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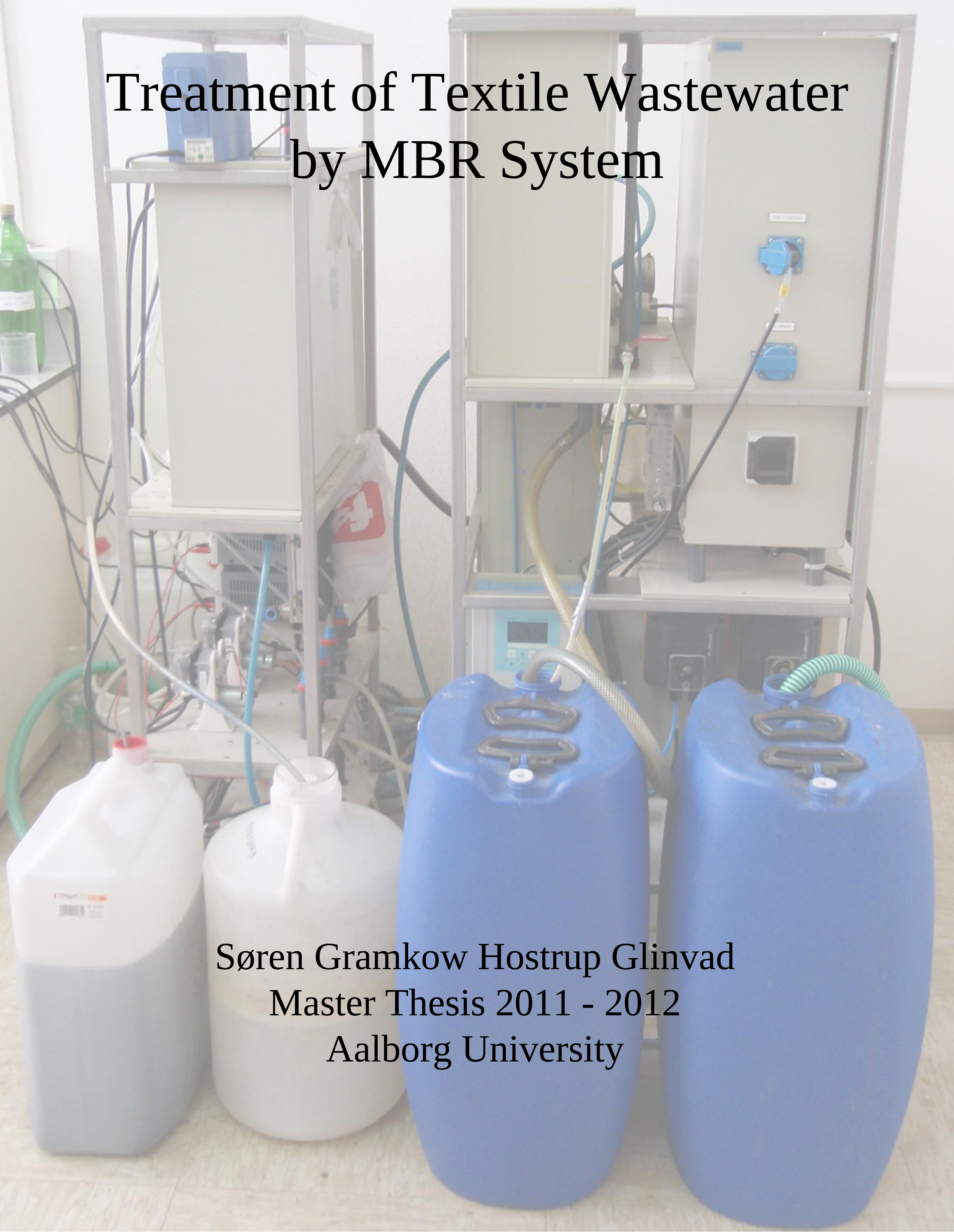

Treatment of Textile Wastewater by MBR System

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Abstract:

The aim of this thesis is to efficiently remove color from textile wastewater using MBR technology and Advanced Oxidation Processes (AOP). MBR technology is of great interest because of its capability to provide a stable and high quality treatment. Fenton's reaction is chosen to be used in the oxidation treatment, since the treatment previously has shown to effectively degrade dyes.

A lab scale MBR system, located at Maribor University, Slovenia was used during this thesis. The MBR system was constructed as an external submerged MBR system. The Fenton's reaction was used to treat both the wastewater and the permeate from the MBR system. The absorbance was measured in order to evaluate the color removal of the MBR system. A clear reduction in the absorbance was observed in the permeate and a highly visible color removal was obtained. The results showed an efficient removal of COD, NH_4^+, NO_3^-, NO_2^- and total nitrogen. The treatment with Fenton's reaction on wastewater and permeate showed efficient color removal both before and after MBR treatment.

It is concluded that MBR treatment is an efficient method for the degradation of dyes in textile wastewater. With optimal operation conditions, a high removal percent of color and nutrients can be obtained. It is concluded that the use of AOP can further improve the quality of the permeate and increase the probability of reusing the water in the dyeing process.

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Spildevand ved brug af MBR

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Synopsis:

Formålet med denne afhandling er ved hjælp af MBR-teknologi og *Advanced Oxidation Processes* (AOP) at reducere farveindholdet i tekstilt spildevand. MBR-teknologi er af stor interesse grundet dets evne til at levere en stabil behandling af høj kvalitet. Som videre behandling er det valgt at benytte *Fenton's reaction*, idet denne behandling tidligere har vist en effektiv nedbrydning af farvestoffer.
I denne afhandling blev der anvendt et MBR system, placeret på Maribor Universitet. MBR systemet er konstrueret som et eksternt neddykket MBR system. Til yderlig behandling blev Fenton's reagent benyttet på både spildevandet og permeatet fra MBR systemet.
For at vurdere farvenedbrydningen i MBR systemet blev absorbansen i permeatet målt. En tydelig reduktion i absorbansen blev observeret og en tydelig farvenedbrydning blev opnået. Resultaterne viste en effektiv fjernelse af COD, NH_4^+, NO_3^-, NO_2^- og total nitrogen. Behandling med *Fenton's reaction* på spildevand og permeat viste en effektiv farvenedbrydning både før og efter MBR behandlingen.
Det konkluderes, at MBR behandling er en effektiv metode til nedbrydning af farvestoffer i tekstilt spildevand. Det er muligt at opnå en høj nedbrydningsprocent af farve og næringsstoffer med optimale driftsbetingelser.
Det konkluderes at anvendelsen af AOP yderligere kan forbedre kvaliteten af permeatet og øge sandsynligheden for at genbruge vandet i farveprocessen.

Preface

This thesis is composed on the basis of work done at the Faculty of Engineering and Science at Aalborg University in the period of September 2011 to June 2012 under the guidance of Kristian Keiding and Morten Lykkegaard Christensen. The experimental work was performed at the University of Maribor, Slovenia in the period of November 2011 to April 2012 under the supervision of dr. Irena Petrinic, research assistant.

The thesis is divided into nine chapters. Chapter one gives a short introduction to the motivation for developing and improving the implementation of membrane bioreactors (MBR) and other technologies. Chapter two and three give a detailed exposition of the principles of MBR and oxidation technologies. Chapter four accounts for the thesis statement followed by chapter five and six, which describes the experimental work and the considerations behind. Chapter seven, eight and nine cover the results, discussion and conclusion of the treatment of textile wastewater using MBR and oxidation technologies.

A CD-ROM is attached to the thesis, containing all the presented results and associated calculations as well as the articles used as source material for this thesis.

Acknowledgement

I would like to thank my supervisor Kristian Keiding for his guidance during my masters thesis and for giving me the opportunity to independently shape my work.

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Contents

Introduction 1

Since the 1990s, the number of installed membrane bioreactor (MBR) plants have increased significantly, showing an increased interest and confidence in MBR technology. It is evident that MBR technology is becoming more and more significant in processes where the environmental footprint needs to be limited and a high water product quality is demanded. The use of MBR technology has reached a global implementation in a wide range of countries, such as China, Japan, Australia, USA and a large part of Europe [1].

The stage of MBR development in each country and geographic region, depends strongly on the legislation on discharge and reuse of wastewater. As a result of stricter legislation in the industrial and developed countries, as compared to the developing countries, the use of MBR technology is more widespread. However globally the legislation is becoming more and more strict and it is expected that the developing countries will follow with these restrictions. This will demand further development and wider use of wastewater treatment plants.[1]
The most significant aspect of the MBR technology, that is affecting its use, is the cost and plant size. MBR technology is more costly than conventional treatment plants, which is mostly due to the energy demand, membrane replacement and sludge management. However the costs have decreased significant since its implementation in the 1990s and continues to decrease today. This still makes MBR technology one of the most established technologies for wastewater treatment, along with the key-fact that MBR systems provide highly consistant quality of water effluents. [1]

Especially in the textile industry a high quality of water effluent is demanded, since textile wastewater can be a major source of color and contaminants when discharged to the environment. The color from the textile wastewater is mainly due to the intense dyeing process, which involves a wide range of different types of dyes, of which only 50 % is biodegradable [2][3]. Many of these dyes can cause environmental problems if released into the aquatic environment, thus causing highly environmental concerns. Because of this and local water scarcity, which is a problem in many regions, reuse of the water effluent has become an important issue in the textile industry. [4]
Both biological and chemical treatment have been proven efficient to some degree in removal of color from textile wastewater. As mentioned, MBR technology is already highly used, but can still be developed to further improve the effluent quality. A possible choice of additional treatment is the use of chemical oxidation technologies. Chemical oxidation technologies are very attractive because of their capability of degrading and mineralizing inorganic and organic contaminants very fast compared to other degrading methods. It is an efficient technology to apply as pre- or post-treatment combined with a MBR system.

Principles of MBR 2

2.1 Configurations of MBR

MBR technology includes biological treatment and membrane filtration. With a MBR it is possible to remove dissolved and suspended organic chemical constituents through biodegradation, as well as bio adsorption, and suspended matter through physical separation like membrane filtration. Most importantly it is necessary to maintain appropriate biological conditions in the bioreactor for retaining a sufficient microorganism environment for removal of the organic constituents. Therefore it is necessary to evaluate several parameters during the process of a MBR, for example the configuration of the reactor, aeration, mixed liquor suspended solids (MLSS), hydraulic retention time (HRT), etc. [1]. A standard measurement of the content of organic constituents in the wastewater and effluent (permeate) is the chemical and biochemical oxygen demand (COD and BOD), with both being an indirect measurement of the content of organic constituents in the sample. COD is the measurement of oxygen needed for oxidation of the organic constituents, while BOD is the measurement of oxygen needed by aerobic biological organisms to degrade organic constituents [1] [5]. The microoganisms in the bioreactor can either be aerobic or anaerobic depending on the desired treatment and conditions in the bioreactor. After the bioreactor treatment they are separated from the water through membrane filtration resulting in a clarified permeate. [1]

The configuration of the MBR system is especially referring to how the membrane module is integrated with the bioreactor and is of high importance. There are two main MBR system configurations; submerged and sidestream MBR. These two configurations are shown in figure 2.1.

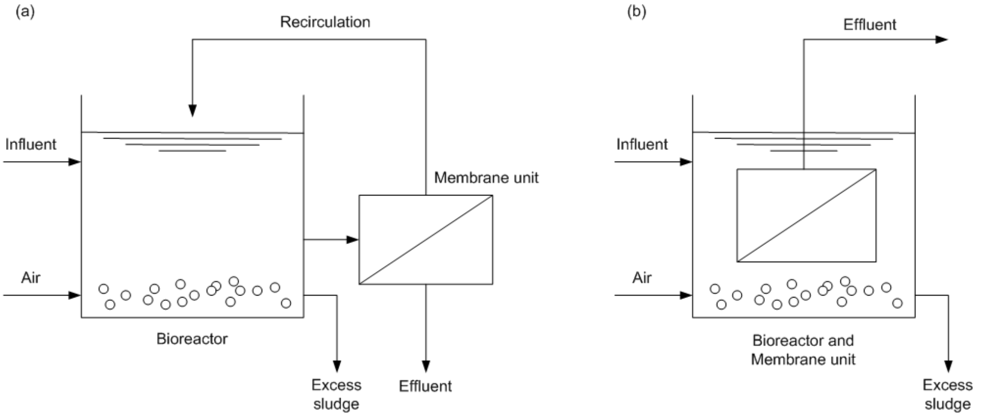

Figure 2.1: Configurations of a MBR: (a) sidestream and (b) submerged. Modified from [1].

A submerged MBR is usually less energy intensive than a sidestream MBR, however recent developments have decreased the extra energy demand and cost for sidestreams MBR. In a submerged MBR the membrane module is installed either in the main bioreactor or a separate tank.

