could also be the cause of the microbial growth in the absorption column. However it is believed that the microbial community first establishes in the absorption column and then some microorganisms follow the water to the desorption column and attaches there. Maybe it is a combination of contaminants in the raw gas and in the air used in the desorption column that causes the extensive growth in the desorption column.

#### 2.4.3 The solution at present date

The growth lowers the upgrading capacity. A plant with two parallel upgrading systems can stop and clean one while the other is running, but if the plant does not have two systems a stop means a period when refined gas can not be upgraded. The stop in operation is especially serious for plants that experience a bigger demand for upgraded biogas [7].

At present date, the upgrading plants clean the pall-rings, the absorption column and the desorption column in order to maintain the capacity. Different plants employs different methods to clean the pall-rings. They either clean them inside or outside the column, and some use detergents and others use only water [6].

Each upgrading plant uses different detergents to clean the pall-rings. The detergents are shown in table 2. Sodium hypochlorite NaClO, sodium hydroxide

(NaOH) and potassium hydroxide (KOH) are common ingredients in the alkaline detergents [6].

Table 2: Detergents used to clean the pall-rings and the absorption/desorption column [6].

Detergents		
Mechanically with hot water		
Hypochlorite (ClO <sup>-</sup> )		
Alkaline detergents		

The time needed to clean the pall-rings varies between six to ten hours and depends on the technique used. A technician at the Linköping upgrading plant said that it could take up to two or three days to clean the pall-rings [7]. How often the plants clean their pall-rings varies between a couple of times a year to every third week [6].

Cleaning the pall-rings outside the column is a time consuming job and if it is done mechanically with water the removal of bacteria is insufficient and the bacteria on the pall-rings soon starts to grow again [7]. Hence the cleaning just removes the clogging and thereby elevates the capacity.

The upgrading plant in Linköping use sodium hydroxide (NaOH) to elevate the pH to around 12 and thereby killing the bacteria within the column which facilitates the cleaning [7]. But since the absorption of carbon dioxide is pH dependent this can not be done while the column is in operation. So it still means a stop in production. The upgrading plant in Linköping is trying prevent or at least decrease the extent of the growth during the summer by lowering the pH, which is done through additions of citric acid ( $C_6H_8O_7$ ) [7].

#### 2.5 Water quality

#### 2.5.1 Water from sewage treatment plant

The effluent from a sewage treatment plant must fulfil the load that set by the law. For a upgrading plant with single pass this could be considered the worst case scenario Table 3. Table 4 gives average concentrations of some constituents in the effluent from sewage treatment plants [9].

Table 3: Regulations on the effluents from sewage treatment plant in Sweden [9].

Parameter	Annular mean	Type of limit
	(mg/l)	
BOD <sub>7</sub>	$15 { m mg~O_2/l}$	threshold
$\mathrm{COD}_{Cr}$	$70 \mathrm{mg} \mathrm{O}_2/\mathrm{l}$	recommended
Total N	$15 \mathrm{mg/l}$	recommended
	(10.000-100.000 pe)	
	$10 \mathrm{mg/l}$	recommended
	$(>100.000 { m pe})$	
Total P	$0.5 \mathrm{mg/l}$	recommended

Table 4: Average concentrations of the effluents from sewage treatment plants in Sweden, 2000 [9].

Parameter	Average concentration
	(mg/l)
BOD <sub>7</sub>	7.2
$COD_{Cr}$	42.2
Total N	13.9
Total P	0.31

#### 2.5.2 Drinking water

Upgrading plants with regeneration use drinking water as their process water. Table 5 gives the European drinking water regulations for some constituents [10]. This could be seen as the worst case scenario for the regenerating plant.

Parameter	Limit
DOC	$4.0 \mathrm{mg/l}$
Nitrate NO <sub>3</sub>	$50 \mathrm{~mg/l}$
Nitrite NO <sub>2</sub>	$0.50 \mathrm{~mg/l}$
Ammonia NH <sub>4</sub>	0.5 mg/l
$[ Hydrogen \ conc \ [H^+] ]$	$\geq 6.5 \mathrm{and} \leq 9.5$
Total organic carbon (TOC)	No abnormal change
Colony count 22 °C	100/ml
Colony count 37 °C	$20/\mathrm{ml}$

Table 5: European drinking water regulations [10].

### 3 Method

To investigate options available for the abatement of microbial growth on pallrings a literature survey was conducted. Literature was collected:

- regarding existing water treatment methods and evaluation of the possibility of applying them to the process.
- concerning systems with recirculating process water, especially systems that could have problems with bacterial growth. That could be compared to water wash with regeneration.
- about filtration of both water and air.

The methods implementation possibilities was evaluated with regard to:

- the efficiency of the treatment.
- if the treatment will result in release of any harmful substances in the gas and or in the water.
- if there is or will be formed any substances that could be corrosive to the equipment.
- if it is economically sustainable.

The databases searched were: ScienceDirect, ENVIROnetBASE Environmental Resources Online, SpringerLink and Wiley InterScience. Searh engines were used to locate some information. A search started with a specific word considered to be important in the context of the query and were followed by addition of words and in some cases restraints until an reasonable list of hits were reached, that is a list with not to many hits in it. Then the titles in the list were reviewed to see if there were any interesting hits.

### 4 Results

The water treatment should aim at either prevention of microbial growth in the absorption column or at keeping the growth under a threshold in order to maintain an acceptable process capacity. The treatment methods to be evaluated were either suggested in the project plan or selected after reading about biofilm formation, reduction and prevention. This preliminary reading resulted in the conclusion that in order to prevent biofilm formation or at least diminish the extent of the growth the treatment method should destroy the microorganisms, inactivate them or remove the available organic matter, thus reducing the sub-strate for new biomass [11]. However, it should be pointed out that one study stated that it was virtually impossible to inhibit biofilm formation by limiting the carbon source [12].

Many of the disinfectants used in water treatment today are oxidising agents. The higher the oxidation potential the easier the compound can oxidise organic materials [13]. Standard potentials for some disinfectants used in water treatment are listed in table 6. Although the disinfection power of a disinfectant is correlated with its oxidation potential, oxidation is not the only factor governing the efficiency [14]. Molecular weight and charge for example influences the efficiency at which it kills or inactivates microorganisms.

Chemical	Standard Potential
	$\rm E^{\circ}$ (volts)
Hydroxyl radical, <sup>•</sup> OH	2.80
Ozone, $O_3$	2.07
Peracetic acid, $CH_3COOOH$	1,81
Hydrogen peroxide, $H_2O_2$	1.76
Perhydroxyl, $HO_2^{\cdot}$	1.70
Chlorine, $Cl_2$	1.36
Chlorine dioxide, $ClO_2$	1.27

 Table 6: Standard Potentials

One also need to consider the fact that the bacteria are not all suspended in the water, in fact they form biofilms on the surfaces available, in this case the pall-rings. Biofilms are more resilient against disinfectants than bacteria in solution. One explanation could be that the films contain a matrix of exoplysaccaridic substances (EPS) that are difficult for the disinfectant to penetrate [15, 12]. To overcome this the treatment may require higher dosages, longer contact time or the water need to be treated before a biofilm develops or perhaps a combination of all three. The biofilm continue to develop even though there are no longer any microorganisms in the water which means that the treatment method focusing on the reduction of microorganisms should treat the biofilms and not only the planktonic cells[8]. Oxidising biocides are more efficient at limiting the biofilm formation since they can destroy the EPS matrix [16].

The efficiency of the biocides/oxidants depends on contact time, intensity of the disinfectant, type and age of the microorganisms, the quality of the water like turbidity and BOD content, pH and temperature. These parameters and byproduct formation, implementation and operational costs need to be considered when designing a treatment method. The primary factors affecting the disinfection of the water are the ability to:

- 1. oxidise or rupture the cell wall.
- 2. diffuse into the cell and interfere with cellular activity.
- 3. remove nutrients from the water.
- 4. leave a residual in the treated water.

It is obvious that the time needed to kill a given percentage of microorganisms decreases as the intensity of the disinfectant increases (cf. equation (4.1)) [17]. However, no inactivation at low concentrations of disinfectants and no further increase in inactivation at higher concentrations of the disinfectant is explained by this simplified equation.

$$t = \frac{k}{I^m} \tag{4.1}$$

where

t =Contact time,

I =Intensity ( ex.concentration (mg/l)),

k =Reaction constant and

m = Constant, makes the relationship more general.

The deactivation of bacteria usually follows first-order kinetics that is m = 1 which gives  $k = C \cdot t$ . The Ct-value is the product of disinfectant concentration and contact time needed to deactivate microorganisms. The deactivation is often expressed as a log reduction.

$$1log reduction = 90\%$$
 deactivation  
 $2log reduction = 99\%$  deactivation  
 $3log reduction = 99,9\%$  deactivation  
 $4log reduction = 99,99\%$  deactivation

Disinfection by-products form during oxidation/disinfection of waters containing natural organic matter (NOM) and/or bromide ions (Br<sup>-</sup>). The maximum contaminant levels of trihalomethanes, THMs, haloacetic acids, HAAs and bromate,  $BrO_3^-$  in the effluent from a water treatment plant in the United States are 80, 60 and 10  $\mu$ g/l, respectively [18]. The European Union states that the limit for total trihalomethanes and bromate is 0.1 mg/l and 0.01 mg/l [19].

The treatment could either be continuous or in chock dosages depending on the aim and type treatment. In a continuous process there is a higher risk of adaptation by the bacteria. A shock dosage program can be necessary when the bacterial growth is extensive. After a shock treatment some kind of physical method may be needed. The cost assessment can be divided into operational and implementation costs. Where the operational costs include chemical and electricity costs.

The costs are linked to the required dosages and they are higly dependent on the experimental conditions. This made it difficult to access the costs of the different treatments, and resulted in a more qualitative description of the costs.