Often membrane configurations used is flat sheets and tubular. An advantage of the submerged MBR is the possibility of incorporating a backwash system through the membrane module without removing it. This is also highly needed since the intensive direct contact with the activated sludge can result in a high fouling degree, however aeration is mainly used to reduce fouling. If the membrane module is in a separate tank, but still submerged, the activated sludge must be recirculated back to the main bioreactor to avoid sludge accumulation. [1]
In a sidestream MBR the membrane module is installed externally to the reactor. A pumping system is then required to transfer the activated sludge to the membrane module and back to the bioreactor. However the membrane module can be placed at lower levels than the bioreactor to utilize the gravitational force and hence to ease the maintenance. The membrane modules can more easily be cleaned chemically without any chemical risk to the activated sludge, and maintenance of the membrane module is more optimal, since they can be replaced relative fast. Both configurations have advantages and disadvantages, and are both used industrial. [1]

Furthermore the configuration of the bioreactor is classified according to process configuration, feeding regime and redox conditions. Process configuration determines the way the wastewater is in contact with the biomass, which for a MBR system is as suspended growth, where the biomass is suspended in the reactor. The feeding regime determines in which way the wastewater is introduced to the bioreactor, which for a MBR system is continuously. Other systems can instead involve a fixed film instead of suspension or feeding batch-wise instead of continuously, like moving bed bioreactor (MBBR) or sequencing batch reactor (SBR). [1]
In a MBR system the redox conditions are established by either dissolved oxygen (DO) being present in aerobic reactors or complete absence of oxygen in anaerobic reactors. Sometimes also an anoxic reactor is used, where oxygen is provided by another chemical compound. The setup of the bioreactor is especially important in order to achieve sufficient removal of organic and nitrogenous matter. In the activated sludge system within the bioreactor several reactions occur, that changes the form of the nitrogenous matter. An overview of this system is shown in figure 2.2. [1] [6]

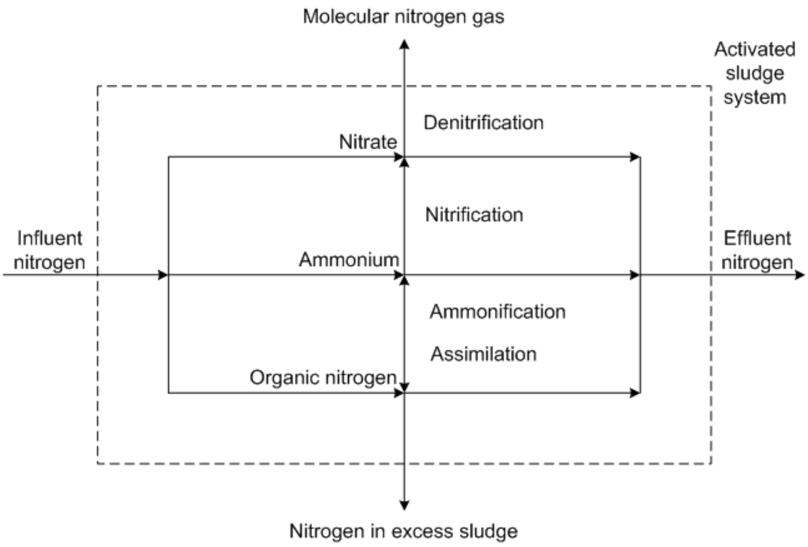

Figure 2.2: Schematic presentation of the forms of nitrogenous matter and their reaction pathways. Modified from Haandel et al. [6]

Nitrogenous matter in wastewater is mainly composed of ammonium nitrogen (present as gaseous NH_3 and ionic $NH_4{}^+$) and organic nitrogen. Traces of the oxidized form of nitrogen can be present, namely nitrate ($NO_3{}^-$) and nitrite ($NO_2{}^-$). The total amount of nitrogen in the influent and effluent is defined by equation 2.1 and 2.2 [6].

$$N_{ti} = N_{ki} + N_{ni} = N_{oi} + N_{ai} + N_{ni} \tag{2.1}$$

$$N_{te} = N_{ke} + N_{ne} = N_{oe} + N_{ae} + N_{ne} \tag{2.2}$$

N_{ti}	Total nitrogen in influent	N_{te}	Total nitrogen in effluent
N_{ki}	Total kjeldahl nitrogen in influent	N_{ke}	Total kjeldahl nitrogen in effluent
N_{ni}	Nitrate in influent	N_{ne}	Nitrate in effluent
N_{oi}	Organic nitrogen in influent	N_{oe}	Organic nitrogen in effluent
N_{ai}	Ammonium in influent	N_{ae}	Ammonium in effluent

The Total Kjeldahl Nitrogen (TKN) is the sum of organic nitrogen and ammonium concentrations, as shown in equation 2.1 and 2.2. This value is often used to determine the content of nitrogenous matter in wastewater instead of total organic nitrogen (TN). As shown in figure 2.2 different reactions occur, known as ammonification/assimilation, nitrification and denitrification. Ammonification is the conversion of organic nitrogen into ammonium, and assimilation is the reverse process. The reaction is described by the following reaction:

$$RNH_2 + H_2O + H^+ \leftrightarrow ROH + NH_4^+ \tag{2.3}$$

Ammonification classically occurs in the aerobic reactor, where ammonium is used in the nitrification stage. Nitrification is the biological conversion of ammonium to nitrate and occurs only under aerobic conditions. Nitrification is divided into two stages, the conversion of ammonium to nitrite and the conversion of nitrite to nitrate. The reactions are as following:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H^+ + 2H_2O \tag{2.4}$$

$$2NO_2^- + 2O_2 \rightarrow 2NO_3^- \tag{2.5}$$

The second reaction step proceeds much faster than the first step, which means that nitrite never accumulates in the bioreactor, as long as sufficient levels of carbon sources and dissolved oxygen are present. The DO level should be above 2.0 mg/L for maintaning growth of the microorganisms in the aerobic reactor. [1] [7]

Denitrification occurs in the anaerobic reactor, where nitrate is converted to gaseous molecular nitrogen. Denitrification occurs under anaerobic conditions, where organic carbon is oxidized using the nitrate ion. A general description is shown in the following reaction:

$$C_{10}H_{19}O_3N + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^- \tag{2.6}$$

In reaction 2.6, $C_{10}H_{19}O_3N$ represents the dissolved organic matter in the wastewater. If there is not enough organic matter in the wastewater, additional carbon can be added in the form of glucose. However most full scale MBR plants recircle the wastewater from the aerobic reactor, which is rich on nitrate. For complete removal of nitrogen both aerobic and anaerobic treatment is necessary [8]. Simpel aerobic MBR systems are however also commonly used without anaerobic treatment, but for industrial high strength wastewater anaerobic treatment is more sufficient [9] [10] [11] [12]. Different setups of aerobic and anaerobic reactors have been used where either the wastewater first enters the aerobic reactor and then the anaerobic reactor or the reverse setup, but with recirculation back to the anaerobic reactor. The latter is however proven to be more efficient when dealing with industrial textile wastewater. [13]

The textile industry produces wastewater containing large quantities of dyes, which most are of synthetic origin and consist of complex aromatic molecules. Different kind of dyes exist and their use is dependent on the types of fibers used in the dyeing process. A selection of dyes that can be named includes acid dyes, basic dyes, direct dyes and reactive dyes. A large part of these dyes are however resistant to biodegradation and cannot be removed by aerobic biological treatment [14]. The aerobic biological treatment mainly involves adsorption, because the aerobic degradation occurs very slowly and often leaves behind non-biodegradable or difficult to degrade intermediates [15]. Instead anaerobic biological treatment have proven to degrade the dyes more rapidly, however it produces toxic aromatic amines, which cannot be further degraded in the anaerobic reactor and will accumulate. A combination of an anaerobic reactor followed by an aerobic reactor is the optimal setup, since the toxic amines can be degraded in the aerobic reactor [16]. A recirculation of the wastewater from the aerobic reactor to the anaerobic reactor is however necessary in order to achieve a proper removal of nitrogen. [17] [18] [19]

When biological treatment of wastewater is not sufficient enough for color removal, chemical treatment can be a more effcient method. It is an efficient technology that can be applied as pretreatment of wastewater, for detoxification and enhancing the biodegradability, before the biological treatment. Thereby the biological process can be concentrated on the nutrient removal.

Oxidation Technologies 3

3.1 Principles of Oxidation

Chemical oxidation technologies can be used as part of the treatment of drinking water, groundwater and wastewater. They are normally combined with other treatment technologies, such as biological treatment and membrane filtration. Chemical oxidation technologies are very attractive because of their capability of degrading and mineralizing inorganic and organic contaminants very fast compared to other degrading methods. It is an efficient technology to apply as pre- and post-treatment of wastewater for detoxification and enhancing the biodegradability before the biological treatment and improve the effluent water.

Most of the recent research on chemical oxidation technologies has concentrated on Advanced Oxidation Processes (AOPs). Several studies have examined the effect of wastewater treated with AOPs and compared it with nontreated wastewater. The results indicated an improved purification of the wastewater and of various other parameters. But to fully determine the efficiency of AOPs, it is necessary to understand the principles of oxidation.
Oxidation is part of a reduction-oxidation (redox) reaction, which involves oxidation and reduction. A redox reaction includes the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant). Oxidation is the removal of electrons and reduction is the gain of electrons. The specie that loses electrons is oxidized, while the other specie gains electrons and is reduced. The number of electrons gained or lost in a process is equal to the change in the oxidation state of the reduced or oxidized specie [20]. The oxidation potential for selected chemical reactants is shown in figure 3.1.

Table 3.1: Oxidation potential for selected chemical reactants [21].

Oxidant	**Oxidation potential, E^0 [V]**
Hydroxyl radical	2.80
Ozone	
acidic	2.07
basic	1.24
Hydrogen peroxide	
acidic	1.78
basic	0.85
Chlorine dioxide	1.71
Chlorine	
acidic (elementary)	1.36
acidic (hypochlorous acid)	1.49
basic (hypochlorite)	0.90

A change in the oxidation state is generated by an oxidant and/or reductant that is powerfull enough to effect this change. The power of an oxidant or reductant is measured by the oxidation potential of the species. A higher oxidation potential results in a more effective oxidation. The higher the oxidation potential of a specie is, the more affinity for electrons it has. An overview of selected oxidants and their oxidation potential is given in table 3.1 [21].

Fluorine is one of the strongest oxidants, as shown in table 3.1. Fluorine is however a highly toxic chemical and it is therefore unattractive as an oxidant in water and wastewater treatment. Hydroxyl radicals, ozone and hydrogen peroxide are also some of the strongest oxidants, as shown in table 3.1. They are even stronger than chlorine and chlorine dioxide, which have previously been used in water and wastewater treatment. This makes them very attractive as usable oxidants. [22] [23]

3.2 Advanced Oxidation Processes

AOPs involve two stages of the oxidation process, as described in section 3.1. First the formation of strong oxidants and then the reaction between oxidants and contaminants. In general, AOPs include processes based on the generation of hydroxyl radicals. As shown in table 3.1 on the preceding page, the hydroxyl radical is very desirable because of its high oxidation potential and fast reaction rate. The hydroxyl radical is so reactive that it reacts with almost any organic contaminants in the solution at high reaction rates in the order of 10^9-10^{10} $M^{-1}\cdot s^{-1}$. [24] [25]

Hydroxyl radicals can oxidize the organic contaminants by a number of pathways, resulting in a radical chain oxidation ending with complete oxidation of the organic contaminants. Hydroxyl radicals can oxidize the organic contaminants by abstraction of protons producing organic radicals, which can be further oxidized. Another possibility is the addition to double bonds, like aromatic rings, where a complex between the hydroxyl radical and the organic contaminant is created, which again can be further oxidized. [23] [26]

The effectiveness of an AOP is proportional to its ability to generate hydroxyl radicals and is dependent on the reaction rate between the hydroxyl radicals and contaminants. One of the most established oxidants used in chemical oxidation technology is hydrogen peroxide. However oxidation by hydrogen peroxide alone is not effective enough for removal of organic contaminants, because of low reaction rates at reasonable hydrogen peroxide concentrations [23]. Therefore, a catalyst must be present to activate the generation of hydroxyl radicals. This can be done with ultraviolet (UV) light, ozone or iron salts, which is known as Fenton's reaction. Compared to other chemical oxidation processes, Fenton's reaction has the advantage of not being an energy and cost intensive process, like processes including ozonation and UV [22]. Likewise the processes can include a lot more complicated setup, whereas treatment with Fenton's reagent can be quite simple.

3.2.1 Fenton's Reaction

In the Fenton's reaction, hydrogen peroxide reacts with ferrous iron from the iron salt to form Fenton's reagent. This reagent is based on the catalytic effect of ferrous iron on the decomposition of hydrogen peroxide. The iron-oxide complex is however unstable and immediately reacts to form hydroxyl radicals. The overall reaction is shown below. [27] [28]

$$\mathrm{Fe}^{2+} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^{-} + \mathrm{OH}^{\bullet} \tag{3.1}$$

The Fenton reaction can be separated into two separated systems. The ferrous system refers to the primary reaction which produces hydroxyl radicals, shown above in reaction 3.1. The ferric system is responsible for the regeneration of ferrous iron in order maintain the generation of hydroxyl radicals. This is shown in reaction 3.2 along with several sidereactions that include ferric and ferrous iron. [29]

$$\begin{align}
\mathrm{Fe}^{3+} + \mathrm{H_2O_2} &\rightarrow \mathrm{Fe}^{2+} + \mathrm{H}^{+} + \mathrm{OH}_2^{\bullet} \tag{3.2}\\
\mathrm{Fe}^{3+} + \mathrm{OH}_2^{\bullet} &\rightarrow \mathrm{Fe}^{2+} + \mathrm{H}^{+} + \mathrm{O_2} \tag{3.3}\\
\mathrm{Fe}^{2+} + \mathrm{OH}_2^{\bullet} &\rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}_2^{-} \tag{3.4}\\
\mathrm{Fe}^{2+} + \mathrm{OH}^{\bullet} &\rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^{-} \tag{3.5}\\
\mathrm{H_2O_2} + \mathrm{OH}^{\bullet} &\rightarrow \mathrm{H_2O} + \mathrm{OH}_2^{\bullet} \tag{3.6}\\
 & \tag{3.7}
\end{align}$$

As shown in the reactions above, ferrous and ferric iron can also participate in other side reactions along with the generated hydroxyl and hydroperoxyl radicals and thus resulting in termination of the generated radicals [27] [29]. The scavenging of radicals by reactions 3.3 and 3.4 is not as important as the scavenging of hydroxyl radicals. The hydroperoxyl radicals are not nearly as reactive as hydroxyl radicals, therefore hydroxyl radicals are of much more importance for the oxidation of organic contaminants [27].

In the presence of organic contaminants, these will react with the generated hydroxyl radicals and be oxidized. Further reaction with ferric iron and water generates new organic products that can be further oxidized until a complete mineralization is obtained [28]. The reaction schemes are shown below:

$$\begin{align}
\mathrm{RH} + \mathrm{OH}^{\bullet} &\rightarrow \mathrm{H_2O} + \mathrm{R}^{\bullet} \tag{3.8}\\
\mathrm{R}^{\bullet} + \mathrm{Fe}^{3+} &\rightarrow \mathrm{R}^{+} + \mathrm{Fe}^{2+} \tag{3.9}\\
\mathrm{R}^{+} + \mathrm{H_2O} &\rightarrow \mathrm{ROH} + \mathrm{H}^{+} \tag{3.10}
\end{align}$$

The above reaction schemes show that ferric iron is also reduced back to ferrous iron when including organic contaminants, which is able to maintain the generation of hydroxyl radicals. The shown reactions are together known as the classical "radical chain" mechanism, which is proposed for simple Fe^{3+} systems involving $\mathrm{OH}^{\bullet}$ and $\mathrm{OH}_2^{\bullet}$. However the mechanism of reaction with Fenton's reagent is relatively complex and may change depending on the reaction conditions [27]. This is especially documented by Yoon et al. [29], where different ratios between iron and hydrogen peroxide shows different reaction pathways. This is further discussed in chapter 8.

The reaction efficiency of Fenton's reagent is however also dependent on other parameters than the chemical ratios. It has been proven that the reaction is strongly dependent on the pH during the reaction. At pH lower than 3.5, the ferrous iron and hydrogen peroxide are more stable in solution, which results in a better redox system. At pH above 4, the ferrous iron can easily form ferric iron which is less stable than ferrous iron. Ferric iron has a high tendency for generating iron hydroxide complexes at pH above 4, which is also why the pH is typical raised after the reaction for removing excess iron as precipitated iron hydroxide complexes [3] [30] [31]. For hydrogen peroxide it applies that in basic solution it is unstable and easily decomposes into water and oxygen gas [30]. Also previous studies have mainly performed the reactions at pH 3 and according to Pignatello et al. [27] the efficiency drops below and above pH 3. Also Oliveros et al. [32] showed that pH 3 is a critical point for the redox system.

A more in depth comparison of the processes is presented in chapter 8. All mentioned processes have been proven to effectively degrade and remove dyes from textile wastewater in experimental studies, however the Fenton's reaction is not as examined in full scale as the other processes [22]. Therefore on the basis of the preceding sections, it is chosen to further evaluate the effect of treatment with Fenton's reagent on textile wastewater in relation to MBR treatment.

Thesis Statement 4

Wastewater released from textile industries can cause environmental and health hazards because of the often toxic content of dyes from the dyeing process. Most of the dyes used in the textile industry and their degradation products are cytotoxic or carcinogenic. Thus, decolorization of textile wastewater is an important environmental concern. Today there is a great focus on reusing the effluent water in the dyeing process. Hence there is an urgent need to develop an economical treatment system for the treatment of wastewater, which can meet the strict quality standards.

This study aims at decolorizing textile wastewater by a MBR system and furthermore study the effect of treatment by Advanced Oxidation Processes (AOP). In order to do so the operating conditions of the MBR system and the influence on the performance must be investigated. The influence of parameters such as aeration, mixed liquor suspended solids (MLSS) and hydraulic retention time (HRT) will be investigated.

The conventional aerobic and anaerobic wastewater treatment processes, such as MBR systems, usually can not efficiently decolorize the effluents contaminated with dyes, due to their complex polyaromatic structure and non-biodegradability. Therefore further treatment in the form of chemical oxidation, such as AOP, can be necessary to achieve a better performance. In this study the efficiency of pre- and post-treatment with AOP and integration into the MBR system will be tested and investigated.

The objectives of this study are therefore:

- Treatment of textile wastewater with a MBR system.
- Evaluate the wastewater treatment of a MBR system.
- Evaluate the wastewater treatment with Fenton's reaction.
- To measure and evaluate the content of COD, ${NH_4}^+$, ${NO_3}^-$, ${PO_4}^{3-}$ and total N.

Experimental Setup 5

5.1 Setup Parameters for Lab Scale MBR

Setup of the lab scale MBR is schematic presented in figure 5.1. The system is a ZeeWeed ® ZenoGem® MBR system provided by Zenon Systems and operated at Maribor University.

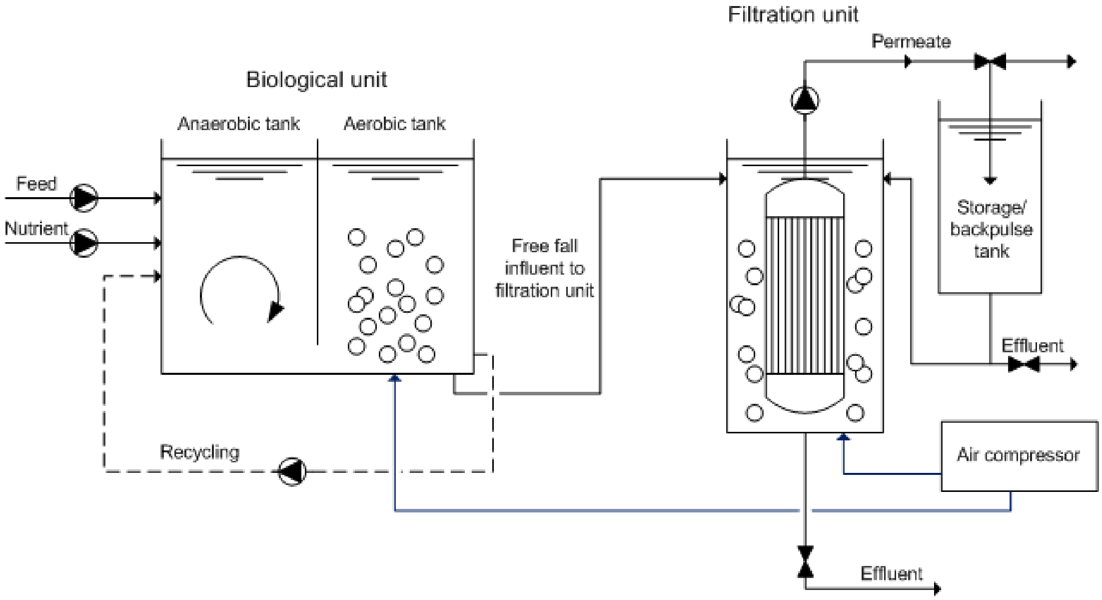

Figure 5.1: Schematic presentation of the lab scale MBR.

The setup included a bioreactor, divided into an aerobic and anaerobic reactor, and an external submerged membrane module. The transmembrane pressure (TMP) was controlled by an air pump, pumping at a constant rate. Every 10 min the pressure was reversed and the membrane was backpulsed with permeate from the storage tank for 30 s. To further prevent fouling on the membrane, an air compressor applied aeration along the membrane surface.

In the bioreactor, the aerobic reactor was supplied with aeration by the same air compressor used for the filtration unit. In the anaerobic reactor, circulation was assured by a mechanical stirrer to avoid settling. The flow balance of the system is shown in figure 5.2.

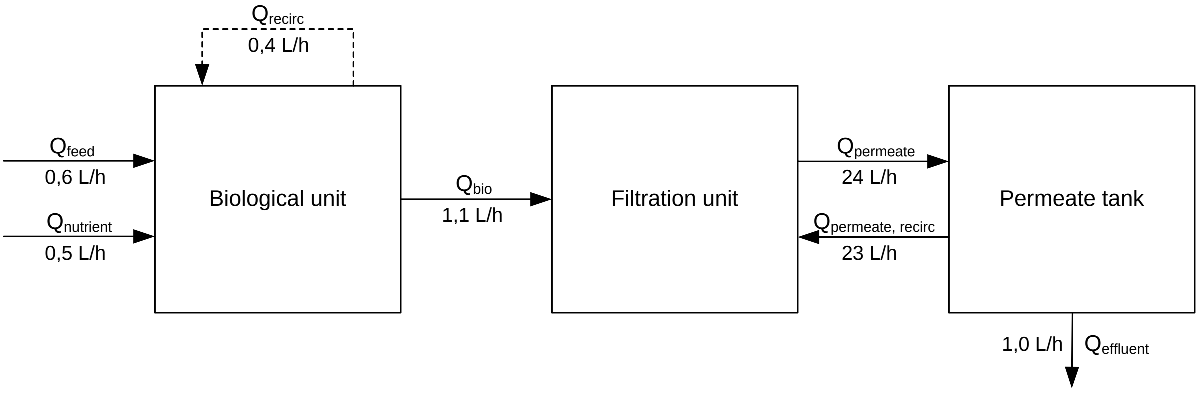

Figure 5.2: An overview of the flow rates in the MBR system.

Due to lack of sludge recirculation, 2 L of sludge was transferred daily from the filtration unit to the bioreactor. This is however not assessed as part of the flow balance in figure 5.2. The system was fed with wastewater at a rate of 0.6 L/h and nutritent solution at a rate of 0.5 L/h for a total period of 40 days. All physical operation parameters are presented in table 5.1.

Table 5.1: Physical parameters for lab scale MBR.

Parameter	**Value**
Volume aerobic tank [L]	23
Volume anaerobic tank [L]	12
Volume membrane tank [L]	25
Volume permeate tank [L]	15
Membrane surface area [m^2]	0.93
Pore size [μm]	0.04
Backpulse	30 s every 10 min

Activated sludge was collected from Maribor Municipal Wastewater Treatment Plant and had an initial MLSS of approximately 10 g/L. The wastewater used as feed was retrieved from Beti Textile Plant in Metlika, Slovenia. Along with the wastewater, a nutrient solution containing additional glucose, ammonium and phosphate sources was also added to the bioreactor. The biological parameters are presented in table 5.2.

Table 5.2: Biological parameters for lab scale MBR.

Parameter	**Value**
Feed COD [mg O_2/L]	∼900
COD load [g COD/g MLSS]	∼0.45
MLSS [g/L]	∼2
HRT [day]	∼2

Sludge samples from the bioreactor and filtration unit were taken every second day for MLSS measurements, as described later in section 6.1.

Each day the DO level and pH-values were monitored, along with the TMP and flow rates of the system. Samples from the wastewater and permeate were taken everyday for UV-Vis measurements and twice a week for nutrient analysis, as desribed later in section 6.1.

5.2 Setup for Fenton's reagent experiments

As mentioned in section 5.1, the wastewater was retrieved from Beti Textile Plant in Metlika, Slovenia. The plant mainly uses acid dyes in the dyeing process, however several more kinds of dyes are also used. In order to determine if Fenton's reaction can be used for the degradation of acid dyes, some preliminary experiments were conducted with Nylosan Yellow E-2RL and Nylosan Red E-BL, which both are acid dyes, provided by Beti Textile Plant. The experiments were conducted based on the previous work done by T. Kurbus [33].

As mentioned in section 3.2, certain reaction conditions must be optimized in order to achieve the optimal treatment with Fenton's reaction. This includes pH, time of reaction and doses of hydrogen peroxide and iron sulfate. As described in section 3.2 the efficiency of the reaction is strongly dependent on pH. Several studies have shown that the maximum reaction rate occurs around pH 3 in most cases. In basic solution the iron will precipitate as $Fe(OH)_3$ and not act as a catalyst for the radical generation [21] [34]. Therefore are all experiments with Fenton's reaction in this study conducted with a pH around 3.

The reaction rates with Fenton's reaction is mainly limited by the generation of hydroxyl radicals, which is dependent on the iron concentration. A too low concentration of iron will result in excessive long reaction rates and a too high concentration of hydrogen peroxide will result in radical scavenging [21] [35] [36]. Typical Fe:H_2O_2 ratios are between 1:5 and 1:10 (w/w), with minimum iron concentrations at 3-15 mg/L. According to US Peroxide [21] a ratio between iron and the desired substrate removed is optimal at 1:10-50 (w/w). However since the wastewater contains an unknown content and type of dyes, it is decided to adjust the iron concentration after the COD level, which is given in mg O_2/L. It is selected on the basis of this to perform three different experiments with an Fe:COD ratio of 1:10, 1:15 and 1:25 (w/w).

According to Alaton et al. [34] and Lucas et al. [35] the optimal ratio between iron sulfate and hydrogen peroxide is between 1:5 and 1:10 molar ratio. Converted to a weight/weight ratio it is 1:3 to 1:6. US Peroxide [21] states that a range from 1:5 to 1:25 (w/w) is usable for treatment with Fenton's reaction, as long as the iron concentration is above the minimal limit. On the basis of this it is chosen that different Fe:H_2O_2 ratios of 1:5, 1:10, 1:15 and 1:20 (w/w) are tested for each of the different Fe:COD ratios.

For the procedure of the treatment with Fenton's reaction several studies show that only a short reaction time is necessary. According to both Alaton et al. [34] and Lodha et al. [3] most of the dye removal occurs during the first few minutes, afterwards the removal effect becomes steady. Generally a reaction time of 30 min is applied, since an effect can still be observed so long [3] [34] [37]. Therefore a reaction time of 30 min is chosen for the experiments in this thesis. Furthermore H_2SO_4 and NaOH is chosen to be used for lowering and raising the pH respectively. Only a simple experimental setup is necessary, with a small sample put under stirring at room temperature. After the reaction the pH is raised in order to precipitate additional iron as ferric hydroxide. The significance of this is later discussed in chapter 8.

Experimental Procedure 6

6.1 Determination of DO, MLSS and pH

The DO levels in the anaerobic and aerobic tanks were measured using an oxygen sensor. DO levels were measured three times every day during the MBR process.

For determination of sludge concentration, 50 ml of samples from both the aerobic and anaerobic reactor in the bioreactor and the membrane module were filtered on a pre-dried and weighed 12 μm filter. Then the filter and filtercake were dried at 105 $^\circ C$ for $2\frac{1}{2}$ h and then weighed again. This procedure was done every second day.

pH was measured with a pH meter equipped with a pH electrode every day during the MBR process. pH measurements were done in the feed tank, permeate tank, aerobic and anaerobic reactor every day.

6.2 Determination of COD and Nutrient Content

All the analysis are performed with LANGE Colorimetric cuvette tests. For heating the samples a HACH LANGE Heater was used and for measuring and calculating the absorbance and concentration a HACH LANGE Spectrophotometer was used. Product informations are shown in Appendix A and on the attached CD-ROM.

For the analysis of COD in wastewater, a HACH LANGE Sample cuvette, containing a mixture of 90 % sulphuric acid, 1.5 % inorganic mercury compounds, 1 % potassium dichromate and 0.5 % silver sulfate, was fist shaken and then added 2 ml of wastewater. Then the cuvette was shaken again and heated to 148° for 2 hours. Afterwards the cuvette was shaken and cooled down until measurement and calculation of absorbance and concentration.
For the analysis of COD in permeate a HACH LANGE Sample cuvette, containing a mixture of 90 % sulphuric acid, 8 % water, 1.7 % inorganic mercury compounds, 0.5 % silver sulfate and 0.1 % potassium dichromate, was fist shaken and then added 2 ml of permeate. Then the cuvette was shaken again and heated to 148° for 2 hours. Afterwards the cuvette was shaken and cooled down until measurement and calculation of absorbance and concentration.