#### 4.1 Chemical methods

Chemical biocides kill or inactivates microorganisms in the water. Chemical oxidants employs oxidation to reduce the COD/BOD levels, and to remove both inorganic and organic compounds from the water. There are chemicals that can accomplish both. After reading more about biofilms it was concluded that the biocide would have to be an oxidising agent in order to be effective at removing the attached microorganisms [20, 21, 12, 16]. The chemicals to be evaluated were selected with regard to this requirement.

A factor to consider when choosing a treatment chemical is if it can be stored or has to be generated on site. Other design parameters are storage of chemicals or reagents for the generation of the chemical, generation equipment, dosage apparatus and what kind of contact tank and mixing is necessary. Is there a need for continuous monitoring of the process? Can the residual concentration of the chemical leave the plant or should it be destroyed? Many of the chemicals used for disinfection/oxidation are strong oxidising agent and therefor should be handled with caution.

#### 4.1.1 Chlorination, Cl<sub>2</sub>

**General** Chlorine is the most commonly used chemical for water disinfection, perhaps because of its ability to provide a residual in the treated water. It is widely used to disinfect drinking water, sewage treatment plant effluent and swimming pool water.

Many of the species of chlorine that provide disinfection can also oxidise natural organic matter by cleavage of carbon-carbon double bonds [14, 18]. Through oxidation chlorine can remove dissolved organics from the water, however the reaction between natural organic substances in the water and chlorine can result in the formation of mutagenic/carcinogenic and toxic by-products.

**Generation** There are three chlorine compounds that are used for water treatment, molecular chlorine  $(Cl_2)$ , calcium hypochlorite  $(Ca(OCl)_2)$  and sodium hypochlorite (NaClO) [14]. The chlorine compounds dissolve in water and forms the chlorine disinfectant hypochlorous acid (HOCl) according to the following reactions.

$$Cl_{2}(aq) + H_{2}O \rightarrow HCl + HOCl$$

$$NaOCl + H_{2}O \rightarrow NaOH + HOCl$$

$$Ca(OCl)_{2} + H_{2}O \rightarrow Ca(OH)_{2} + 2 HOCl$$

The hypochlorous acid reacts further and a mixture of hypochlorous acid and hydrochlorite ions,  $OCl^-$  are formed. These species of chlorine are called the free chlorine. As can be seen in reaction (4.2) the ratio of the chlorine disinfectant is pH dependent. Hypochlorous acid dominates below pH 7.6 and hydrochlorite ions above 7.6.

$$HOCl + H_2O \leftrightarrow H_3O^+ + OCl^-$$

$$(4.2)$$

Aqueous chlorine is not stable in the presence of sunlight. Sunlight contains ultraviolet light that drives the reaction that causes the hypochlorous acid to break up.

$$2 \operatorname{HOCl} \rightarrow 2 \operatorname{H}^{+} + 2 \operatorname{Cl}^{-} + \operatorname{O}_{2}$$

**Function** When chlorinating water the chlorine is initially added to oxidise any reducing compound present. Then the concentration of hypochlorous acid is increased to form chloramines with the ammonia and organic nitrogen present in the water. The concentration is increased further in order to destroy the chloramines and finally it is increased to build up the free chlorine residual so that the disinfection can begin [17, 22]. Since chlorine reacts with chemicals in the water it has to be added in amounts sufficient to meet the chlorine demand if it is to provide residual (longterm) disinfection. Ammonia and organic nitrogen present in the water binds to the free chlorine to form organic and inorganic chloramines according to the following reactions.

$$\begin{aligned} \mathrm{NH}_3 + \mathrm{HOCl} &\rightarrow \mathrm{NH}_2\mathrm{Cl}(\mathrm{monochloramine}) + \mathrm{H}_2\mathrm{O} \\ \mathrm{NH}_2\mathrm{Cl} + \mathrm{HOCl} &\rightarrow \mathrm{NHCl}_2(\mathrm{dichloramine}) + \mathrm{H}_2\mathrm{O} \\ \mathrm{NHCl}_2 + \mathrm{HOCl} &\rightarrow \mathrm{NCl}_3(\mathrm{trichloramine}) + \mathrm{H}_2\mathrm{O} \end{aligned}$$

All the chlorine disinfectants reduces to the chloride ion  $(Cl^-)$  when they oxidises other substances. Free residual chlorine can be calculated using Equation (4.3). It can be difficult to maintain a free chlorine residual in waters having high chlorine demand.

Free residual chlorine = 
$$[HOCl] + [OCl^{-}]$$
 (4.3)

The mechanism of which chlorine deactivates bacteria is not clear, but hypochlorous acid is belived to alter the permeability of the membrane [20]. Hypochlorous acid (HOCl) and hypochlorite ions (OCl<sup>-</sup>) penetrate the cells and reacts with certain enzymes within the cell, thus disrupting vital metabolic reactions in the microorganism and thereby kill it. Hypochlorous acid is the most effective disinfectant because it penetrates the cell walls relatively easy, due to its low molecular weight and its electrical neutrality [13]. Chlorine could be a good choice for the treatment of biofilms since it does not only kill microorganisms but also remove the EPS and thereby making it more difficult for the bacteria to attach to the surfaces [12].

**Efficiency** The speciation of chlorine and thus its disinfection efficiency is dependent of the chemistry of the solution, that is the pH, the amount of ammonia, concentration of organics, temperature and suspended solids [14, 23].

Hypochlorous acid is more efficient as a disinfectant than the hydrochlorite ion [17]. This means that the disinfection efficiency decreases with increasing pH. A higher pH requires a longer contact time since the disinfectant is less active. The efficiency of gaseous chlorine and hypochlorite at the same pH after addition is the same. Addition of gaseous chlorine will decrease the pH, while the addition of hypochlorite will increase the pH of the water. Therefore without pH adjustments to maintain the pH, gaseous chlorine will have a greater disinfection efficiency [24].

The amount of ammonia in the water will affect how much of the free chlorine that will form chloramines. Trichloramine is produced at very low pH so it is mostly mono- and dichloroamine that is produced. The free chlorine, hypochlorous acid and hydrochlorite ions have a higher disinfection ability than the chloramines, thus the efficiency increases with decreasing amount of ammonia[14].

Chlorine oxidises any reducing compound in the water before it is available as a disinfectant so the disinfection efficiency is increasing with decreasing amounts of organics in the water. The inactivation of microorganisms increases with increasing temperature [24]. Chlorination is effective against many bacteria, but it has lower efficiency against spores and there are microorganisms that are relatively resistant to chlorination [25]. Initial mixing and effective contact time is important for a good process performance.

**Process design** The treatment system contains a storage tank of the chlorine compound used, chlorinators that apply the chlorine to the water, and mixing chambers [23]. The residual concentrations of chlorine can easily be measured and monitored [20]. There are restrictions on the concentration of residual chlorine in the effluent, thus dechlorination is needed. Dechlorination is an oxidation-reduction reaction, where sulfur dioxide, sodium sulfite, sodium meta sulfite or activated carbon are used as reducing agents [17]. The dechlorination process require no contact tank, since its a fast reaction, so the equipment needed is storage of the dechlorination reagent and some sort of injection apparatus. Chlorine gas and chlorine solutions are very corrosive and should therefore be transported in plastic pipes and need to be stored in corrosion resistant containers.

Biofouling could be controlled at continuous residuals of 0.8mg/l, however growth could be visible at higher dosages. This may be attributed to the biofilm matrix, which serves as a barrier and leads to poor penetration and failure to reach the target organism [26]. Where disinfection of waters require dosages of about 1mg/l of chlorine, biofilms is more difficult to remove by chlorination and dosages as high as 1.5mg/l may not be sufficient to penetrate the biofilms and inactivate the bacteria [20]. For the prevention of biofouling low level continuous dosing is more effective than high level and short contact and the opposite is true for already established biofilms. Low concentrations may only hinder the bacterial duplication whereas higher concentrations completely kills the bacteria [26].

**Environmental aspects** Chlorine reacts with a wide range of organics, and thereby forms disinfection by-products (DBPs), the most common being trihalomethanes (THMS) and haloacetic acids (HAAs) [18].

**Costs** Chlorination is a relatively cheap method for disinfection of waters [19].

**Summary** The advantages with chlorine as a disinfectant are:

- Relatively low costs.
- Ease of application and proven reliability.
- Familiarity with its use.
- Easily measured residual concentration.

The disadvantages are:

- Production of disinfection byproducts.
- The need of dechlorination.

#### 4.1.2 Chlorine dioxide, ClO<sub>2</sub>

**General** Chlorine dioxide is a strong disinfectant perhaps as effective as chlorine. Chlorine dioxide is unstable as a gas and breaks down to chlorine gas,  $Cl_2$ , oxygen,  $O_2$  and heat so it has to be generated on site. It produces less disinfection byproducts than chlorine [27]. When produced and handled properly, chlorine dioxide is an effective biocide and oxidiser. It has been used extensively in the pulp and paper industry, in sewage water and cooling water disinfection [19]. Its possible use in the municipal water treatment are being increasingly investigated.

**Generation** Although chlorine dioxide is stable in aqueous solution it is not as a gas stable over a long time and it is explosive at concentrations above 10 percent by volume in air and under pressure, and therefore has to be produced on site. For drinking water applications, chlorine dioxide is generated from sodium chlorite solutions by the reaction with gaseous chlorine (4.4), hypochlorous acid (4.5) or hydrochloric acid (4.6) [17]. At very low pH aqueous chlorine solution, hypochlorous acid can be directly oxidised to chlorine dioxide (4.7) [17].

$$2 \operatorname{NaClO}_2 + \operatorname{Cl}_2 \to 2 \operatorname{NaCl} + 2 \operatorname{ClO}_2 \tag{4.4}$$

$$2 \operatorname{NaClO}_2 + \operatorname{HOCl} \to 2 \operatorname{ClO}_2 + \operatorname{NaCl} + \operatorname{NaOH}$$

$$(4.5)$$

$$5 \operatorname{NaClO}_2 + 4 \operatorname{HCl} \rightarrow 5 \operatorname{NaCl} + 4 \operatorname{ClO}_2 + 2 \operatorname{H}_2 O$$
 (4.6)

$$2 \operatorname{HClO}_2 + \operatorname{HOCl} \to \operatorname{HCl} + \operatorname{H}_2 \operatorname{O} + 2 \operatorname{ClO}_2$$

$$(4.7)$$

**Function** Chlorine dioxide can be used as a disinfectant and an oxidant in water treatment. It is a relatively small, volatile and highly energetic molecule and a free radical, which makes it highly reactive. At high concentrations it reacts violently with reducing agents producing chloride,  $Cl^-$  (4.8) and chlorite,  $ClO_2^-$  (4.9) as final products [28].

$$ClO_2 + 4 H^+ + 5 e^- \rightarrow Cl^- + 2 H_2O$$
 (4.8)

$$\operatorname{ClO}_2(\operatorname{aq}) + \operatorname{e}^- \to \operatorname{ClO}_2^-$$
 (4.9)

Chlorine dioxide is soluble in water, most of it does not hydrolysis but remains in solution as a dissolved gas. Above 11-12 °C the free radical is found in gaseous form. However, it is extremely volatile and can easily be removed from dilute aqueous solutions with minimal aeration or recarbonation with carbon dioxide.