For the analysis of phosphate, a 0.5 ml sample of either wastewater or permeate was transferred to a HACH LANGE Sample cuvette containing a mixture of 95 % water and 1 % sulphuric acid. Then a cap, containing a sample of 71 % sodium peroxydisulfate and 21 % sodium metaborate, was added on the cuvette and shaken until homogenized. Then the cuvette was heated to 100° for 1 hour. After being cooled down, 0.2 ml solution of 80 % water, 16 % sulphuric acid, 2 % ammonium heptamolybdate tetrahydrate and 1 % sulfamic acid and potassium antimony(III)oxide tartrate hemihydrate was added along with a new cap containing 50 % ascorbic acid, 25 % sodium metaborate and 15 % dextran. Then the cuvette was shaken until homogenized and after 10 min the absorbance and concentration were measured and calculated.

For the analysis of total nitrogen in wastewater, a 0.2 ml sample of wastewater was mixed with 2.3 ml solution of 98 % water and 2 % sodium hydroxide and one tablet of 65 % dipotassium peroxodisulphate, 20 % sodium metaborate and 15-20 % disodium tetraborate anhydrous. The mixture was then heated at 100° for 1 hour. After being cooled down a capsule containing 70 % sodium sulfite and 0.7 % sodium azide was added and then shaken until dissolved. Then 0.5 ml of the mixture was transferred to a HACH LANGE Sample cuvette containing 60 % sulphuric acid, 33 % phosphoric acid and 7 % water. Then 0.2 ml solution of 75 % water, 20 % isopropanol, 1 % 2,6-xylenol and isopentyle acetate was added and mixed. After 15 min the absorbance and concentration were measured and calculated.

For the analysis of ammonium, a 0.5 ml sample of either wastewater or permeate was transferred to a HACH LANGE Sample cuvette containing a mixture of 95 % water and 0.2 % sodium hydroxide. Then a new cap, containing a sample of 76 % D(-)-Mannitol, 12 % troclosene sodium dihydrate and 12 % sodium nitroprusside dihydrate, was added on the cuvette and shaken until homogenized. After 15 min the absorbance and concentration were measured and calculated.

For the analysis of nitrite, a 0.2 ml sample of either wastewater or permeate was transferred to a HACH LANGE Sample cuvette containing a mixture of 97 % water and 3 % citric acid. Then a new cap, containing a sample of 70 % D(-)-Mannitol, 25 % 1-Naphthylamine sulfonic acid salt, 0.25 % sodium hydroxide, was added on the cuvette and shaken until homogenized. After 10 min the absorbance and concentration were measured and calculated.

For the analysis of nitrate, a 0.2 ml sample of either wastewater or permeate was transferred to a HACH LANGE Sample cuvette containing a mixture of 60 % sulphuric acid, 33 % phosphoric acid and 7 % water. Then 1 ml solution of 95 % water, 5 % isopropanol, 1 % 2,6-xylenol and isopentyle acetate was added and the cuvette shaken until homogenized. After 15 min the absorbance and concentration were measured and calculated.

6.3 Preliminary Experiments with Fenton's Reaction

In order to determine that the Fenton's reaction can be used to degrade acid dyes, a preliminary experiment with the dyes Nylosan Yellow E-2RL and Nylosan Red E-BL was made. For both dyes, the following method applies:

A sample of 250 ml dye solution was put under stirring in a conical flask with a magnetic stirrer. First the pH was adjusted to 3.0 with 1M H_2SO_4 and then a dose of 0.1M $FeSO_4{\cdot}7H_2O$ solution was added. Finally a dose of a 0.1M H_2O_2 solution was added and the reaction started. Samples were taken every minute during the first five minutes of reaction. Afterwards samples were taken every 10 or 20 minutes as the reaction proceeded.

The samples were analysed with UV-Vis spectroscopy. The absorbance of the Nylosan Yellow E-2RL samples was measured at 381 nm and for the Nylosan Red E-BL samples the absorbance was measured at 521 nm. Two standardsolutions were prepared for both dyes, which were used to obtain two standardcurves and determination of the maximum absorbance wavelength. These standardcurves along with calculations are shown on the attached CD-ROM.

6.4 Treatment with Fenton's Reaction

In order to determine the optimal conditions for the Fenton's reaction treatment, several experiments were performed with different concentrations of the Fenton's reagents in order to determine the optimal Fe:H_2O_2 and Fe:COD ratio. For all experiments, the following method applies:

A sample of 100 ml wastewater (50 ml for the permeate) was put under stirring in a conical flask with a magnetic stirrer. First the pH was adjusted to 3.0 with 1M H_2SO_4 and then a dose of a 0.1M $FeSO_4{\cdot}7H_2O$ solution was added. Finally a dose of a 0.1M H_2O_2 solution was added and the reaction started.

The mixture was left stirring for 30 min, whereafter the reaction was stopped by adjusting the pH to 12 with 5M NaOH. Then the mixture was filtered through a 12 μm filter and the precipitate was removed. The procedure was the same for treatment of the permeate.

6.5 UV-Vis Measurements of MBR Samples

Each day samples were taken from the feed and permeate tank for UV-Vis measurements. Before measurements, the samples were filtered with a 12 μm filter in order to remove interfering particles. A full UV-Vis spectrum from 200 to 800 nm was measured for each sample. Demineralized water was used as a reference.

Furthermore full UV-Vis spectra were also done for the wastewater and permeate samples treated with Fenton's reaction in the range 200 to 800 nm. Demineralized water was used as a reference.

Results and Interpretation 7

The results are divided into two sections. First section presents the analytical measurements from the MBR system along with the UV-Vis measurements of the permeate. Second section presents the results from the treatment with Fenton's reaction on the dye solutions, wastewater and permeate.

7.1 Analytical measurements

During the MBR process the COD level was regularly measured, as described in section 6.1. COD is used to indirectly measure the amount of organic compounds in the wastewater and permeate. The basis of the COD measurements is that nearly all organic compounds can be fully oxidized and the result shows the mass of oxygen consumed in the oxidation per liter of solution. Table 7.1 shows the COD values in the wastewater and permeate from the MBR system, along with the percentage removal efficiency:

Table 7.1: Wastewater/permeate COD and percentage overall removal.

	Wastewater (mg/L)	Permeate (mg/L)	Removal (%)
Day	COD	COD	COD
1	607	-	-
8	783	38,2	95.1
15	607	33,6	94.5
19	881	-	-
21	-	34,4	-
25	868	47,2	94.6
27	925	41,2	95.6
29	858	45,0	94.8
32	950	53,2	94.4
34	1135	43,8	96.1
36	1013	51,8	94.9
39	1008	59,5	94.1
41	-	54,8	-
43	944	43,1	95.3

From table 7.1 it is shown that the COD removal efficiency of the MBR system is steady around 95 %. The COD level in the wastewater differs between 600 and 1100 mg/L, which is quite low compared to conventional wastewater with COD levels up to 2000 mg/L. The COD level in the permeate differs between 30 and 60 mg/L, which is well below the ordinary limit of 125 mg/L.

Furthermore also the content of phosphate, total nitrogen, ammonium, nitrate and nitrite in the wastewater and permeate was measured, as described in section 6.1. These results are given in table 7.2.

Table 7.2: Wastewater/permeate PO_4-P and total N, and permeate NH_4-N, NO_3-N and NO_2-N.

	Wastewater (mg/L)		Permeate (mg/L)				
Day	PO_4-P	Total N	PO_4-P	Total N	NH_4-N	NO_3-N	NO_2-N
1	-	16.6	-	-	-	-	-
8	0.9	15.8	5.3	22.0	0.06	21.8	0.05
15	-	16.6	7.6	57.2	2.89	20.7	0.05
19	1.0	16.7	-	-	-	-	-
21	-	-	6.1	21.2	-	-	-
25	8.4	48.7	5.0	3.7	0.15	1.0	0.02
27	1.6	39.2	4.4	0.9	0.08	0.0	0.04
29	0.9	36.5	2.5	0.8	0.06	0.0	0.03
32	2.8	29.8	2.2	9.4	0.67	3.9	0.08
34	1.5	27.5	4.8	4.1	0.19	3.0	0.02
36	1.3	25.3	7.7	7.9	1.82	6.5	0.05
39	3.2	60.1	6.7	13.3	7.01	4.1	0.11
41	-	-	4.4	13.8	9.38	3.1	0.08
43	0.8	23.3	4.7	10.4	4.81	4.4	0.09

From table 7.2 it is observed that the removal efficiency of total nitrogen is fairly variable, since quite significant changes of the content in the permeate are shown. The content of ammonium, nitrate and nitrite is at reasonable low values, indicating efficient nitrification and denitrification. However at the end of the MBR process an increase in the content of ammonium and nitrate is observed. This is probably due to the addition of further nutrient content, as mentioned in section 5.1. This is further discussed in chapter 8. An increase of the phosphate content is observed from the wastewater to the permeate during the entire MBR process.

Regularly during the MBR process samples from the wastewater and permeate were taken for UV-Vis measurements. A spectrum from 200 to 800 nm was measured for both the wastewater and permeate. A section of the permeate spectrum is illustrated in figure 7.1.

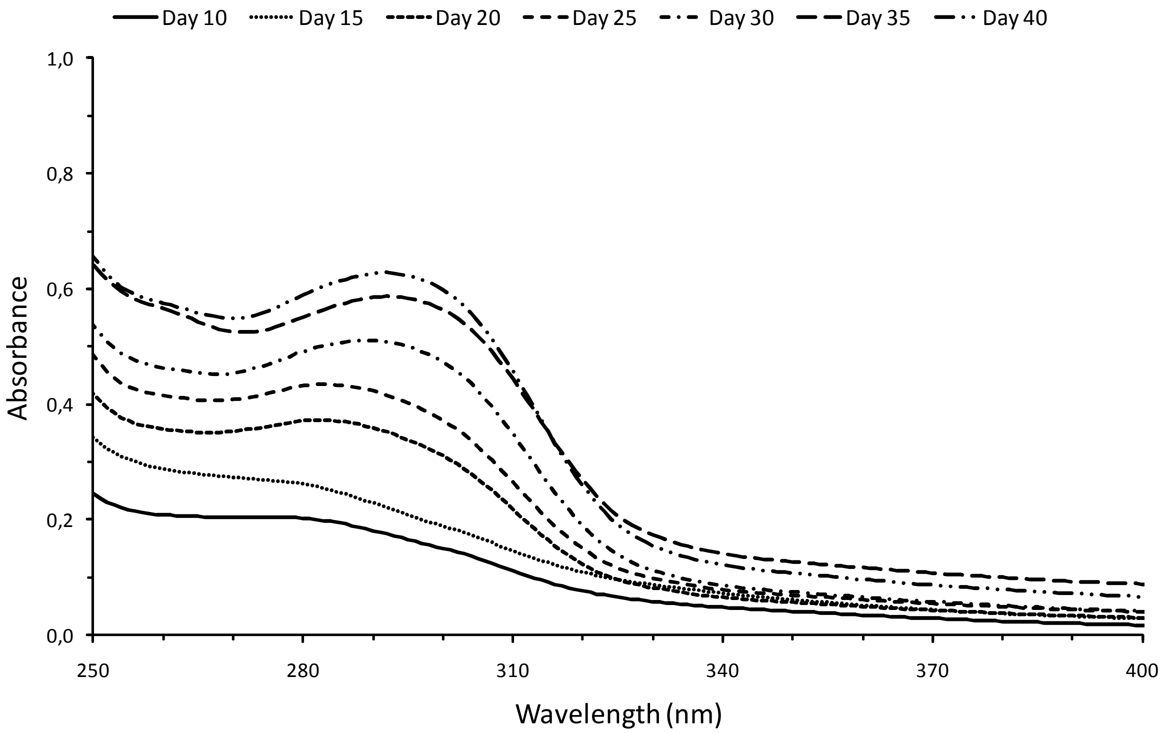

Figure 7.1: Section of the UV-Vis spectrum for selected permeate samples. The figure illustrates how the absorbance increases during the MBR process.

Figure 7.1 illustrates a section from 250 to 400 nm of the full UV-Vis spectrum for the permeate. It is illustrated how the absorbance increases during the MBR process. The same tendency is observed for the wastewater samples, which is illustrated in figure B.4 in Appendix B. The full UV-Vis spectrum for the permeate samples is likewise presented in Appendix B.

7.2 Treatment with Fenton's Reaction

For determining if treatment with Fenton's reaction effectively degrades acid dyes, two dye solutions of Nylosan Yellow E-2RL and Nylosan Red E-BL were treated with Fenton's reaction. Samples were taken during the experiments for measuring the absorbance of the dyes. The results show a significant reduction in the absorbance after treatment with Fenton's reaction. The absorbance as a function of the reaction time for both dyes is shown in figure 7.2.