The chlorine dose must first satisfy the oxidant demand before it can act as and disinfectant. Due to the limited reactions between chlorine dioxide and organic compounds in the water compared to chlorine, more is left for disinfection. Chlorine dioxide disinfects by oxidation. It disrupts the permeability of the outer membrane proteins and lipids causing an increases of the permeability and thereby kills the microorganism [29]. The microorganisms can not develop resistance to chlorine dioxide. There is no significant mineralisation of organic matter, but chlorine dioxide can oxidise the EPS matrix and can thereby be an option for the destruction or prevention of biofilm formation [19].

**Efficiency** Chlorine dioxide is efficient over a wide range of pH from 5 to 9.5 [28]. The efficiency increases with increasing temperature [29].

**Process design** Chlorine dioxide is a poisonous gas, that can be explosive so it is important that it is handled and produced with caution. The treatment consists of storage tanks of the reagents, chlorine dioxide generator, mixing and contact generator and equipment for flow and chlorine residual monitoring [30].

For the reduction of organic pollutants recommended dosages are between 0.5 and 2.0 mg/l with contact times usually as low as 15 to 30 minutes, depending on the water characteristics. As a disinfectant in drinking water treatment the dosages ranges from 0.07 to 2.0 mg/l [29]. At these dosages the residual chlorite is such that it does not constitute any health hazard. Maximum residual of chlorine dioxide is 0.8 mg/l and the maximum of chlorite is 1.0 mg/l [29]. For the prevention of biofilm formation continuous or intermittent low level dosing is used. To treat already established biofilms higher dosages are necessary [28].

Dilution of the sodium chlorite solution promote the production of chlorate in stead of chlorine dioxide (4.12). Because of this some systems function best as intermittent batch generators that produces high concentrations of chlorine dioxide by using high initial sodium chlorite solutions rather than as continuous generators that produce lower concentrations of chlorine dioxide

**Environmental aspects** Chlorine dioxide directly oxidises the natural organic matter constituents by electrophilic abstraction rather than via substitution reactions as chlorine does. Thus, the use of chlorine dioxide results in lower levels of halogenated organic byproducts, however, it does form the inorganic by products chlorate- and chlorite ions.

The chlorate ion  $(\text{ClO}_3^-)$  is one of the most undesired byproducts in the chlorine dioxide generators. Chlorate can be produced by reactions with the intermediate dimer ( $\{\text{Cl}_2\text{O}_2\}$ ). The chlorite ion can produce the dimer instead of being converted to chlorine dioxide (4.10). In some generators at a low initial concentration of reactant a substantial amount of chlorate is formed by reactions with this dimer [29]. Acidic conditions forces the degradation of  $\{\text{Cl}_2\text{O}_2\}$  to chlorate (4.11) and the direct oxidation of chlorite to chlorate (4.12).

$$\operatorname{Cl}_2 + \operatorname{ClO}_2^- \to \{\operatorname{Cl-ClO}_2\} + \operatorname{Cl}^- \tag{4.10}$$

$$\operatorname{ClO}_2^- + \operatorname{HOCl} \to \operatorname{ClO}_3^- + \operatorname{Cl}^- + \operatorname{H}^+$$
 (4.11)

$$ClO_{2}^{-} + Cl_{2} + H_{2}O \rightarrow ClO_{3}^{-} + 2Cl^{-} + H^{+}$$
 (4.12)

The presence of chlorate in the treated water is mainly due to the chlorine dioxide generator and could perhaps be lowered by improving the production technology [27]. The formation of inorganic byproducts such as chlorite and chlorate poses a potential risk to health. The chlorite level can be held under the maximum contaminant level if chlorine dioxide is dosed at minimum levels needed for disinfection or it can be chemically reduced by the addition of for example sulphur or iron compounds. Even though chlorine dioxide as a disinfectant may result in the formation of disinfection byproducts, it does so in a much lower extent than chlorine [31].

**Costs** Treatment with chlorine dioxide is 5 to 10 times more expensive than chlorine, but less than ozonation depending on the chemicals used to produce chlorine dioxide [19]. This treatment has a high chemical and capital cost [29].

Summary The advantages are:

- It does not react with bromides or ammonia.
- Highly reactive with regards to a number of structures.
- It does not lead to a significant formation of halogenated organic compounds.
- Efficient over a wide range of pH.
- Can provide residual concentrations.

The disadvantages are:

- Poisonous gas, that can be explosive.
- Formation of chlorate/chlorite.

#### 4.1.3 Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>

**General** Hydrogen peroxide  $H_2O_2$  contains the peroxide ion  $(O-O)^{2-}$ , that is a strong oxidising agent. Hydrogen peroxide is not in itself a disinfectant, it has to be converted to radicals such as the hydroxyl radical (·OH), which reacts with cell components in order to inactivate microorganisms [20]. It is an effective oxidising agent and a source of active oxygen.

**Generation** Hydrogen peroxide is produced by self oxidation according to reaction (4.13) [32]. It decomposes in the presence of light to water, oxygen and heat, reaction (4.14). This causes safety problems and lowers the disinfection efficiency. Hydrogen peroxide is completely soluble in water, where it acts as a weak acid which dissociates to yield the hydroperoxide ion,  $HO_2^-$  as shown in reaction (4.15) [33].

$$H_2(g) + O_2(g) \to H_2O_2(g)$$
 (4.13)

$$2 H_2 O_2 + \text{light} \rightarrow 2 H_2 O + O_2 + \text{energy}$$
 (4.14)

$$H_2O_2 + H_2O \leftrightarrow HO_2^- + H_3O^+$$
 (4.15)

**Function** Hydrogen peroxide oxidises both organic and inorganic pollutants and thereby lowers the BOD and the COD. Hydrogen peroxide can react with organic matter present in the water directly or indirectly. In the direct mechanism hydrogen peroxide behaves as an oxidant (4.16) or as a reductant (4.17) in redox reactions [33]. The indirect reactions are through the oxidising action of free radicals that are formed when hydrogen peroxide reacts with inorganic compounds such as ozone or  $Fe^{2+}$  or when it is photolysed (see section 4.3 on page 27). These radicals might be needed for the degradation of more resistant substances. Hydrogen peroxide reacts slowly with most organic compounds at least for water treatment applications and in many cases it does not completely oxidises organic compounds [33]. Inorganics reacts faster than organics with hydrogen peroxide [32].

$$H_2O_2 + Reductant \rightarrow Reductant - O + H_2O$$
 (4.16)

$$H_2O_2 + Oxidant \rightarrow Oxidant - H_2 + O_2$$
 (4.17)

The disinfection property of hydrogen peroxide could result from a direct molecular action, but it is belived that it is mostly the free radicals that are responsible for the disinfection. This means that hydrogen peroxide alone is not an effective disinfectant. Some microorganisms may be protected against hydrogen peroxide by their catalase enzyme activity. Hydrogen peroxide is a metabolite that many organisms produces and catalase is an enzyme that they use to detoxify it by breaking it down to water and oxygen [25]. Hydrogen peroxide does not inactivate bacteria effectively even at high dosages [34]. Hydrogen peroxide can supply oxygen to the microorganisms when it dissociates to oxygen and water and can thereby actually promote growth [32].

**Process design** The efficiency of hydrogen peroxide depends on pH, temperature, peroxide concentrations, and reaction time [32]. The disinfection efficiency of hydrogen peroxide is low [25]. It is a less powerful oxidiser than many other chemicals. However, the equipment for it is less complicated compared to other detoxifiers. It accomplish less than 0.2log microbial reductions even at dosages as high as 150 mg/l [25]. The equipment needed for hydrogen peroxide treatment is storage, injection into the system and mixing.

**Environmental aspects** Hydrogen peroxide does not produce disinfection by-products such as trihalomethanes.

**Costs** Low investment and operational costs, since investment costs for new equipment is low and the chemical is inexpensive.

Summary The advantages are:

- $\bullet~{\rm H}_2{\rm O}_2$  is easy to handle and safer than many other chemicals.
- There is no formation of disinfection by-products.
- Nonexpensive treatment.

The disadvantages are:

• It is not very effective as disinfectant/oxidant.

#### 4.1.4 Peracetic acid, CH<sub>3</sub>COOOH

**General** Peracetic acid, PAA is a strong oxidant and disinfectant. It is available in a equilibrium mixture containing acetic acid, hydrogen peroxide, peracetic acid and water [35]. Although hydrogen peroxide contributes to the over all disinfection, peracetic acid is the stronger disinfectant of them.

It is used in disinfection of ion exchangers, cooling towers, as a disinfectant in food and beverage processing, in medical and pharmaceutical applications and as a decoloring agent in textile and pulp and paper industries. [35]. **Generation** Peracetic acid can be produced by a reaction between hydrogen peroxide and acetic acid [35],

$$\begin{split} \mathrm{CH}_3\mathrm{CO}_2\mathrm{H} + \mathrm{H}_2\mathrm{O}_2 &\leftrightarrow \mathrm{CH}_3\mathrm{CO}_3\mathrm{H} + \mathrm{H}_2\mathrm{O}\\ \mathrm{CH}_3\mathrm{CO}_2\mathrm{H} &= \mathrm{Acetic} \ \mathrm{acid}\\ \mathrm{CH}_3\mathrm{CO}_3\mathrm{H} &= \mathrm{Peracetic} \ \mathrm{acid}\\ \mathrm{H}_2\mathrm{O}_2 &= \mathrm{Hydrogen} \ \mathrm{peroxide}. \end{split}$$

The decomposition products of peracetic acid are acetic acid, hydrogen peroxide, oxygen and water. There are three reactions in which peracetic acid is consumed, spontaneous decomposition, hydrolysis and transition-metal catalysed decomposition [35].

**Function** Peracetic acid is a strong oxidising agent and will thus oxidate organic matter in the water. In order to leave a residual concentration for disinfection, peracetic acid must be added in an amount to overcome the peracetic acid demand [36]. It is considered to be an effective disinfectant even in the presence of organic matter in the water.

Peracetic acid disinfection are similar to other peroxides. Its disinfection activity is based on the release of active oxygen. It is thought that the sensitive sulfhydryl and sulfur bonds in proteins, enzymes and other metabolites are oxidised. Peracetic acid may inactivate catalase, an enzyme known to detoxify free hydroxyl radicals [25, 35].

The use of peracetic acid may lead to an increase of the organic content in the water, due to the residual acetic acid [35]. Acetic acid is easily biodegradable and may result in microbial regrowth if peracetic acid levels is to low to cause disinfection.

Efficiency The disinfection efficiency is dependent on the organism that is to be inactivated, temperature, pH, suspended solids (TSS) and the biochemical oxygen demand (BOD). Peracetic acid functions over a wide range of temperatures, and the microbial reduction increases with increasing water temperature [35]. Higher activity occur with low pH, but there is relatively small difference between pH 5 and 8 [35]. The efficiency increases with decreasing TSS and BOD.

**Process design** Most of the reduction occurs during the first 10 minutes of contact time, the inactivation curve showing first-order kinetics [35]. Peracetic acid is bactericidal at 0.001%, fungicidal at 0.003% and sporicidal at 0.3% [35]. A dose of 500ppm of peracetic acid with 30 minutes of contact time guarantees total inactivation of the bacteria [37].

The treatment system consists of storage tank, dosage apparatus and contact tank [30]. Peracetic acid is a powerful oxidiser but diluted to their effective concentration as disinfectant it seem to present no danger. However in concentrated solution caution is recommended [35].

**Environmental aspects** Peracetic acid produces no to little toxic or mutagenic by-products in the reaction with organic material present in the water. No halogenated by-products, but aldehydes may be produced when treating waters containing amino acids, phenols, and other aromatic substances [35]. **Costs** The capital investment is low. Currently the major drawback for the use of peracetic acid as disinfectant is the high chemical costs, which makes it more suitable for applications that do not need to disinfect daily [35].

Summary The advantages are:

- Relatively easy to handle.
- Disinfects even in the presence of organic matter.
- Produces no or small amounts of disinfection by-products.
- Low capital investment

The disadvantages are:

• High operational costs due to the high chemical costs.

#### **4.1.5** Ozone, O<sub>3</sub>

**General** The primary application of ozone in water treatment is as a disinfectant, but it is increasingly being used as an oxidant [20]. Ozone is unstable in water and decomposes in to hydroxyl radicals, 'OH, which are strong oxidisers. While disinfection primarily occurs by ozone itself, oxidation processes may occur through the action of both ozone and hydroxyl radicals. Hydroxyl radicals reacts with many dissolved compounds, while ozone is highly selective [38].

**Generation** Ozone is unstable, having a half-life of only 20-30 min and therefore has to be generated on site. This means that this treatment method does not need large storage volumes. Ozone is typically generated within an enriched oxygen feed gas using an electrical corona discharge, using 10kWh of electricity to produce 1.0 kg of ozone [39]. Ozone is produced by the introduction of dried and dehumidified air between two electrically and opposite charged plates, according to the following reaction.

$$3O_2 \rightarrow 2O_3$$

This reaction proceeds more rapidly with increasing temperature and decreasing pressure.

The major secondary oxidant formed in the decomposition of ozone is hydroxyl radicals. The stability of ozone depends on the water matrix, the type and amount of natural organic matter, the alkalinity and especially the pH, since the pH level determine the extent of the decomposition of ozone (4.18)[38]. Hydroxyl radicals are produced when ozone decomposes at high pH (4.19) [38].

$$O_3 + OH^- \to HO_2^- + O_2 \tag{4.18}$$

$$O_3 + HO_2^- \to OH + O_2^{--} + O_2$$
 (4.19)

**Function** Ozone can react through two different mechanisms directle with the molecular ozone called ozonation and indirectly with the radical species that are formed when ozone decomposes in water [32]. Ozone can react directly with organic matter by addition, electrophilic and perhaps nucleophilic reactions, and directly with inorganic compounds in redox reactions where ozone acts as an oxidising agent (4.20) [33].

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$$
 (4.20)

The indirect reaction is through hydroxyl radicals that are formed when ozone decomposes. Decomposition is accelerated by contact with solid surfaces, contact with chemical substances and by heat. Ozone can produce hydroxyl radicals under high pH according to reaction (4.19). For more information on the enhancement of the hydroxyl radical production see section 4.3 on page 27 and subsections therein. However, the formation of hydroxyl radicals from ozone lowers the disinfection efficiency, since disinfection with ozone is more efficient than with hydroxyl radicals.

Ozonation of waters containing organic matter accomplish little reduction in total organic matter. It is perhaps so that ozone does not mineralises the natural organic matter in the water, but alters its chemical structure [40].

An ozone demand must be overcome before the actual disinfection process can take place [17]. Ozone oxidation can kill microorganisms, but disinfecting the water requires maintaining a certain dissolved ozone concentration for a given contact time [39]. Some spore-forming organisms can not be inactivated by ozone. Ozone can react with natural organic matter in the water and thereby produce low-molecular-weight oxygenated by-products. These by-products are gnerally more biodegradable than their precursors and thus they could promote growth if they are not removed [20].

**Efficiency** The chemical oxygen demand (COD) removal efficiency increases with increasing pH [41]. The disinfection efficiency drops when ozone decomposes to hydroxyl radicals and the oxidation efficiency increases. This means that the disinfection efficiency decreases with increasing pH.

**Process design** The treatment system consists of ozone generator, ozone transfer into the water by fine bubble ceramic diffusers, contact tank, water cooling system since the temperature increases by the production of ozone and ozone concentration measurement instruments [30]. Residual ozone has to be removed before discharge, which can be achieved by extended contact time, aeration, intense UV light doses, or with hydrogen peroxide [39]. The contact tank is a column equipped with diffusers through which the ozone is fed. Depending on the water the treatment system could contain more than one column and perhaps a column in which no gas is fed, where the residual ozone can circulate [33]. Typical water treatment dosages ranges from 1.0-5.3 kg ozone/1000m<sup>3</sup> consuming 10-20kW/kg ozone [17].

**Environmental aspects** Ozone is rapidly decomposed, which means that there is no residues of ozone in the discharge. During disinfection and oxidation

Table 7: Dosages and contact time used to reduce the number of microorganisms and organic matter.

Concentration	Contact time	Removal	Reference
0.1-0.3 ppm	15-30 min	$10^7 \text{ cells/ml}$	[15]
0.1-2.0 mg/l	1-10 min	disinfection	[39]
$2.15 \mathrm{kg} \mathrm{O}_3 / \mathrm{kg} \mathrm{COD}$		COD	[41]

ozone and OH radicals can react with water components to form undesirable byproducts. The bromate ion  $BrO_3^-$  may be formed during ozonation of brominecontaining waters [18, 42].

**Costs** High operational costs since the process require a continuous feed of energy for process maintenance and high capital costs of the ozone generator [33].

Summary The advantages are:

- Ozone is a highly effective disinfectant for all groups of microorganisms.
- Rapid reaction rate.
- Produces few disinfection by-products.
- Ozone generators can treat large volumes of water.
- Oxygen is produced as an end product.

The disadvantages are:

- It do not leave any residual effect.
- Less effective in cold water.
- Produces bromate as a disinfection by-product only if the water contains bromine.
- High operational and capital cost.

#### 4.2 UV radiation

**General** In UV-light treatment of water the wavelengths that are effective for disinfection are also able to initiate photochemical reactions of organic and inorganic compounds. UV-light was first used for disinfection, but the advantages of UV radiation as an oxidation technology as since then been discovered. However the primary objective of UV radiation is still disinfection. It has a negligible effect on total organic matter when using dosages needed for disinfection. In order to remove total organic carbon (TOC) higher dosages are necessary [40]. The disinfection can take place directly through photolysis or indirectly by the formation of free radicals.

**Generation** UV radiation can be generated by a low- or medium pressure mercury lamp. The lamp is a glass tube of quartz with electrodes on each side and filled with argon gas and small doses of liquid mercury [43]. When a current is applied the electrons in the mercury atoms is excited and when they changes their orbital states photon energy is released at specific wavelengths [44].

The low pressure lamp emits two wavelengths at 184.9nm and 253.7nm with input power ranges from 8 to 300 watts. The medium pressure lamp emit a range of wavelengths from 170nm to 400nm and input power ranging from 250 watts to 30 kilowatts [44]. The high pressure lamps are not as useful as the low and medium pressure lamps [44].

**Function** When UV light is used alone there is an increase in dissolved organic carbon in the water due to the decomposition of the microorganisms, because the decomposition rate of the microorganisms are higher than the UV oxidation of the dissolved organic carbon [45]. The photons can directly excite the molecule of the organic compounds in the water, leading to the direct photochemical destruction by cleavage of molecular bonds according to the following reactions [32].