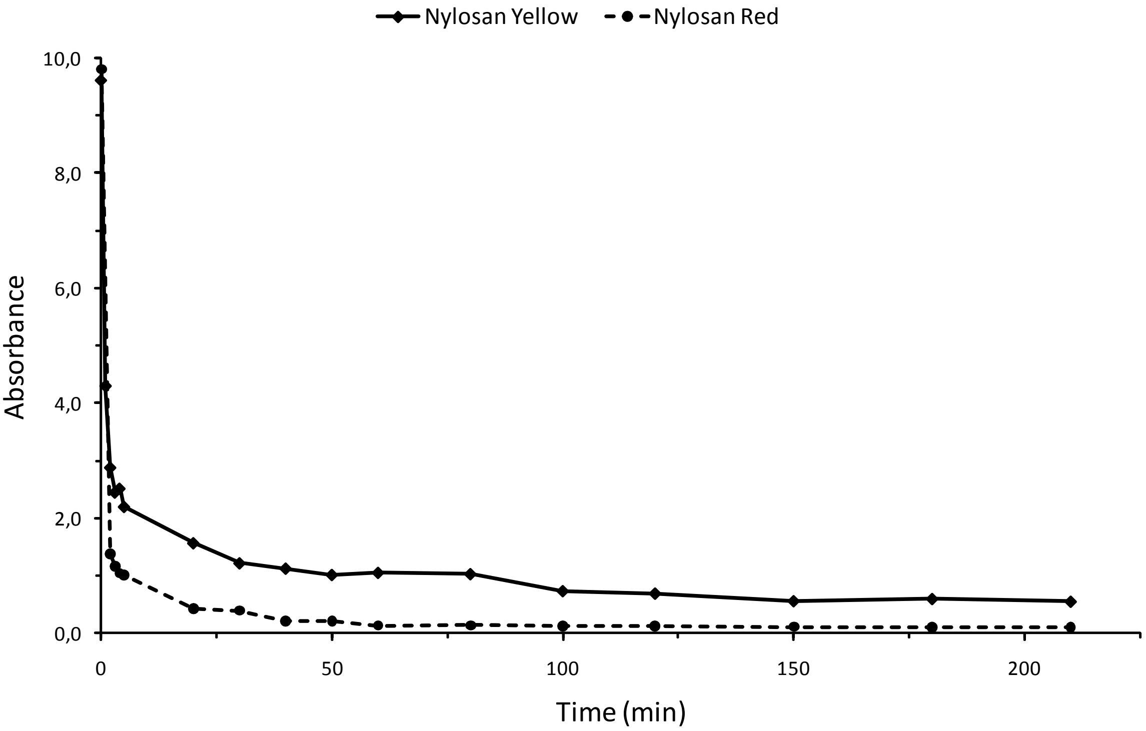

Figure 7.2: Absorbance as a function of reaction time for Nylosan Yellow E-2RL and Nylosan Red E-BL solutions treated with Fenton's reaction.

Figure 7.2 shows a significant reduction in the absorbance relatively fast. Most of the degradation of the dyes occurs during the first five minutes of the reaction, and afterwards the decrease in absorbance occurs more slowly. For both dyes the starting concentration was 10 mg/L and both experiments ended with a concentration below 1 mg/L. For Nylosan Red E-BL the concentration was even below 0.5 mg/L. For Nylosan Yellow E-2RL a degradation percent of 94 % was obtained, while for Nylosan Red E-BL a degradation percent of 98 % was obtained. This indicates that treatment with Fenton's reaction is useful for treating the wastewater and permeate.

For determination of the optimal amount of reagents and the optimal ratio (w/w) between ferrous sulfate and hydrogen peroxide a series of experiments were conducted. With these results the optimal conditions for treating the wastewater and permeate from the MBR system can be determined.

After each experiment the treated samples were analyzed with UV-Vis spectroscopy, as mentioned in section 6.4. For both the wastewater and permeate samples, it was clear that the oxidation became less effective at higher amounts of added hydrogen peroxide. This was evident at all Fe:COD ratios, indicating that no matter the iron concentration, a small ratio between iron and hydrogen peroxide is preferred. For both wastewater and permeate samples, the Fe:COD ratio of 1:10 (w/w) resulted in the best reaction efficiency. At lower doses (1:25) of iron the efficiency decreases quite significant and at higher doses (1:5) the efficiency was also lower. Comparing all the graphs together, the best result was proven to be a Fe:COD ratio of 1:10 (w/w) and a

Fe:H_2O_2 ratio of 1:5 (w/w). The UV-Vis measurements for these ratios for both wastewater and permeate are shown in figure 7.3. The results for the rest of the experiments are shown in Appendix C.

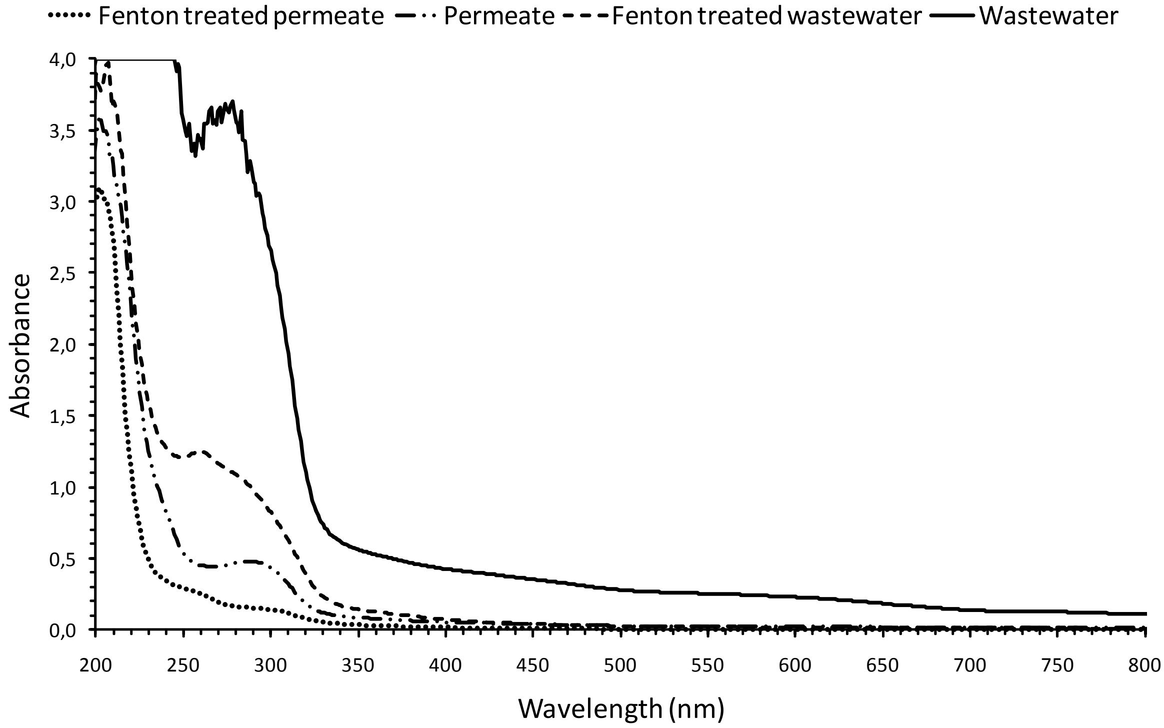

Figure 7.3: UV-Vis spectrum of the wastewater and permeate treated with Fenton's reagent with ratio 1:10 (w/w) Fe:COD and 1:5 (w/w) Fe:H_2O_2.

In figure 7.3 it is shown that the MBR treatment and treatment with Fenton's reaction both are relatively effective. Both methods show almost complete color removal in the visible spectrum from 400 to 700 nm, although the MBR treatment shows a little higher removal than the treatment with Fenton's reaction. Additional treatment with Fenton's reaction on the permeate results in a further decrease in the absorbance in the low range of the visible spectrum and in the ultraviolet range.

By studying the ultraviolet range, the difference between the samples is more obvious shown. The wastewater sample shows a significant peak around 270 nm, which has been considerably decreased in the permeate and moved to around 285 nm. In the wastewater treated with Fenton's reaction the peak is more apparent at 260 nm, but still with an indication of a peak around 270 nm. In the permeate treated with Fenton's reaction, the same tendency can be observed as in the wastewater treated with Fenton's reaction. The peaks are however significant decreased and moved slightly. A more close-up spectrum can be seen in figure 7.4.

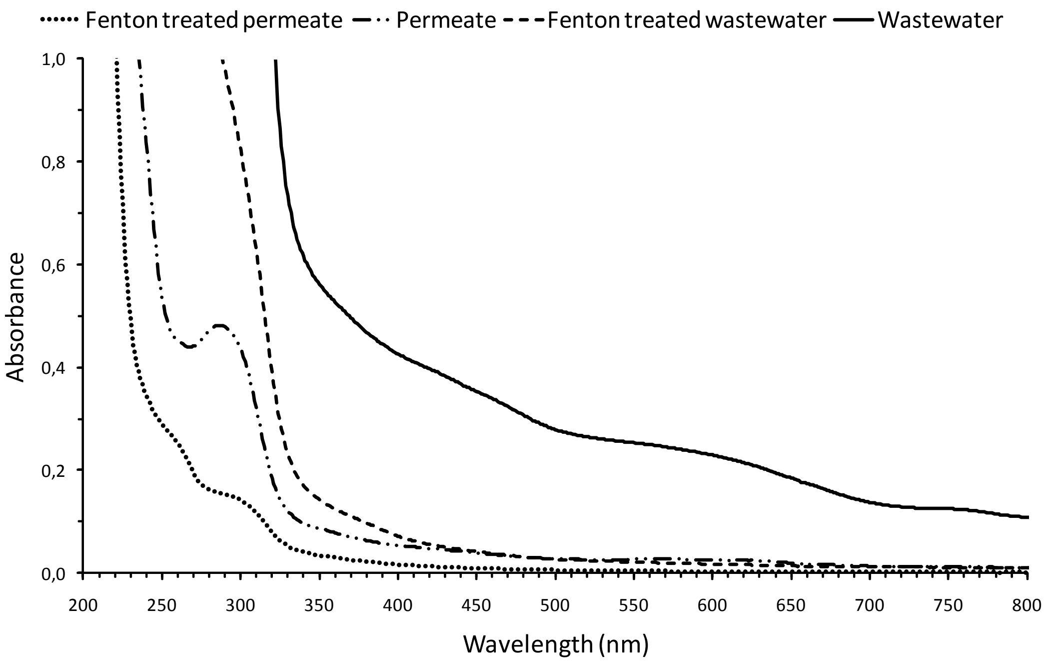

Figure 7.4: UV-Vis spectrum of the wastewater and permeate treated with Fenton's reaction with ratio 1:10 (w/w) Fe:COD and 1:5 (w/w) Fe:H_2O_2.

Figure 7.4 shows more clearly the small amount of absorbance around 390-400 nm in the wastewater treated with Fenton's reaction and permeate from MBR treatment. It is only below 400 nm that the difference between these two samples are visible, otherwise no difference in the rest of the visible spectrum is observed. The curve for permeate treated with Fenton's reaction shows a decrease in absorbance in the whole spectrum. This observed color reduction is shown in figure 7.5.

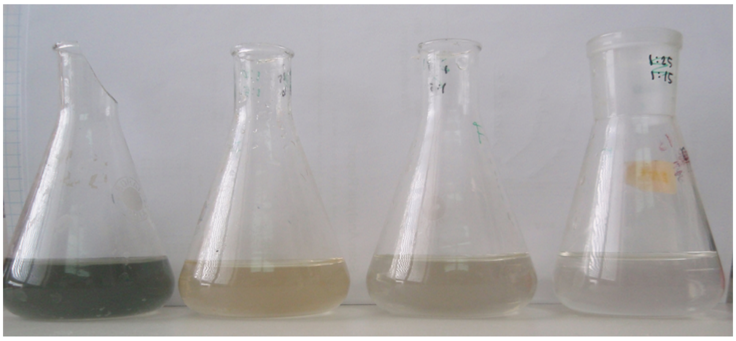

Figure 7.5: From the left: Wastewater, wastewater treated with Fenton's reaction, permeate, permeate treated with Fenton's reaction.

Figure 7.5 shows the color removal efficiency for the MBR and treatment with Fenton's reaction. The blue color from the wastewater is completely removed in both treatments, however the permeate from MBR is less yellow than the wastewater treated with Fenton's reaction. Almost complete color removal is obtained with treatment of permeate with Fenton's reaction.

Discussion 8

8.1 MBR Operation and Analytical Measurements

In figure 7.1 in section 7.1, a UV-Vis spectrum for the permeate samples is illustrated. The spectrum is shown in the range from 250 to 400 nm in order to more clearly illustrate the changes in absorbance during the MBR process. The figure illustrates how the absorbance increases during the process from day 10 to day 40. Directly this could indicate a decreasing performance and color removal efficiency, however the same tendency is observed for the wastewater. The UV-Vis spectrum for the wastewater samples taken during the MBR process is shown in figure B.4 in Appendix B. Although this tendency is not as obvious as for the permeate, the absorbance of the wastewater still has a major influence on the permeate quality. On the assumption that the biological conditions are stable during the entire MBR process, then the removal degree of color would be almost steady. This would mean that a higher absorbance in the wastewater would result in a higher absorbance in the permeate, as compared to a lower beginning absorbance in the wastewater. So the increased absorbance in the permeate can partially be explained by a varying and higher absorbance in the wastewater. However the increase can still be explained by a decrease in the performance efficiency of the MBR system, since the MBR did not operate under optimal conditions. This is discussed later in this chapter.

From the UV-Vis spectra of the wastewater and permeate shown in figure 7.3 in section 7.2, as well as from visible observation, a clear reduction in color was obtained from MBR treatment. The blue color in the wastewater is completely removed, leaving only a yellow color. It is also observed that the decrease in absorbance from wastewater to permeate is almost steady in the visible spectrum. The absorbance curve for the permeate does not change shape from the curve for the wastewater, which could indicate adsorption of the dyes to the biomass instead of biodegradation. With biodegradation of the dyes it would have been expected that the peaks would change shape, as new intermediates is created when breaking down the dye molecules. On the basis of this observation, samples from the bioreactor were studied with a microscope. With this it was possible to notice that the biomass was colored blue or surrounded by blue color both in the aerobic and anaerobic reactor. As mentioned in section 2.1 adsorption of dyes to the biomass is most likely to occur in the aerobic reactor, however this was also observed in the anaerobic reactor. This could indicate that the dyes present in the wastewater is non-biodegradable or that both biodegradation and adsorption is occuring. Even though adsorption is the primary removal mechanism in aerobic treatments, it is not all dyes that are adsorbed by activated sludge. The adsorption depends strongly on the dye structure, coloring groups and solubility. Cationic dyes have been shown to adsorb better than anionic dyes to activated sludge [38].

To obtain sufficient treatment, the operational conditions of the MBR must be optimized. An highly important parameter is the MLSS. Under normal conditions it would take the bioreactor approximately one month for the microorganisms to stabilize and adjust to the wastewater. During this period the MLSS value is typical steady around 1-2 g/L, whereafter it begins to increase before stabilizing around 10-15 g/L [39]. This is for a MBR system operating under perfect conditions, which is not valid in this thesis. Figure B.1 in Appendix B shows the change in MLSS during the MBR process. Immediately in the beginning of the process a decrease is observed in the MLSS concentration, whereafter the concentration is steady around 1-2 g/L, however slightly decreasing from 2 g/L towards 1 g/L. No increase in the MLSS is indicated during the process. This is most likely due to the high hydraulic retention time (HRT) of approximately two days. Because of limited supplies of raw wastewater, the influent to the bioreactor had to be kept at a relatively low flow, which resulted in a low COD loading. This means that the microorganisms had limited recources for feeding and cell growth, resulting in the low and decreasing MLSS concentration. The MLSS concentration in the anaerobic reactor is lower than in the aerobic reactor, which could be because anaerobic treatment is more efficient for high strength wastewater. Since the wastewater was low strength and relatively low temperature could occur, this could induce low biomass growth and growth rate, which would make it more difficult to sustain a sufficient biomass concentration. Further complications leading to a low MLSS concentration, could be because of no recirculation of the biomass from the membrane module to the bioreactor. However this is considered as not having as much an influence on the MLSS, since a decrease in MLSS in the membrane module tank also was observed, see figure B.1 in Appendix B. In order to sustain the biomass concentration in the bioreactor, 2 L of biomass was transferred manually each day from the filtration unit to the bioreactor. Furthermore a solution of glucose was added simultaneously to the bioreactor to ensure enough carbon sources for the microorganisms to feed on. It is believed this maintained the MLSS concentration at a steady level instead of further decreasing.

Despite the non optimal conditions of the MBR, efficient removal of nutrients was still achieved. As shown in table 7.1 in section 7.1 the COD removal was stable around 94 % for all measurements conducted. This indicates a stable system in the bioreactor, which further supports the discussion about the changes in absorbance, as described in the beginning of this chapter. The COD level was well below the limit of 125 mg/L as imposed by European legislation [40]. Table 7.2 in section 7.1 shows the measured concentrations of phosphate and total nitrogen in the wastewater along with phosphate, total nitrogen, ammonium, nitrate and nitrite concentrations in the permeate. An obvious tendency of increasing concentrations of phosphate, when comparing the wastewater and permeate, is observed. Biological phosphorus removal requires different operational conditions than the removal of nitrogen, i.e. high biomass yields and short sludge retention times. To effectively remove phosphate from the wastewater an anaerobic and aerobic reactor is needed. Sufficient biological phosphoruos removal in a MBR is done by poly-phosphate accumulating organisms (PAOs). PAOs require anaerobic conditions for the assimilation of organic matter, such as volatile fatty acids, with the release of phosphorus from intracellular polyphosphate granules. Then under aerobic conditions, phosphorus removed from solution by PAOs, resulting in phosphoruos-rich wastage [40] [41]. If the subsequent removal of phosphate in the aerobic reactor is not sufficient enough, this would result in an increased concentration of phosphate in the permeate. This is clearly observed in the measurements of the phosphate concentrations. So the high concentration of phosphate in the permeate is due to the release of phosphate from the sludge. This indicates that to optimize the removal of phosphate, another post-treatment must be performed.

By studying table 7.2 it is shown that an efficient removal of nitrogen was obtained. In the beginning of the MBR process, mixed results were obtained with increasing concentrations of nitrogen and nitrate in the permeate. The ammonium concentration in the wastewater was measured to be around 7 mg/L. The ammonium concentration in the permeate is measured to be below this concentration at all measurements, except during the last week of the process. The efficient removal of ammonium indicates a successful nitrification in the aerobic reactor, where ammonium is converted to nitrite and nitrate. Nitrite is effectively converted to nitrate, which the results also show, since only very small traces of nitrite are found in all the samples. In the beginning of the MBR process the microorganisms have not yet adapted to the environment, so the efficiency of the nitrification and denitrification is expected to be limited. This is as mentioned shown by the increased concentrations of nitrate, which could indicate an unefficient denitrification. In the anaerobic reactor nitrate is used in oxidizing organic carbon, however if anaerobic conditions have not been established, then a efficient denitrification can not be obtained and the nitrate can not be removed from the wastewater.

During the last week of the MBR process, a significant increase in the concentration of total nitrogen, ammonium and nitrate was observed. This is due to the addition of nutrient solution to the bioreactor. In order to maintain the growth of the microorganisms, a solution of glucose, ammonium chloride and dipotassium phosphate was added. This was done so the microorganisms would have enough carbon, nitrogen and phosphorus for cell growth and reproduction. As mentioned before this is believed to be the reason why a steady MLSS concentration was obtained. However by adding the nutrient solution, large amounts of ammonium and phosphate was added compared to the starting concentrations in the wastewater. Calculations of the nutrient solution are found on the attached CD-ROM. This means that with these much higher concentrations of nitrogen, ammonium and phosphate being added to the bioreactor, a higher concentration is expected to be present in the permeate. The microorganisms can only consume a certain amount of nutrients, which means that a larger amount of nutrients is left in the wastewater, resulting in a higher concentration in the permeate. This difference can however be neglected by describing the kinetics of the nitrification and denitrification. A range of equations and mass balances can be used to evaluate the biosystem and determine the removal efficiency of the nutrients. Thereby can the difference in concentration caused by the added nutrient solution be eliminated. This however requires, that the biokinetic constants are know for the specific system, in order to describe the efficiency of the biosystem. This was not done in this thesis, but could be of great interest in future studies.

8.2 Treatment with Fenton's Reaction

As illustrated in figure 7.2 it was possible to effectively degrade the acid dyes Nylosan Yellow and Nylosan Red. The degradation of the dyes was relatively fast and mainly occured in the first few minutes of the reaction, whereafter the degradation slowed down. This is dependent on the reagent concentrations compared to the dye concentration, which has a great influence on the reaction rate. Overall this indicates that treatment with Fenton's reaction can efficiently be used for treating textile wastewater containing acid dyes. This is further confirmed in figure 7.5 in section 7.1 which shows a clear reduction in color when treating both wastewater and permeate with Fenton's reaction. The blue color in the wastewater has been completely removed both in the wastewater and permeate treated with Fenton's reaction. This indicates a successful degradation of the dyes responsible for the blue color. However it was not possible to obtain complete color removal, when only treating the wastewater with Fenton's reaction, since a yellow color is still visible, as shown in figure 7.5. Also it is clear that the chemical treatment of the wastewater was not as efficient as the biological treatment, since the permeate from the MBR shows less coloring. It is surprising that the biological treatment shows greater effect on the color removal than the chemical treatment, since textile wastewater contains large amounts of non-biodegradable dyes, as mentioned in section 2.1. The wastewater is however of low strength due to the relatively low COD content and clarity in color compared to previously experiments with textile wastewater, and can therefore be expected to be less toxic for the microorganisms. Although as previous mentioned the high efficiency in color removal from the MBR could be because of adsorption occuring instead of biodegradation.

When studying the permeate results, from figure 7.5 in section 7.2, a complete color removal when treating the permeate with Fenton's reaction is observed. This shows that the wastewater can efficiently be further treated after the MBR treatment and treatment with Fenton's reaction as a post-treatment can improve the water quality. This is confirmed from the UV-Vis spectrum in figure 7.4 in section 7.2, where the permeate curve does not show any absorbance in the visible spectrum. It it clearly observed that the permeate treated with Fenton's reaction achieved a further decrease in absorbance and thereby a further degradation of the dyes. Also in this figure the absorbance of the wastewater can be further studied. There is indications of absorbance peaks around 440 and 590 nm, however not very significant because of the influence of the large peaks in the ultraviolet range. The peak around 590 indicates a blue color and the peak around 440 indicates a yellow color, which is still present at lower amounts after treatment. This consist with the fact that the color of the wastewater was blue, with indication of green color coming from the mixture of yellow and blue [42].

A complete indication of the dyes present in the samples is however not obtainable. The wastewater is a mixture of different dyes with unknown structures and other chemicals that has been used during the dyeing process. The dyes and chemicals used in the dyeing process is a commercial secret, so the actual chemical name and structure is not obtainable. A wide range of different types of dyes are expected to be used, so it is difficult to precisely determine the origin of the peaks in the spectrum. Especially the peaks present in the ultraviolet range are difficult to identificate, since several chromophores absorb UV radiation. However the peak around 254 nm, which is only present in the samples treated with Fenton's reaction, could be an indication of hydrogen peroxide. The main peak just below 300 nm, which is present in all samples, could be an indication of the amount of organic contaminants still present in the samples. A wide range of ultraviolet absorbing chromophores exist, of which many can be present in dye molecules and intermediates [43].

The results show that when treating raw wastewater with Fenton's reaction it was not possible to obtain the same degree of color removal as with the MBR treatment. However further treatment with Fenton's reaction of the permeate showed further color removal, resulting in an almost colorless sample. This suggest that the use of Fenton's reaction is better used as a post-treatment instead of a pre-treatment to biological treatment. However to fully compare the results it would be necessary to use wastewater treated with Fenton's reaction in a MBR system in order to see if the pre-treatment of Fenton's reaction followed by biological treatment would result in better color removal. It is however questionable if the implementation of Fenton's reaction to MBR treatment is beneficial. The pre-treatment with Fenton's reaction would mean the use of large amounts of chemicals when applied industrial, which would further result in large amounts of iron precipitate. The excess iron is removed after treatment by raising the pH and precipitate it as $Fe(OH)_3$. This would result in large amounts of precipitate that needs to be securely eliminated, which would increase the maintenance and cost significantly. Therefore a post-treatment would be preferred over a pre-treatment. However the efficiency of post-treatment with Fenton's reaction can be discussed, since the effect is not that significant as the results show. The color removal did in fact improve, but it is questionable how high a water quality is needed for the textile industry to reuse the water in the dyeing process. This must be considered by the manufacturers before a final decision can be taken, on whether a post-treatment is feasible. The extra maintenance alone can eliminate the option of using Fenton's reaction, since the whole process must be under pH-controlled conditions, which requires more maintenance and extra costs. These are the biggest disadvantages of the Fenton's reaction, so comparing the obtained results and the disadvantages of the process, it is questionable that the use of Fenton's reaction in practice can be implemented.

8.3 Alternative Choices of AOP

Instead of using Fenton's reaction as treatment several other AOPs can be used, as previous mentioned in section 3.2. These processes includes H_2O_2/O_3, H_2O_2/UV and O_3/UV. The advantages of Fenton's reaction compared to the other processes, is its low energy demand and the use of relatively low cost chemicals. Previous studies have shown that color removal efficiency with Fenton's reaction can be achieved just as high as processes including H_2O_2/O_3, H_2O_2/UV and O_3/UV. In some studies an even higher removal efficiency, but also lower removal efficiencies have been shown [37] [44] [45]. However, as described previously, several disadvantages with the Fenton's reaction exist and highly influence the use of the process in practice. Whereas treatments with ozone and UV are already more tested in full scale [22] [46]. The advantages and disadvantages of H_2O_2/O_3, H_2O_2/UV and O_3/UV processes are listed in table 8.1 along with a brief description of the process.

Table 8.1: Brief description, advantages and disadvantages of different AOP technologies [22].

AOP Technology	Description	Advantage	Disadvantage
H_2O_2/O_3	O_3 and H_2O_2 react to form hydroxyl radicals in aqueous solution.	More effective than O_3 and H_2O_2 alone. An already established technology.	May require ozone off-gas treatment. Higher costs.
O_3/UV	Hydroxyl radicals are generated when UV light is applied to ozonated water.	More efficient at generating hydroxyl radicals than H_2O_2/UV processes.	Energy and cost intensive process. Turbidity can interfere with UV light. May require ozone off-gas treatment.
H_2O_2/UV	Direct photochemical cleavage of H_2O_2 generates hydroxyl radicals.	An already established technology. No off-gas treatment required. Not limited by mass transfer relative to O_3 processes	Energy and cost intensive process. Turbidity can interfere with UV light.

As with the Fenton's reaction, several studies have already shown that with treatments including H_2O_2/O_3, H_2O_2/UV or O_3/UV it is possible to obtain COD and color removal over 90 % [37] [47]. According to Melin et al. [22] the treatment with O_3/UV or H_2O_2/UV have a higher efficiency than treatment with H_2O_2/O_3 or Fenton's reaction, which is because of the UV light. Several other studies have proven that when applying UV light to treatments with either ozone, hydrogen peroxide or Fenton's reaction, the efficiency in color removal increases significant [37] [44]. However treatments including UV light are more influenced by the wastewater quality, since the UV light can be highly affected by high turbidity in the wastewater and thereby decreasing the process efficiency. Also the possibility of components in the wastewater absorbing the UV light can be relatively high, for example nitrates and UV light absorbing chromophores from dyes [22] [48].

Other disadvantages with ozone and UV involving processes is the cost of the equipment and processes. For ozone treatments an off-gas treatment system would be required, since there are strict laws for releasing ozone into the atmosphere, which would further increase the maintenance cost. For both treatments with ozone and/or UV the operational cost would increase, when installing the equipment for the processes. However compared to treatment with Fenton's reaction, which deals with less expensive chemicals and equipment, the treatment with H_2O_2/O_3, H_2O_2/UV or O_3/UV would still be preferred. The processes are close to being equally efficient and advantages and disadvantages can be named for all processes However treatments with ozone and UV are more widely tested in both lab scale and full scale. The Fenton's reaction suffers especially from the pH adjustment and large amounts of iron sludge that needs to be disposed, which increases the maintainance severely.

Conclusion 9

The aim of this thesis was to treat textile wastewater with MBR treatment and improve the effluent quality by further treatment with Fenton's reaction. This was successfully achieved and the conclusion is as following:

On the basis of the results obtained in this thesis, it is concluded that MBR treatment is an efficient method for treating textile wastewater with focus on removing the color. In this study, textile wastewater was efficiently decolorized through biological treatment and membrane filtration. The biological treatment efficiently decreased the content of COD, total nitrogen, ammonium, nitrate and nitrite in the wastewater and an approved effluent quality was obtained. The results however showed that improvements can still be made with respect to the content of phosphate in the effluent. Even though the bioreactor was constructed to obtain optimal removal of phosphate, higher concentrations were still obtained in the effluent. On the basis of this, it it concluded that further phosphate removal treatments can be necessary.