## $M + h\nu \rightarrow M^*$ M<sup>\*</sup> $\rightarrow$ Products

The mechanism is more complicated in the presence of oxygen. The the electron in the excited state can be transferred to one oxygen molecule in ground state and thereby forms the superoxide ion radical (4.21), or the organic molecule may firstly undergo homolysis of a carbon-hydrogen bond followed by a reaction with oxygen to yield peroxyl radicals (4.22), (4.23).

$$M + h\nu \rightarrow M^*$$

$$M^* + O_2 \to M^{\cdot} + O_2^{\cdot -}$$
 (4.21)

$$M-H + h\nu \to M^{\cdot} + H^{\cdot} \tag{4.22}$$

$$M' + O_2 \to MO_2' \tag{4.23}$$

UV-light is not in itself very effective for the degradation of organics, it is more effective as a disinfectant [46]. The high energy photons targets the DNA and destroys it, leaving the membranes and enzymes intact, thus disables the organisms ability to reproduce [42, 47]. Some organisms have the ability to recover and repair their DNA damage. However they can not develop immunity mechanisms against the UV light.

The medium pressure lamp emits multiple wavelengths and thereby have the added affect of destroying enzymes, proteins and also damages the cell wall [44]. This provides a high degree of lethality and also protects against photo reactivation (or light repair) and enzymatic dark repair where damaged DNA is repaired within the cell. Low pressure lamps do not offer this protection [44]. Medium pressure systems are best suited for high water flows and lower water quality where higher UV doses are required. Low pressure lamp systems are best suited for low-flow processes and to treat higher water qualities [44]. **Efficiency** The inactivation depends on the wavelength of the UV light, the quantity of the transmitted energy, UV absorbance by the substrate, presence of other competitive UV absorbents, the physical state of the microorganisms (biofilm, growth phase), the diversity of the microorganisms and their ability to repair the damage caused by the UV light [32, 48]. The UV absorbance of organic and inorganic matter in the water can be included in the calculations of the needed dosage [47]. The reduction of bacteria with UV light is achieved by photons with a wavelength in the UVC-band, i.e. 200-280nm but a wavelength of 254nm is the most effective [20, 39].

**Process design** The equipment needed for the treatment of water with UVlight is an UV-lamp. In the system the lamps are suspended over the liquid to be disinfected or immersed in it [17]. Relatively short contact time is needed for the inactivation of many microorganisms. However, the radiation must reach the bacteria, so the distribution of the light in the water is important. Light intensity measurements could be necessary in order to monitor the process. Photoreactors are usually cylindrical chambers that contain inner quartz sleeves, where UV lamps are placed. These sleeves need to be cleaned to avoid the problem with reduced light transmittance [32].

The dosages needed to inactivate microorganisms vary from  $2mWs/cm^2$  to more than  $230mWs/cm^2$  (at 254nm), depending on the target organism and the required killrate [39]. Typical dosages in drinking water treatment are in the order of  $4.0 \cdot 10^{-2}Ws/cm^2$  to achieve a 2log inactivation of most microorganisms [40]. The UV dose is calculated using the following equation.

UV dose = Intensity · Contact time  $[1mJ/cm^2 = 1000mWs/cm^2]$ 

**Environmental aspects** Low pressure UV produces almost no byproducts [47].

**Costs** High capital cost of photoreactors and perhaps high operational costs mainly due to the requirement of continuous feed of energy for process maintenance [33].

**Summary** The advantages are:

- Does not require the additions of chemicals.
- It need relatively short contact time.
- Does not produce any toxic byproducts in the water.
- Requires very little maintenance.
- Low running costs.

The disadvantages are:

- The efficiency is dependent on the quality of the water.
- There is no way of measuring the actual dose.
- There are no residual effect.
- High capital and perhaps operational costs.

#### 4.3 Advanced oxidation processes

When searching the literature for methods to reduce the available substrate for new biomass advanced oxidation processes emerged as a viable option, since they could be operated at a complete mineralisation and thereby not leaving any organic matter in the water that would have to be removed through some kind of filtration.

All advanced oxidation processes (AOPs) enhances the production of hydroxyl radicals ('OH), a reactive oxidising agent that promotes the degradation of individual pollutants or the reduction of the organic load. Since the hydroxyl radical is highly reactive and unstable, it must be generated on site by chemical or photochemical reaction processes [41]. Advanced oxidation processes has been applied for the degradation of pollutants, disinfection, maintenance of swimming-pools and treatment of cooling water, leachates and domestic wastewater.

The AOP involves two steps, (1) the generation of free radicals, (2) oxidation of polluting compounds by these free radicals. However, ozone and UV radiation by them self may have an affect on the water quality both in the reduction of microorganisms and the organic load.

Reactions involving free radicals can be divided into three categories initiation, propagation and termination reactions. Initiation reactions leads to a net increase in the number of radicals, propagation reactions involves reactions in which the total number of radicals remains the same and termination reactions results in a net decrease in the number of free radicals. It is the initiation reaction that separate the AOPs. The propagation and termination reactions are basically the same for all of them [33].

Hydroxyl radicals is highly reactive and has a high redox potential and they react non selectively with organic matter present in the water. They are able to mineralise the majority of organic compounds, that is reduce them to carbon dioxide, water and mineral salts [32]. However in many applications it is not necessary to operate the process to this level of treatment.

Oxidation by the hydroxyl radicals is primarily achieved either by hydrogen abstraction (4.24) or hydroxylation (4.25), but can also take place through electron transfer (4.26) depending on the nature of the compound [33]. These organic radicals react with  $\cdot$ OH radicals to produce the final products carbon dioxide, water and inorganic salts [32, 37].

$$^{\circ}\mathrm{OH} + \mathrm{RH} \to \mathrm{H}_{2}\mathrm{O} + \mathrm{R}^{\circ} \tag{4.24}$$

 $^{\circ}\text{OH} + \text{PhX} \rightarrow \text{HOPhX}^{\circ}$  (4.25)

$$^{\circ}\mathrm{OH} + \mathrm{RX} \to \mathrm{RX}^{*+} + \mathrm{OH}^{-} \tag{4.26}$$

UV radiation targets the DNA while chemical disinfectants damages the microbial cell walls membranes and enzymatic or transport systems. In advanced oxidation processes the microbial repair system may be overloaded, making the microorganisms unable to repair their injuries, which leads to death, hence a combination of two disinfection methods could perhaps destroy a wider range of microorganisms [25]. For example some microorganisms are UV resistant, but more sensitive to chemical disinfectants and for others the opposite is true [25]. However, for disinfection purposes ozone alone is probably the most effective treatment. Carbonate  $(CO_3^{2^-})$  and bicarbonate  $(HCO_3^-)$  ions in the water consume the hydroxyl radicals and thereby lowers the efficiency of the advanced oxidation process (4.27),(4.28) [45]. Although the carbonate radical may act as an oxidant, its oxidation potential is lower than that of the hydroxyl radical.

$$OH + HCO_3^- \to H_2O + CO_3^{--}$$

$$(4.27)$$

$$^{\circ}\mathrm{OH} + \mathrm{CO}_{3}^{2-} \rightarrow \mathrm{OH}^{-} + \mathrm{CO}_{3}^{--} \tag{4.28}$$

The AOP require different costs associated with the investment in equipment (ozone generator, UV lamps, photoreactor and ozonation chambers), process control, operating and maintenance costs (electrical power requirements and manpower). The treatment costs are also affected by the nature of the water to be treated and experimental conditions such as water flow rate, oxidant, UV doses etc. Thus, the presence of particulates, turbidity, and natural hydroxyl radical scavengers (carbonates) are factors negatively affecting the performance of advanced oxidation processes [33]. This means that the necessary dosages needs to be experimentally determined before any cost assessment can be done.

In the following sections some advanced oxidations processes will be discussed further.

#### 4.3.1 $UV/H_2O_2$

This process can degrade organic contaminants either by direct photolysis, see section 4.2 on page 24, or indirect by the formation of hydroxyl radicals [32]. Hydroxyl radicals are formed by photolysis of hydrogen peroxide (4.29).

$$H_2O_2 + h\nu \rightarrow 2 \text{ OH} \tag{4.29}$$

Organic compounds react foremost with 'OH radicals, but some can react direct with UV-light which in turn can increase theirs ability to be oxidised by hydrogen peroxide [32].

The efficiency of this process is dependent on the UV- and hydrogen peroxide dose, pH and the water matrix. The efficiency increases with increasing UV dose, which can be accomplished by an increase in exposure time or UV intensity [32]. The required hydrogen peroxide dose is dependent on the concentration of the organic matter in the water, but there is an optimum dose and a further increase will not lead to a higher efficiency. If overdosed, the hydrogen peroxide may act as a hydroxyl scavenger, by the formation of the less reactive radical HO<sub>2</sub> shown in reaction (4.30), resulting in lower oxidation efficiency [32, 45]. The optimum DOC removal was obtain, when the hydrogen peroxide dose was between 0.01 - 0.1% [45].

$$\mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{OH} \rightarrow \mathrm{H}_{2}\mathrm{O} + \mathrm{HO}_{2}^{\cdot} \tag{4.30}$$

The oxidation efficiency is at its highest at acidic conditions, but pH independent below 5, when carbonic acid dominates the fraction of  $[CO_3^{2-}, HCO_3^{-}, H_2CO_3^{-}]$ . The efficiency is drastically reduced with increasing pH above 5, when the bicarbonate ion is the dominant species, which scavenge the hydroxyl radical. Increasing the pH beyond 7 results in that the carbonate is the dominant species, which has an even higher reactivity towards hydroxyl radicals [32, 41, 46].

Photochemically induced reactions often have a low activation energy, thus the temperature will not have a large affect on the degradation rate of the contaminants. The rate of degradation is instead highly dependent on the structure of the substrate [46]. Absorbance of the UV-light by natural organic matter will lower the radical production [32]. Photolysis of hydrogen peroxide is an effective AOP, if the substrate does not absorb significant amounts of UV light [32].

This technique can be used for the reduction of the biological oxygen demand, the chemical oxygen demand and the total organic matter. The main application is treatment of low contaminated water and has primarily been used to treat low levels of pollutants (ppm), since transmittance of the UV light is important. One paper states that the combination of hydrogen peroxide and UV had no synergistic effect [25].

The UV/H<sub>2</sub>O<sub>2</sub> treatment system consists of three major components. (1) UV reactor, (2) electrical supply and UV lamp controller and (3) dosage equipment to add hydrogen peroxide, and storage of hydrogen peroxide. This treatment requires low capital investment, and is a cost effective source of hydroxyl radicals, with a simple operation procedure [49].

#### 4.3.2 $O_3/H_2O_2$

In the advanced oxidation process with ozone and hydrogen peroxide oxidation can take place in two ways, where the first is slow compared to the second:

- 1. Direct oxidation by aqueous ozone.
- 2. Indirectly by the formation of hydroxyl radicals that form during ozone decomposition.

As stated in section 4.1.5 on page 22 ozone decomposes to hydroxyl radicals at elevated pH. The hydroxyl formation can be enhanced by the addition of hydrogen peroxide. In aqueous solution hydrogen peroxide is found in an acid base equilibrium, and ozone reacts with the hydroperoxide ion,  $HO_2^-$ , which can be seen in the following reactions [46].

$$\begin{aligned} \mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{H}_{2}\mathrm{O} &\leftrightarrow \mathrm{H}_{3}\mathrm{O}^{+} + \mathrm{HO}_{2}^{-} \\ \mathrm{O}_{3} + \mathrm{HO}_{2}^{-} &\rightarrow \mathrm{OH} + \mathrm{O}_{2}^{-} + \mathrm{O}_{2} \end{aligned}$$

The efficiency is dependent on the ozone dose, the hydrogen peroxide/ozone ratio, contact time, pH and the composition of the water [50]. The  $H_2O_2/ozone$  ratio is important since an excess amount of hydrogen peroxide can act as a hydroxyl scavenger. Ozone decomposition will increase with increasing pH, since the hydrogen peroxide dissociate to the hydroperoxide ion.

This is the advanced oxidation process to choose, if the UV transmission is low, or where fouling is an issue, since it is more tolerant of poor water quality than other advanced oxidation processes.

#### 4.3.3 UV/O<sub>3</sub>

The oxidation of organic compounds by ozone occurs via two competing pathways, direct oxidation by the ozone molecule and indirect oxidation by hydroxyl radicals. The hydroxyl radicals are formed during ozone decomposition and this decomposition to hydroxyl radicals is enhanced by UV-light. The treatment utilising UV light and ozone inactivates microorganisms in two ways:

- 1. UV light destroys RNA, DNA and other nuclear biomaterials.
- 2. Rupture of cell walls through oxidation by ozone and hydroxyl radicals.

and reduces suspended solids and organics in two ways [40].

- 1. Direct chemical oxidation by ozone.
- 2. Direct chemical oxidation by hydroxyl radicals.

Ozone decompose in water to form hydroperoxide ions (4.31). The photolysis of ozone in solution is represented by reaction (4.32), since hydroxyl radicals in close proximity will from hydrogen peroxide. The hydrogen peroxide formed dissociate to hydroperoxide ions. Hydroxyl radicals are then formed by the reaction between ozone and the hydroperoxide ion according to reaction (4.33). Hydroxyl radicals could also form by photolysis of hydrogen peroxide (4.34).

$$OH^- + O_3 \to HO_2^- + O_3^-$$
 (4.31)

$$O_3 + H_2O + h\nu \rightarrow [2 OH] + O_2 \rightarrow H_2O_2 + O_2$$

$$(4.32)$$

$$\mathrm{HO}_{2}^{-} + \mathrm{O}_{3} \to \mathrm{^{\circ}OH} + \mathrm{O}_{2}^{\cdot -} + \mathrm{O}_{2} \tag{4.33}$$

$$H_2O_2 + h\nu \to 2 \text{`OH} \tag{4.34}$$

The decomposition rate is affected by pH, ozone dose, UV radiation and presence of free-radical scavengers. The optimum pH is near or above neutral for most organic pollutants [41, 51]. There are an optimum ozone dose, and if added above that, it will reduce the removal efficiency. The removal efficiency increases with increasing UV intensity. Low alkalinity of the water makes the oxidation of the naturally occuring organic matter more efficient since the hydroxyl radicals are not consumed by carbonate and bicarbonate [40]. The ozone is fed to the water prior to the photoreactor or directly into it [33]. The system only requires air and electricity to operate. No storage is needed.

This method is effective at oxidising the organic matter in the water. Although the chemical characteristics of the organic matter changes rapidly the mineralisation process is slower [40]. High UV intensity and initial ozone concentration may be necessary in order to remove more resistant compounds, which implies high operational costs. Higher total organic carbon (TOC) removal and trihalomethane (THM) forming potential reduction with the combination of ozone and UV than ozone alone [46]. The COD removal increases with increasing contact time up to a point where an increase in contact time does not correspond to an increase in removal [41].

#### 4.3.4 $O_3/H_2O_2/UV$

Ozone, hydrogen peroxide, and or UV radiation can react individually or photolysis directly with the organic matter in the water and in combination they can produce radicals that oxidises the contaminants. The production of hydroxyl radicals by ozone and hydrogen peroxide is enhanced by the addition of UV light, that is the photochemical generation of hydroxyl radicals [46]:

1. Direct chemical oxidation by ozone.

- 2. Direct photolysis by UV.
- 3. Indirect oxidation by hydroxyl radicals, formed from ozone decomposition enhanced by UV light and or hydrogen per

The COD removal is higher under acidic conditions. Excess amounts of hydrogen peroxide lowers the removal efficiency, which may be due to the formation of the less reactive radical  $HO_2$ , which in turn is formed by the reaction between hydroxyl radicals and excess hydrogen peroxide [41].

The main reactions of the advanced oxidation process involving ozone, hydrogen peroxide and UV radiation [33] are:

$$O_3 + H_2O + h\nu \to 2 \text{ OH} \to H_2O_2 \tag{4.35}$$

$$H_2O_2 + h\nu \to 2 \text{ OH} \tag{4.36}$$

$$O_3 + OH^- \to HO_2^- + O_2 \tag{4.37}$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+$$
 (4.38)

$$HO_2^- + O_3 \to OH + O_2^- + O_2$$
 (4.39)

#### 4.3.5 UV/CH<sub>3</sub>COOOH

The combination of peracetic acid and UV increases the disinfection and show synergistic benefits. The synergistic effect may be contributed to the interaction of peracetic acid and UV to produce radicals by the photolysis of peracetic acid [25].

$$CH_3CO_3H + h\nu \rightarrow CH_3CO_2^{\cdot} + OH$$
 (4.40)

$$\operatorname{CH}_3\operatorname{CO}_2^{\cdot} \to \operatorname{CH}_3^{\cdot} + \operatorname{CO}_2$$
 (4.41)

Peracetic acid can react with hydroxyl radicals according to the following reactions.

$$CH_3CO_3H + OH \rightarrow CH_3CO_4H_2 \rightarrow CH_3CO_2H + OOH$$
 (4.42)

$$CH_3CO_3H + OH \rightarrow CH_3CO + O_2 + H_2O$$

$$(4.43)$$

The presence of hydrogen peroxide contributes to the formation of new peracetic acid as soon as it is consumed but also to the formation of new hydroxyl radicals [37].

#### 4.3.6 $Fe^{2+}/H_2O_2$

In Fenton's reaction hydroxyl radicals are created by the oxidation of iron at low pH during consumption of hydrogen peroxide. The treatment has a high reduction rate and can be used to reduce the COD in the water. The presently accepted scheme for the Fenton's reagent chain is as follows [52]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$$
 (4.44)

$$RH + OH \rightarrow H_2O + R \rightarrow Further oxidation$$
 (4.45)

$$R^{\cdot} + Fe^{3+} \to R^{+} + Fe^{2+}$$
 (4.46)

 $^{\circ}\mathrm{OH} + \mathrm{Fe}^{2+} \rightarrow \mathrm{OH}^{-} + \mathrm{Fe}^{3+}$  (4.47)

When the amount of  $\text{Fe}^{2+}$  exceeds that of  $\text{H}_2\text{O}_2$  the treatment leads to chemical coagulation, if the opposite is true chemical oxidation uccurs [52]. However, it is important to remember that hydrogen peroxide can act as a hydroxyl radical scavenger, thus it is important to determine the appropriate hydrogen peroxide dose.

The reaction (4.46) competes with reaction (4.47) and (4.45). This competition of hydroxyl radicals between  $\text{Fe}^{2+}$ , RH and  $\text{Fe}^{3+}$  leads to the non-productive decomposition of hydrogen peroxide and limits the yield of hydroxylated (oxidised) organic compounds. Therefore the stoichiometric relationship between them has to be established to maximise the efficiency of the degradation process [52].

Maximum amount of hydroxyl radicals is produced under acidic conditions, with optimum above 2 but below 4 [53]. This means that pH adjustment is necessary. If the concentrations of the reactants are not limiting the organic matter in the water can be fully converted to carbon dioxide, water and inorganic salts.

This treatment provides hydroxyl radicals at the lowest oxidant cost, however the process requires pH and temperature adjustments [49]. This treatment is known to be effective in the removal of many organic pollutants from wastewater [53]. Iron is abundant and a non toxic element and hydrogen peroxide is easy to handle and an environmentally benign chemical. However, the treatment may require sludge removal.

#### 4.4 Filtration

#### 4.4.1 Water filtration

The destruction of the microorganisms generates new substrates for the bacteria, encouraging regrowth. The removal of organic matter could, if not operated at a complete mineralisation level, f leave some easyily biodegradable substances which also could promote growth. This means that some sort of filtration may be necessary. A filter system in itself could be a treatment option, since organic matter can be removed from the water, and thereby lower the available substrate for new biomass and microorganisms are removed from the water.

Membrane technologies are efficient and economically acceptable for the removal of natural organic matter and microorganisms [54]. Reverse osmosis and nanofiltration can be used to remove natural organic matter. Ultratfiltration and microfiltration can be employed for microbial removal [55].