Furthermore the treatment with Fenton's reaction was performed on the wastewater and permeate from the MBR system. The results showed that it was possible to obtain an efficient color removal in both the wastewater and permeate. The treatment with Fenton's reaction on the wastewater showed less efficient color removal than the MBR treatment, while the treatment of permeate from the MBR system showed improved effluent quality. On the basis of these results it is concluded that post-treatment with Fenton's reagent is more desirable than pre-treatment of the wastewater. However it is necessary to further test the use of Fenton's reaction as a pre-treatment for obtaining a definite conclusion.

Even though post-treatment with Fenton's reaction is concluded as being efficient, it is still concluded that further improvements of the treatment must be made, before the treatment with Fenton's reaction is sustainable. The maintenance is still too high compared to other Advanced Oxidation Processes. Processes including ozone and UV treatment is far more desirable because of their easier implementation into the industrial sector. The use of these processes is already being implemented, while the treatment with Fenton's reaction needs further investigation before it can be sustainable.

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Chemicals and Apparatus A

Chemicals

Iron(II) sulfate heptahydrate
$FeSO_4 \cdot 7H_2O$
Producer: Fluka Chemika
Cas: 7782-63-0
Assay: >99.5 %
Batch No: 326730/1 993

Hydrogen peroxide
H_2O_2
Producer: Sigma-Aldrich
Cas: 7722-84-1

Sulfuric acid
H_2SO_4
Producer: Panreac Quimica
Cas: 7664-93-9
Assay: 93-98 %

Sodium hydroxide
NaOH
Producer: Sigma-Aldrich
Cas: 1310-73-2

Ammonium chloride
NH_4Cl
Producer: Fluka Chemika
Cas: 12125-02-0

Dipotassium phosphate
K_2HPO_4
Producer: Kemika
Cas: 7758-11-4

Apparatus

Spectrophotometer
Model: HACH LANGE DR 2800
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany
SRN: 1233542

Spectrophotometer
Model: Agilent 8453 UV-Vis
Producer: Agilent Technologies
Origin: Germany

Heater
Model: HACH LANGE LT 200
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany
SRN: 1234034

pH-meter and DO-meter
Model: inoLab Multi 720
Producer: WTW
Origin: Germany
SRN: 10350609

Filter paper
Model: MN 614
Producer: Macherey-Nagel GmbH
Origin: Düren, Germany
Type: Fast filtration

HACH LANGE Cuvette Tests

COD cuvette test
Product code: LCK 314 COD
Range: 15-150 mg/l O_2
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany

COD cuvette test
Product code: LCK 514 COD
Range: 100-2000 mg/l O_2
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany

Ammonium cuvette test
Product code: LCK 305 Ammonium
Range: 1.0-12 mg/l NH_4-N
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany

Nitrate cuvette test
Product code: LCK 340 Nitrate
Range: 5.0-35 mg/l NO_3-N
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany

Nitrite cuvette test
Product code: LCK 342 Nitrite
Range: 0.6-6.0 mg/l NO_2-N
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany

Phosphate cuvette test
Product code: LCK 348 Phosphate
Range: 0.5-5.0 mg/l PO_4-P
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany

Total nitrogen cuvette test
Product code: LCK 138 LatoN
Range: 1-16 mg/l TN
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany

Total nitrogen cuvette test
Product code: LCK 338 LatoN
Range: 20-100 mg/l TN
Producer: HACH LANGE GmbH
Origin: Düsseldorf, Germany

MBR Operational Conditions B

MLSS Results

Every second day during the MBR process the MLSS value was determined for the aerobic reactor, anaerobic reactor and the membrane unit tank. Figure B.1 shows the change in MLSS as a function of time:

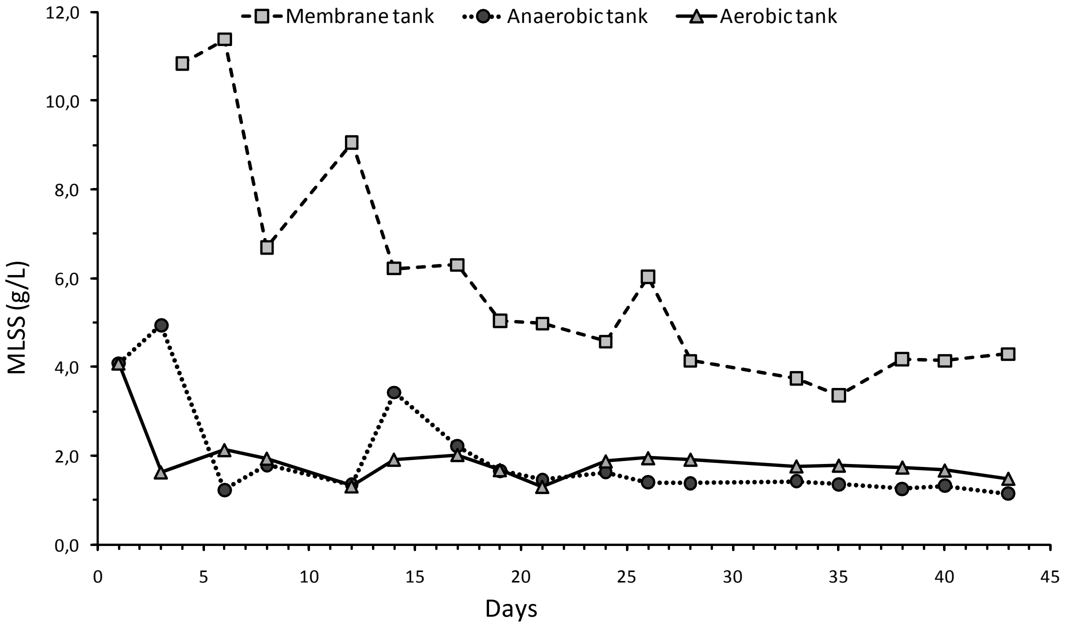

Figure B.1: MLSS change over time for the aerobic reactor, anaerobic reactor and membrane unit tank.

MLSS is observed to be steady over time both in the aerobic and anaerobic reactor, but a small descrease is observed. In the membrane unit tank a obvious decrease in MLSS is observed. This is directly opposite the expected tendency, which is an increase in MLSS [7].

Dissolved Oxygen Results

Every day during the MBR process the DO level was measured in the aerobic and anaerobic reactor. The measurements were conducted three times every day in order to observe the change in DO more specific. The change in DO as a function of time is presented in figure B.2:

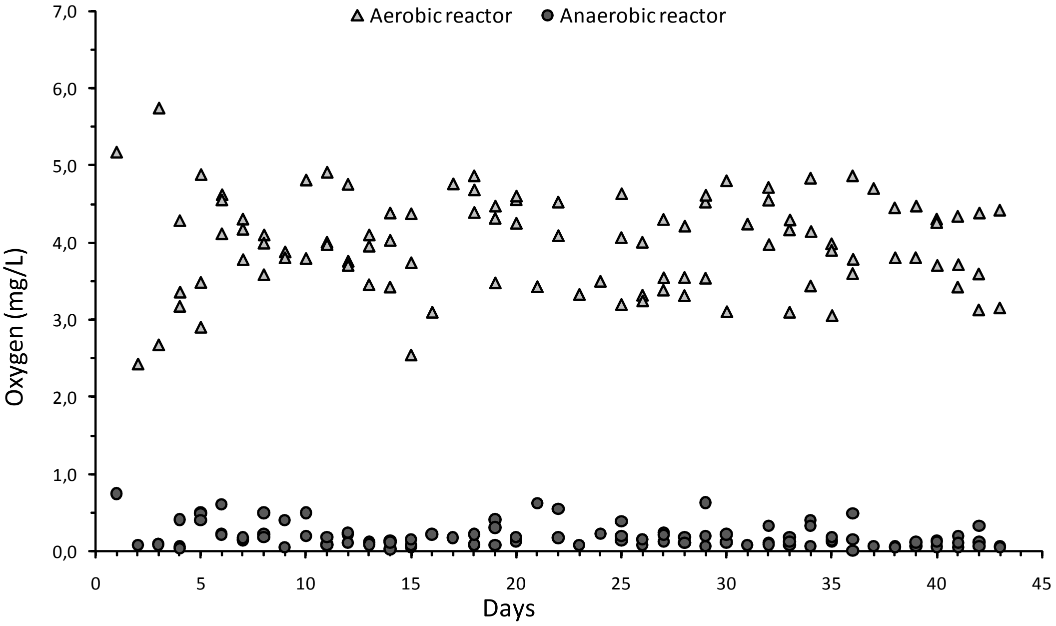

Figure B.2: DO change over time for the aerobic reactor and anaerobic reactor.

An adequate level of DO must be kept in the aerobic reactor for the nitrification process to take place properly. According to literature the DO level must be above 2 mg/L for this to happen. Meanwhile the DO level in the anaerobic reactor must be below 1 mg/L, since the presence of oxygen is an obstacle for the denitrification.

From figure B.2 it can be concluded that the right operational conditions have been present for the microorganisms. The aerobic reactor had a DO level between 3 and 5 mg/L, while in the anaerobic reactor the DO level was mostly kept below 0.5 mg/L.

pH Results

Every day during the MBR process the pH level was measured in the aerobic reactor, anaerobic reactor and permeate. The change in pH as a function of time is presented in figure B.3:

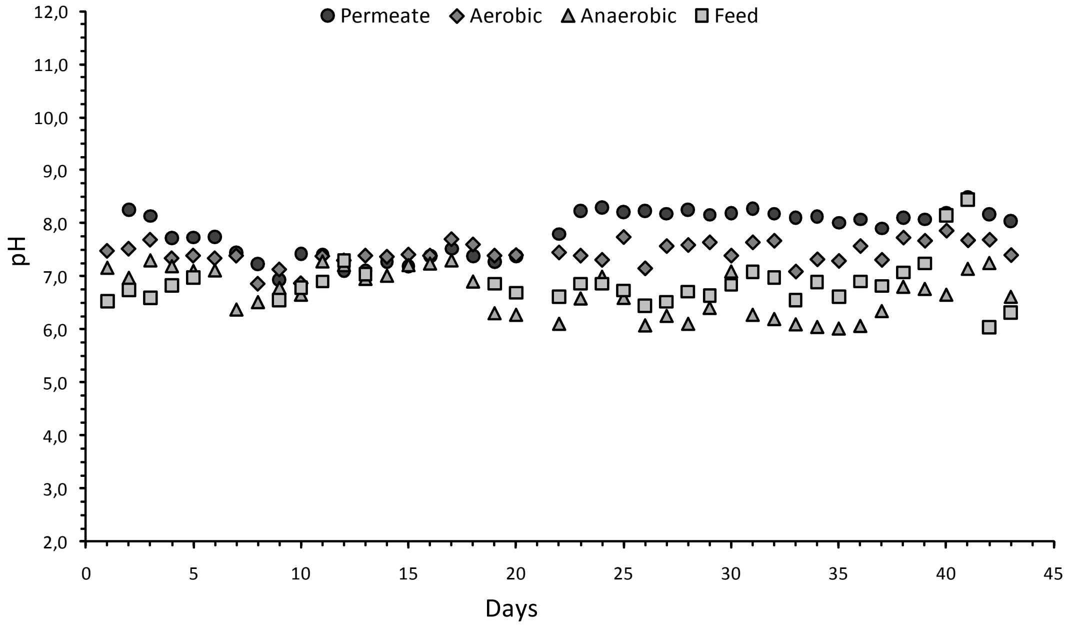

Figure B.3: Change in pH in the aerobic and anaerobic reactor, feed and permeate.

Figure B.3 shows that the pH for the wastewater (feed) change around pH 6-7 with a short increase in the end of the MBR process. In the first half of the operation periode, the pH levels were almost at the same level in both the aerobic and anaerobic reactor and in the permeate. After this the pH levels became quite different. The anaerobic reactor had generally a pH level lower than the aerobic reactor around pH 6, whereas the pH level in the aerobic reactor was steady just above pH 7. The permeate had the highest pH level around 8 with almost little change in the pH level.

UV-Vis Measurements

The following figures present the UV-Vis results for wastewater and permeate. The first and last measurements are marked on the graphs. The results can also be found on the CD-ROM.

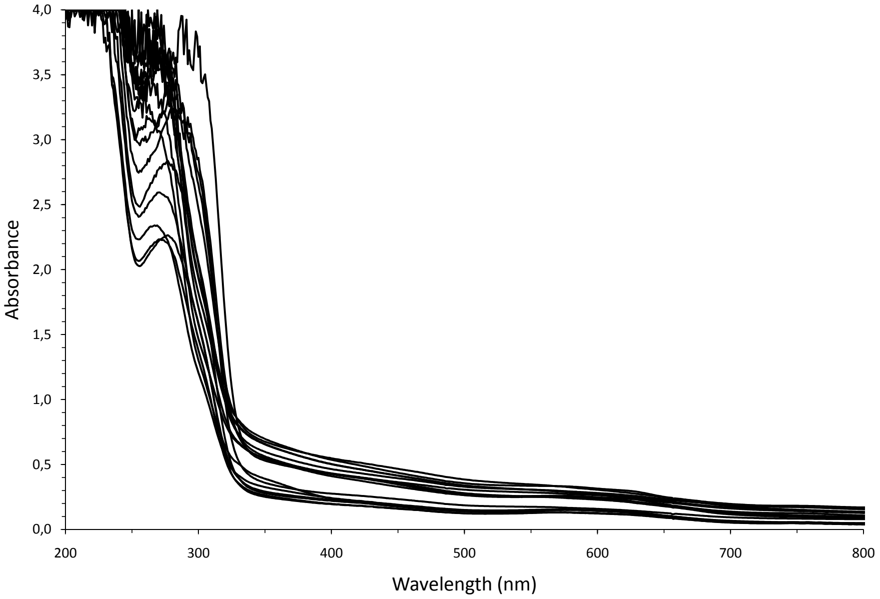

Figure B.4: UV-Vis spectrum of wastewater samples during the MBR process.