#### 4.4.2 Air filtration

Microorganisms and organic matter could enter the system with the raw biogas and the air used in the desorption column. A better filtration of the incoming biogas and the air could perhaps be a way to lower the amount of growth. The filter should allow the gas to move freely through it and capture the microorganisms and the organic matter. Particles in the air offers surfaces for the mikroorganisms to grow on in an otherwise harsh environment. A filter that removes the particles will have an indirect effect on the amount of microorganisms in the air. A filter that traps the microorganisms will clog more quickly and shows a higher resistance to the airflow which perhaps will result in higher energy requirements [56].

#### 4.5 Summary

Table 8 summarises some qualities of the treatments methods mentioned in the earlier sections; environmental impact (Env.), by-products (BP), efficiency when removing organic matter (Efficiency o.m.), efficiency when removing microorganisms (Efficiency m.o.), investment costs (Invest. costs) and operational costs (Oper. costs). The gradings are in a gliding scale from bad to good --, -, +/-, +, ++.

The the efficiency is highly dependent on several experimental parameters such as water quality and water flow. In the table below the efficiency is based on that the treatment method is used in its appropriate application. For example when the water has a high UV transmittance then the inactivation efficiency of microorganisms with UV-light is high and if not the efficiency is low.

	Env.	BP	Efficiency	Efficiency	Invest.	Oper.
			o.m.	m.o.	$\cos ts$	$\cos ts$
$Cl_2$			_	+	+	++
ClO <sub>2</sub>		+/-	++	++	++	+
$H_2O_2$	++	++			++	+
CH <sub>3</sub> COOOH	++	++	++	++	++	
O <sub>3</sub>	+	+	++	+	—	+
UV	++	++	+	++	+/-	++
AOPs						
$\rm UV/H_2O_2$	++	++	++		++	++
$O_3/H_2O_2$	++	+	++	_		++
UV/O <sub>3</sub>	++	+	++	_		
$\mathrm{UV}/\mathrm{O}_3/\mathrm{H}_2\mathrm{O}_2$	++	+	++	_		
UV/CH <sub>3</sub> COOOH	++	++	++	++	++	
$\mathrm{Fe}^{2+}/\mathrm{H}_{2}\mathrm{O}_{2}$		++	++		++	++

Table 8: Advantages and disadvantages with the different treatments.

### 5 Discussion

The requirements on a chosen treatment method for the cleaning of the pallrings and the columns are the following; First and foremost the treatment should be able to be carried out while the upgrading process is running. This implies that it should work at the pH and the temperature of the upgrading process, since the absorption of carbon dioxide is dependent on these parameters. The treatment should not release any harmful substances in the gas or in the water, not contain any corrosive substances and it should be economically sustainable.

The treatment alternative to chose can not be decided until operational costs have been investigated, after the needed dosages has been determined in some form of laboratory or pilot plant study. This is needed since the efficiency of the treatment methods is highly dependent on conditions such as water quality and flow rate.

When deciding on a treatment method the first thing to consider is whether the main purpose is to reduce the microorganisms or the organic matter or if a combination of both is the best way to tackle the problem. This means that considerations should be given to the following; type of upgrading plant, the water quality the water flow through the absorption column and the needed process capacity.

The efficiency of the treatments employed varies with pH and since the pH of the process varies throughout the upgrading system, it is important to take into account where the treatment should be employed. Thus, a treatment that functions best at low pH should be employed in the absorption column and treat the water there. If the system is regenerating, this treatment could function up to the desorption column. After the desorption column in this system and prior to the absorption column in the single pass plant the treatment should be efficient at neutral or slightly above. The treatment in itself can influence the pH and that has to be compensated for in order to maintain the upgrading capacity.

**Reduction of organic matter** If the best way to maintain an acceptable process capacity is by a reduction of the organic matter, things to consider is to what degree the treatment is needed to operate at, and where in the system to employ it. One also need to be aware that some of the decomposed organic matter can become more biodegradable and thus could serve as nutrients for the microorganisms and thereby promote microbial growth. In the latter case some type of filtration will be required.

**Reduction of microorganisms** If destruction of the microorganisms is the aim of the chosen treatment, the next thing to consider is if it is enough to treat the water before the absorption column or if it is necessary to leave a residual in the water and if that is possible. A biofilm continues to develop even if there are no microorganisms in the water. This imply that, if some microorganisms could enter the system with the raw biogas the treatment method would have to stretch into the absorption column, or if the only source of the microorganisms is the water it could be enough to treat the water prior to the column.

When determining which disinfectant to use it is important to have knowledge on the microorganisms to be destroyed or inactivated. This has been studied in a master thesis at the department of water and environmental studies at Linköpings Universitet [6]. It is important to apply the disinfectant at the correct dose and at the correct frequency. The exact doses and contact times can only be determined through laboratory and pilot-plant studies. However, low level continuous dosing is belived to be the best way to prevent biofouling, and high level dosing with short contact time is best suited for removal of already established biofilms [26]. One more thing to consider is the possibility that the microorganisms could develop resistance or that they may repair the damage caused by the treatment.

#### 5.1 Single pass

The single pass upgrading plant takes its process water from a sewage treatment plant. Since this method require large volumes of water it is not economically sustainable to use drinking water. This means that the process water is of poorer water quality compared to plants using drinking water (cf. section 2.5 on page 9).

Just limiting the organic matter could be an overwhelming task in the case of single pass process water. It would have to be very efficient in order to keep the microorganisms below an acceptable level. This need to be accomplished prior to the absorption column in order to keep the microorganism level low in the absorption column, which may prove to be costly. An alternative could be to operate the treatment at a lower level in combination with some kind of filtration. However, eventually some sort of treatment to remove the microorganisms is necessary, because it probably would be difficult to remove all the substrate for new biomass. The conclusion is that the removal of organic matter is not a permanent solution in the case of single pass process water. A combination of the friction caused by the passing water and reduction of organic matter may keep the growth under an acceptable level and thus, maintaining it there. This means that the same number of microorganisms that are flushed out regrows due to the amount of organic matter that enters the absorption column. The shear forces caused by the water can limit biofilm development [21]. However, the rate of which the nutrients are transported to the microorganisms affects the biofilm development, that is a higher transport rate will lead to a faster development.

In this type of plant the process water passes through the absorption column only once. Thus, if it is possible to hinder the attachment of microorganisms to the surfaces it could be possible to prevent clogging, since both the microorganisms and the organic matter would be flushed out. If this is possible the poorer quality of the water compared to that used in the regenerating plant would not be that important. This is valid, if it does not have a negative effect on the efficiency of the treatment method.

• The conclusion is that for the upgrading plant with single pass the best way to handle the problem with bacterial growth is through some kind of treatment focusing on the reduction of the amount of microorganisms.

The next thing to decide on is if the treatment should be continuous or intermittent. Here it is important to account for the needed process capacity, the possibility of adaptation (continuous) and the best choice from an economical point of view. Intuitively a continuous treatment would have to be operated in such a way that no microorganisms attaches to the pall-rings, otherwise it would eventually be necessary to remove the attached bacteria. These are more difficult to remove since they are not only attached to a surface but they could also have developed resistance to the treatment method. Since it is very difficult to hinder all microorganisms from attaching to the surfaces an intermittent treatment is perhaps better. The intermittent treatment would have to be done at intervals still allowing an acceptable process capacity to be maintained.

• The conclusion is that an intermittent treatment is the viable option.

Microorganisms do not only enter the system from the water, but also from the raw gas that enter the system in the absorption column, the treatment should extend to the absorption column. It seems that it will not be enough to treat the water prior to the absorption column, however, this might need to be evaluated in some kind if pilot plant study.

#### 5.1.1 Treatment method

Upgrading plants with single pass process water need a treatment method that is not influenced by the amount of organic matter in the water. The treatment should either be employed prior to the absorption column to treat the water and leave a residual in the water to treat the microorganisms that enters the water from the raw gas or be employed in the absorption column to treat it all in the same time. In some cases it may be enough to just treat the incoming water. The addition of the chemical should not alter the pH of the water, or if it does that need to be compensated for in order to maintain the upgrading capacity. It should be efficient at reducing the amount of microorganisms and it must be economically possible to implement it in the process.

**Chlorine** requires a relatively low investment cost and it is an effective disinfectant that is widely used. It can be added to the water prior to the absorption column and leave a residual in the water. However, the high amount of organic matter in the water raises the question of disinfection by products, which certainly would be formed. Another consequence of the high organic content in the water is that the chlorine must satisfy the chlorine demand, before it can act as a disinfectant. This means that it would have to be added in high doses and that in turn means high costs. The formation of disinfection by-products may not be a problem, since the water is returned to the sewage treatment plant, where the chlorine residual and the disinfection by-products likely are removed. The efficiency of chlorine is at its highest at low pH. The addition of for example chlorine gas will lower the pH, which would have to be compensated for in order to maintain the upgrading pH. This means that it will be efficient in the absorption column. Chlorine gas and chlorine solutions are corrosive, which has an adverse effect on the equipment. This together with the low microorganism inactivation with regard to the expected chemical amounts needed and the necessary pH adjustment is why this treatment is not recommended.

**Chlorine dioxide** functions over a wide range of pH and it is less reactive towards organic matter compared to chlorine, which is advantagous, since more

is left for disinfection. Since chlorine dioxide reacts far less with organic matter it also produces less halogenated by-products. However, it does produce chlorate as a by-product which poses a potential risk to health. This treatment is belived to be more expensive than chlorine because of the higher chemical costs. This could perhaps be compensated for by the lower amount needed. However, the investment costs will be substantial. It is a dissolved gas in the water, which means that it does not hydrolys, and does not lower the exchange between the carbon dioxide and the water. However, the gas is poisonous and can be explosive under pressure which make it difficult to handle and therefore requires a well educated staff. Together with the higher expected operational and investment costs is why this method is not recommended.

**Hydrogen peroxide** does not seem to be a very efficient disinfectant, but perhaps that can be compensated by the fact that this method does not require investments in new equipment and that the chemical is relatively non-expensive. However, the required chemical amount need to be determined experimentally before that statement can be validated or rejected. The efficiency is also dependent on the temperature, which means that the efficiency would fluctuate with the seasonal variations in water temperature, requiring higher dosages during the winter. This method does not seem promising, since one study states that even high dosages up to 150mg/l would not achieve more than 0.2log microbial reduction. The efficiency of hydrogen peroxide is at its highest at high pH and that means that it will not be efficient in the absorption column where the pH is low. This means that this treatment will probably not be efficient enough and is therefore not recommended.

**Peracetic acid** must be added to overcome the peracetic acid demand before it can disinfect, but it is thought to be an effective disinfectant even in the presence of organic matter, although the efficiency increases with decreasing amount of organic matter. An advantage is that this treatment does not require much equipment, which means low capital investments. Peracetic acid has its highest efficiency at low pH, which means that it could effectively treat the water in the absorption column. It is also a weak acid meaning that a significant amount will remain as peracetic acid and not ionise in the water. This and the fact that only small dosages are needed, since it is bactericidal and fungicidal at dosages of 1-3ppm. This means that it will not significantly affect the pH. This treatment is also dependent on the water temperature, but the main problem is the chemical costs. However, an intermittent treatment would perhaps keep the costs low enough. This could be the solution, if the chemical costs versus efficiency is acceptable.

**Ozone** must firstly overcome the ozone demand before it can act as a disinfectant. It is an effective disinfectant, and functions best at low pH, which means that it is efficient in the absorption column. It has a high reaction rate and in order to leave a residual in the absorption column. The fast reaction rate and the high ozone demand may result in high dosages, which in turn means high operational costs. This treatment have high investments costs. The treatment can produce the disinfection by-product bromate, if the water contains bromine. This treatment is temperature dependent and since the water comes

from a sewage treatment plant higher dosages will be necessary during the winter. The anticipated high operational and investment cost is why this treatment is not recommended.

**UV radiation** is an excellent way of disinfecting water. Since it is a physical process that only requires electricity and at intervals replacement of the UV lamps it would perhaps require less operational costs both with regard to the fact that no chemicals are used and that the maintenance requires less attention. Although it might not require high operational costs, there are substantial investment cost. So if UV light is to be used the electricity requirementsneed to be determined in order to evaluate the costs.

One important thing is that it requires relatively short contact time, which is good because of the high flow through the system. Another advantage is that it will not affect the pH of the water and is independent of the pH. However, if this treatment is to be considered the water must have an high enough UV transmittance, which only can be determined in a pilot plant study.

This treatment is dependent on if it is enough to treat the water prior to the absorption column, since the UV light does not leave any residual for deactivation of microorganisms in the water. This is because the main disinfection by UV light is through the action of the photons. However radicals are formed and can follow the water into the absorption column. The pall-rings in the absorption column make it difficult to employ the treatment here. A treatment method that only treat the water prior to the absorption column would need to have a filtration step in order to limit the organic matter that enters the absorption column and there serves as substrate for new biomass. Two studies have shown that nanofiltration in combination with UV-disinfection could be used in the food and beverage industries to make the process water reusable [57, 58]. Thus this treatment could produce process water of drinking water quality. This raises the question: does the water need to be of drinking water quality or does it need to be of higher quality. Perhaps drinking water in combination with the fact that the process water passes the absorption column only once is enough to maintain an acceptable process capacity.

- The most promising method for the actual reduction of microorganisms seems to be the addition of peracetic acid.
- UV radiation in combination with some kind of filtration could also be possible (if the incoming process water is responsible for the growth).

#### 5.2 Regenerating

In plants with regenerating process water the microorganisms that enters the system from the water, raw biogas and air are ,trapped, which leads to an accumulation of microorganisms in the system. Drinking water is used instead of water from the sewage treatment plant which means that there is a slower accumulation of microorganisms and a slower development of the biofilms in the absorption column, compared to the system with single pass because of the much better water quality.

For disinfection to be an alternative some sort of filtration would be necessary, since the system is recirculating. Otherwise there would be a build of organic matter in the water. Thus, the combination of a disinfectant and some type of filtration perhaps could be an effective way of handling the problem, if economically sustainable. If a lower capacity level is acceptable, an intermittent treatment with higher dosages in combination with filtration to remove the dissolved organic matter could be possible. Otherwise a continuous treatment is recommended in the literature for the prevention of biofilm formation, but one need to remember that the microorganisms could develop resistance to a treatment.

A treatment that only remove organic matter from the water would not be a solution, if not operated at such a level that microbial growth is below an acceptable level. This treatment would then eventually need some sort of treatment to remove biofilm formed. Some sort of filtration is necessary if the oxidation process does not completely mineralise the organic compounds in the water. However, since drinking water is used only low levels of organic matter are expected to enter the system from the process water. Thus, it could perhaps be possible to remove the available substrate for new biomass by a treatment method specified to remove organic matter.

• The conclusion is that for the upgrading plant with regenerating process water both treatment options, destruction of microorganisms or reduction of organic matter could be viable options.

#### 5.2.1 Treatment method

Since this type of upgrading plant uses drinking water, as process water it is assumed that most of the microorganisms enters the system with the raw gas in to the absorption column and with the air that enters the desorption column. Perhaps intensive filtering of the incoming raw gas and air could hinder microorganisms from entering the water and thus preventing growth. If that is not possible, some other treatment is necessary.

The pH of the water is an important factor when deciding on a treatment and where to employ it. In the regenerating plant the pH of the process water varies: before the absorption column it is neutral or slightly above between the absorption and desorption column the water is acidic. This is because carbon dioxide dissolves in the water and forms carbonic acid and thereby lowers the pH in the absorption column and in the desorption column the dissolved carbon dioxide is removed and thereby elevates the pH again.

**Reduction of microorganisms** If disinfection is to be an alternative it will probably not be enough to treat the water prior to the absorption column, since the main part of the microorganisms enters the system in the columns. Some microorganisms would circulate and those would be taken care of, but some would attach to the surfaces in the columns and a biofilm would eventually develop if the treatment does not stretches into the columns.

The addition of a chemical seems to be the simplest way out and would also offer a solution with the low investment costs. Compared to the situation with single pass process water with poor water quality in this case the treatment could be employed in a preventative way because of the lower oxidant demand of the water. However, this requires that it is economically sustainable to dose it continuously. Neither chlorine nor chlorine dioxide is chosen for the same reason as mentioned in the section above for the single pass system. Hydrogen peroxide and peracetic acid could perhaps be efficient in the prevention of biofilm formation. Which one to choose depends on the efficiency versus the chemical costs, and that would have to be determined with a laboratory or pilot plant study. Peracetic acid comes in a equilibrium solution containing peracetic acid and hydrogen peroxide and where peracetic acid functions best under low pH, hydrogen peroxide is more efficient under high pH, which means that the peracetic acid solution could be added to treat the water throughout the system.

Ozone could perhaps be added in such a way that it treat the water in the absorption column and or the desorption column. A drawback is the fact that it will require high investments and perhaps operational costs. However, this problem is less compared with the process with single pass due to the higher water quality.

UV-light in itself will not be a possible solution, since it probably will be difficult and costly to implement it in the absorption/desorption column. If UV light could be implemented in the columns this would be the feasible treatment, but since the columns are packed with pall-rings this does not seem possible. A possible alternative would be to treat the water between the columns both prior to and after the absorption column in combination with filters to remove the decomposed microorganisms and the organic matter. A pilot plant study would need to be conducted to determine if that is enough.

- The most promising method for the reduction of microorganisms seem to be the addition of peracetic acid as a preventative measure. With some sort of filter to remove the decomposed microorganisms.
- UV-light in combination with some kind of filtration could perhaps be a solution (if it is enough to treat the water between the columns).

**Removal of organic matter** may be a viable option if the treatment is operated at such a level that there is no net increase of microorganisms in the system over time. This could be accomplished by operating the oxidation process at a very high level (could be expensive, or perhaps not since drinking water is used) or in a combination with some sort of filter.

An advanced oxidation process could perhaps offer both oxidation of organic matter and destruction of microorganisms. That could be employed in such a way that it could treat the water both between and within the columns. The efficiency of the advanced oxidation processes is compound specific and highly affected by the water quality, the final choice can only be made after preliminary laboratory tests.

• A UV based advanced oxidation process offers an attractive alternative, since it could be employed to treat the water through out the system both with regard to the organic matter and the microorganisms.

## 6 Conclusions

The current cleaning methods mentioned in section 2.4.3 on page 8 all imply a stop in operation even though the cleaning can be done "in column". Since they highly affect the temperature and the pH of the process water, they can not be added while the upgrading system is running. Hot water and alkaline detergents that have a high pH have a negative effect on the exchange between the water and the carbon dioxide. The addition of a pH lowering substance, although it reduces the amount of microorganisms and make it more difficult for them to attach to the surfaces, is not a solution since a low pH lowers the carbon dioxide exchange.

#### 6.1 Single pass

- The treatment method should focus on the reduction of microorganisms.
- The addition of the chemical biocide should be applied intermittently.
- Peracetic acid appears to be a solution that could be applied in the absorption column and reduce the amount of microorganisms there.
- UV-light in combination with filtration could be a possible solution, if it is enough to treat the water prior to the absorption column.

#### 6.2 Regenerating

- The treatment could focus on both the reduction of microorganisms and the removal of organic matter.
- For the reduction of microorganisms the addition of peracetic acid seems to be a viable option that could treat the water throughout the system.
- An advanced oxidation treatment could be employed to remove both organic matter an microorganisms and it could treat the water through out the system.

#### 6.3 What to do next?

- Determining to what level the water must be cleaned in order to maintain an acceptable process capacity.
- A laboratory and pilot plant study to determine the needed dosages.
- More thorough estimations of the investment and operational cost of the suggested methods.
- Determen how to implement the treatment in the existing process.

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## A Flowchart of the regenerating process



Figure 6: Absorption with water wash with regeneration [4].

## **B** Flowchart of the single pass process



Figure 7: Absorption with water wash without regeneration [4].



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