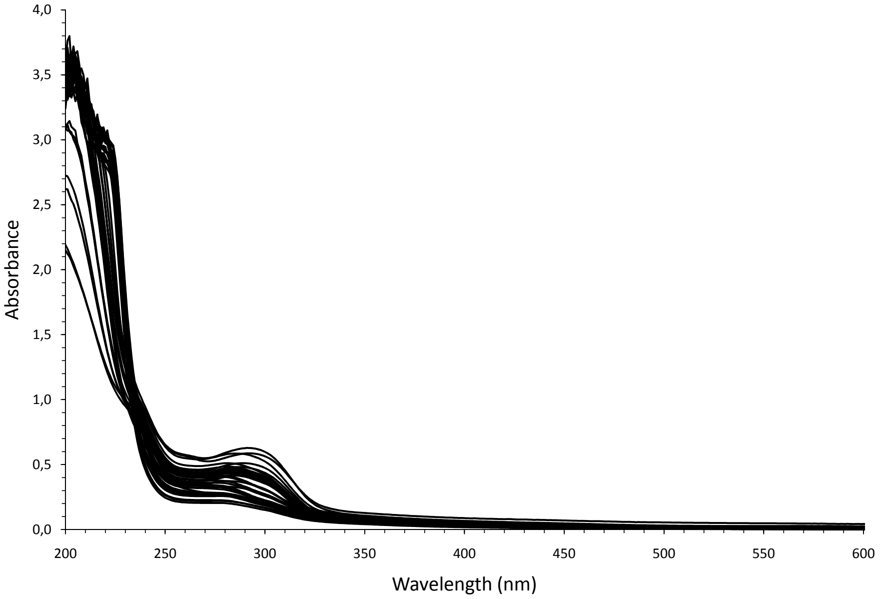

Figure B.5: UV-Vis spectrum of permeate samples during the MBR process.

Fenton's Reaction Results C

The following figures present the results obtained from treating raw wastewater with Fenton's reagent using different amounts of reagents and different Fe:H_2O_2 ratios.

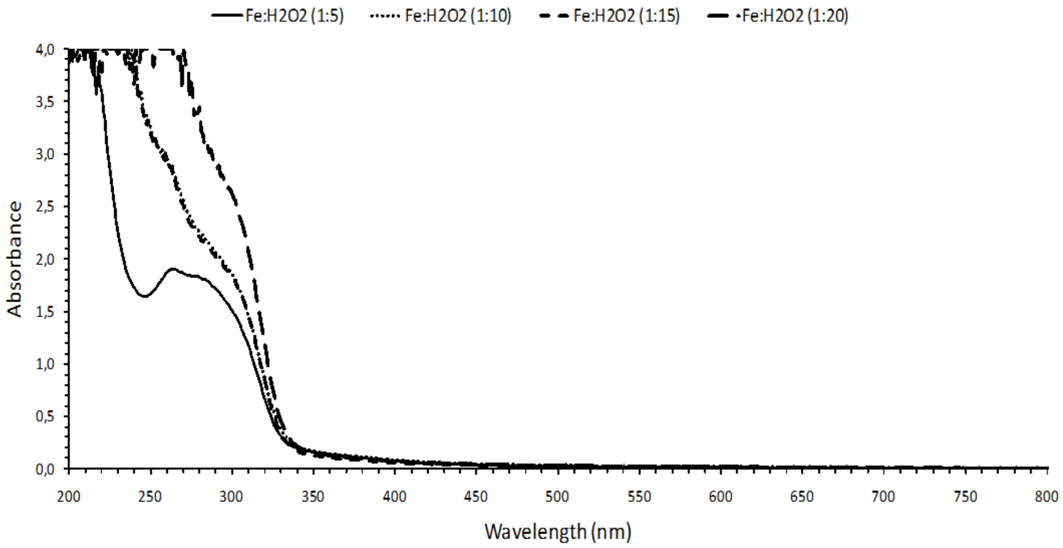

Figure C.1: UV-Vis spectrum of wastewater treated with Fenton's reagent with ratio 1:5 (w/w) Fe:COD.

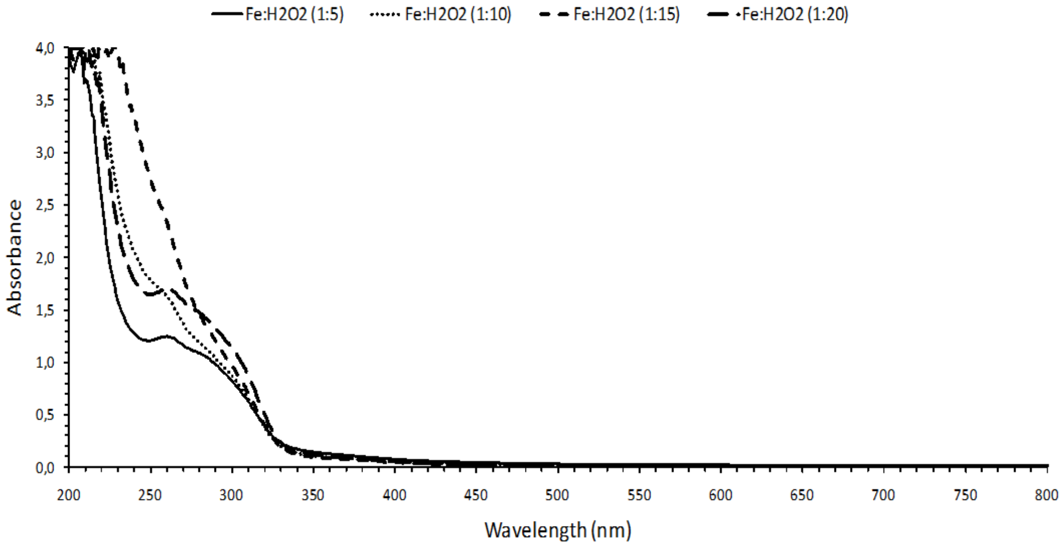

Figure C.2: UV-Vis spectrum of wastewater treated with Fenton's reagent with ratio 1:10 (w/w) Fe:COD.

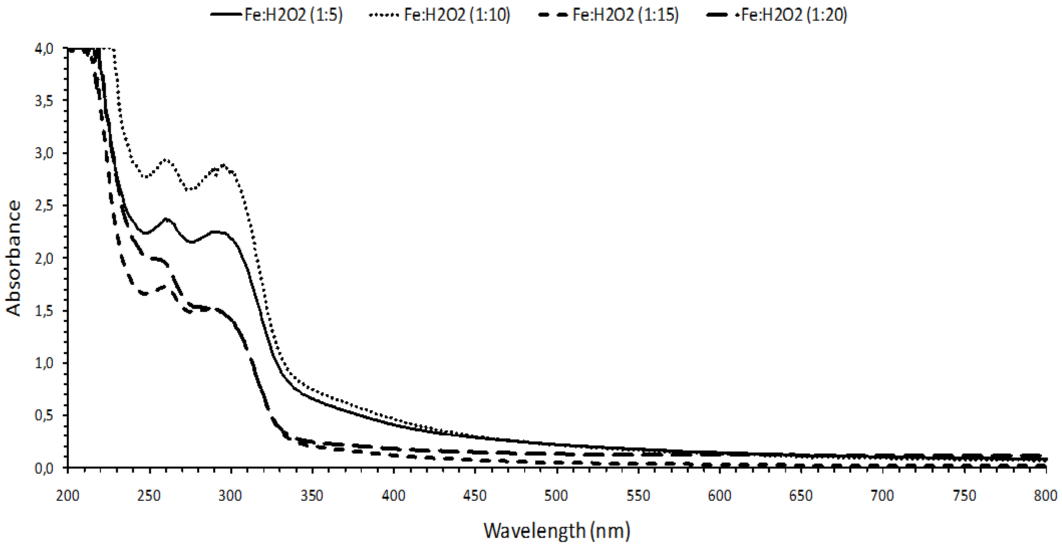

Figure C.3: UV-Vis spectrum of wastewater treated with Fenton's reagent with ratio 1:25 (w/w) Fe:COD.

The following figures present the results obtained from treating the permeate with Fenton's reagent using different amounts of reagents and different Fe:H_2O_2 ratios.

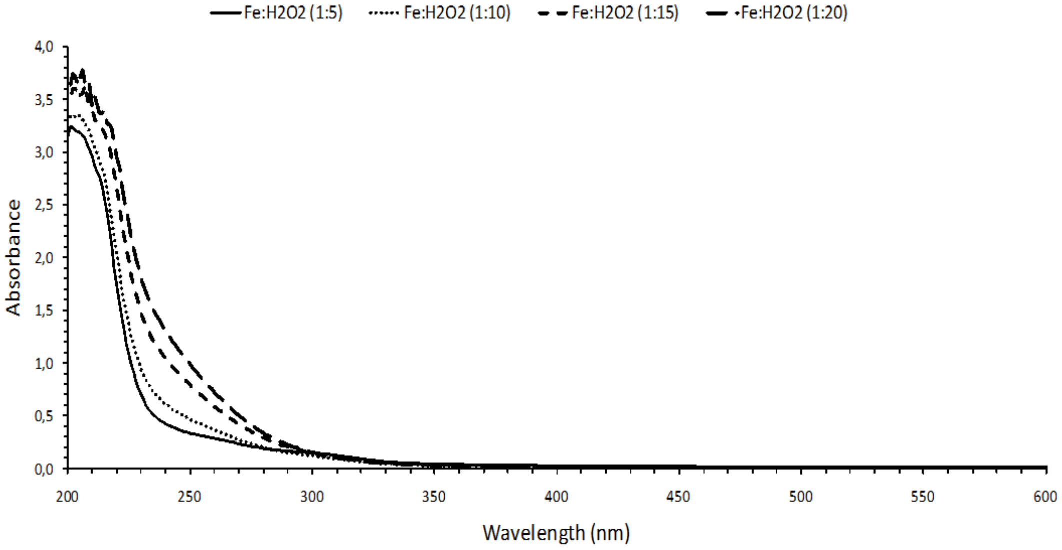

Figure C.4: UV-Vis spectrum of permeate treated with Fenton's reagent with ratio 1:5 (w/w) Fe:COD.

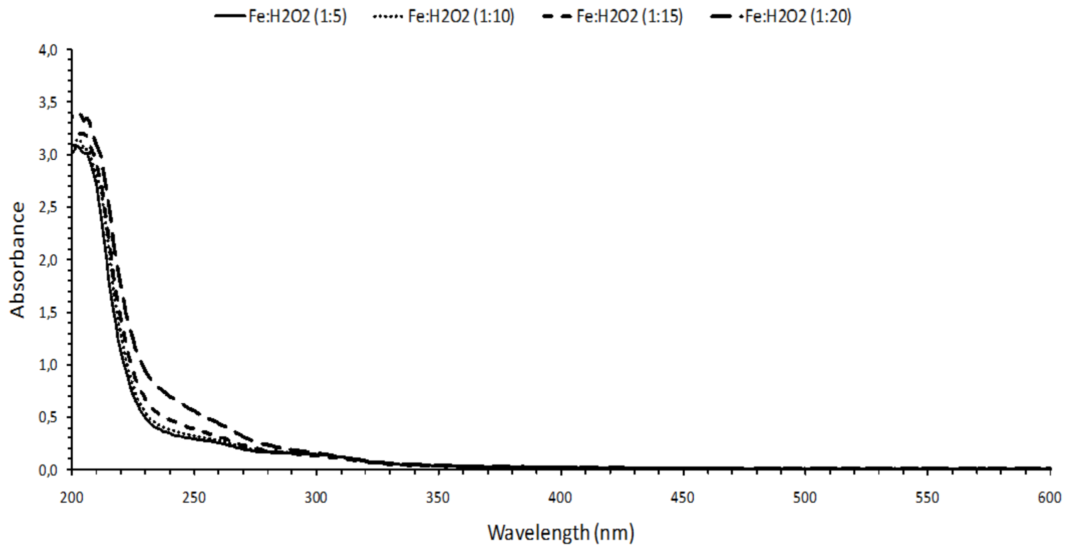

Figure C.5: UV-Vis spectrum of permeate treated with Fenton's reagent with ratio 1:10 (w/w) Fe:COD.

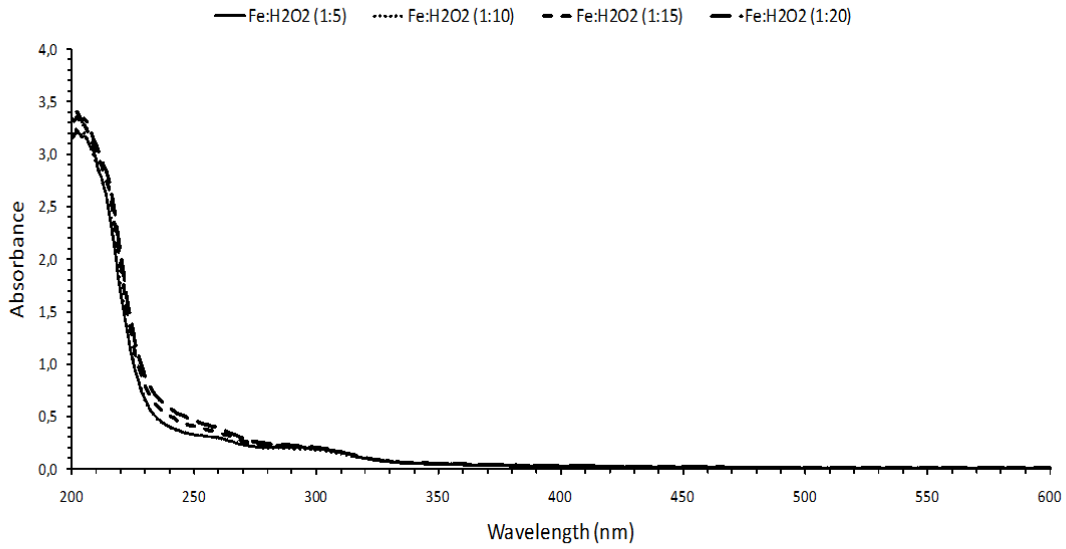

Figure C.6: UV-Vis spectrum of permeate treated with Fenton's reagent with ratio 1:25 (w/w) Fe:COD.