Treatment of wastewater generated by wood-based dry industries: advanced oxidation processes and electrocoagulation

Henrik Hansson

Abstract

Hansson, Henrik (2014) *Treatment of wastewater generated by wood-based dry industries: advanced oxidation processes and electrocoagulation*, Linnaeus University Dissertations No 186/2014, ISBN: 978-91-87925-11-5. Written in English.

Wood is a material with an enormous number of applications. For decades, the development of wastewater treatment technologies tailored for the wood sector has focused on those industries that have water as an integral part of the industrial production, such as paper and pulp. However, there is a large and potentially growing sector that has been neglected, which is formed by industries in which water is not part of their production line, as for example, the wood floor and furniture industries (named wood-based dry industries). These industries still produces relatively low volumes of highly polluted wastewaters, with COD up to 30,000 mg/L, due to cleaning/washing procedure (named cleaning wastewaters). These cleaning wastewaters are often sent to the municipal wastewater treatment plant after dilution with potable water. Once there, recalcitrant pollutants are diluted and discharged into recipient water bodies or trapped in the municipal wastewater sludge. Another type of contaminated water these "dry industries" often generate in high volumes, and which is usually discharged with no previous treatment, is storm-water containing contaminants that have leached from large wood storage areas. The overall aim of this thesis was to increase the level of knowledge and competence and to present on-site wastewater treatment options for wood-based dry industries using the wood floor industry as a case-study, with a focus on combined treatment methods and solutions applicable to both the cleaning wastewater and storm-water. Among the treatment technologies investigated, electrocoagulation was studied both as a standalone treatment and combined with sorption using activated carbon. The combined treatment achieved a COD reduction of approximately 70%. Some advanced oxidation processes (AOP) were also studied: a COD reduction of approximately 70% was achieved by photo-Fenton, but the most successful AOP was ozone combined with UV light, were a COD reduction around 90% was achieved, with additional improvement in the biodegradability of the treated effluent. Ozone also proved to be effective in degrading organic compounds (approximately 70% COD reduction) and enhanced the biodegradability of the storm-water runoff from wood storage areas. The results have shown that the application of ozone can be considered an option for treatment of cleaning wastewaters and possibly for storm-water biodegradation enhancement.

Keywords: Advanced oxidation processes; Electrocoagulation; Fenton; Industrial storm-water; Ozone; Respirometry assays; Wastewater; Wood floor industry.

Svensk sammanfattning

Trä är ett material med ett stort antal möjliga användningsområden. Inom träindustrin har utvecklingen av vattenbehandlingsmetoder varit inriktat på de branscher som har vatten som en del av produktionen, såsom papper- och massaindustrin. Men det finns en stor och potentiellt växande sektor inom träindustrin som har försummats, den utgörs av industrier som inte har vatten som en del av produktionen, t.ex. trägolv och trämöbel industrier. Trots detta så producerar dessa industrier fortfarande relativt kraftigt förorenade avloppsvatten med t.ex. COD-värden upp till 30000 mg/l men i relativt låga volymer. Dessa avloppsvatten uppkommer vid rengöring av maskiner och städning av lokaler, varefter de oftast efter utspädning med dricksvatten skickas till det kommunala reningsverket. Väl där späds det förorenade vattnet vidare ut med annat inkommande vatten men passerar dock till stor del obehandlat och släpps ut i mottagande vattendrag eller så fastnar föroreningarna i avloppsslamet. Dagvatten är en annan typ av förorenat vatten från dessa "torra industrier" som ofta genereras i stora volymer och innehåller föroreningar som lakats från de trämaterial som förvaras i de stora upplag som ofta förekommer vid denna typ av industrier. Det övergripande syftet med avhandlingen var att öka kunskapen och kompetensen för att kunna miljömässigt riktigt och ekonomiskt billigt behandla industriavloppsvatten lokalt på plats inom trävaruindustrin, genom att använda en trä-golvsindustri som fallstudie. Fokus lades på kombinerade behandlingsmetoder och lösningar som skulle kunna vara lämpliga både för industriavloppsvatten och dagvatten. Ett antal behandlingstekniker har undersökts; elektrokoagulering studerades både som en fristående behandling och i kombination med aktivt kol. Den kombinerade behandlingen gav en COD-reduktion på ungefär 70 %. Flera avancerade oxidationsprocesser (AOP) studerades också, och en COD-reduktion på cirka 70% uppnåddes med en kombination av UV-ljus och Fenton behandling. Den mest framgångsrika behandlingen var ozon i kombination med UV-ljus där en COD-reduktion runt 90 % uppnåddes varvid en avsevärd förbättring av den biologisk nedbrytbarhet på det behandlade avloppsvattenet erhölls. Ozon visade sig också vara effektivt för nedbrytning av organiska föreningar (ca 70% COD reduktion) och förbättrade den biologiska nedbrytbarheten av föroreningarna i dagvattnet från den studerade industrin. Resultaten har visat att ozon kan anses vara ett lämpligt alternativ för att behandla industriavloppsvatten inom trävarusektorn och möjligen för att öka den biologiska nedbrytbarheten av dagvattnet från dessa industrier.

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PREFACE

Wood is a material with a very diverse range of uses. It is also a material that is having a revival as structural bundling material for houses; not only single- and two-storey houses, but skyscrapers made of wood are built, such as a 10-storey building in London in 2009 and an 8-storey building finished in 2013 in Stockholm. About 4,000 apartments in wood high-rise buildings are planned in Stockholm. Meanwhile, this type of innovative construction is funded by numerous sources, including the government of the USA. However, for these types of novel buildings, the good old-fashioned timber beam is not sufficient. Instead, innovative glued mass timber panels are used. These new products, together with well-established uses for glued wood products, such as wood floors and wood furniture, enable the existence of a growing industry, which produces low volumes of highly contaminated wastewater. This type of industrial wastewater has for a long time been neglected.

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In addition, these types of wood-based industries often store large amounts of wood outdoors, which in contact with rainfall generate large volumes of polluted storm-water and wood leachate. The present thesis investigated treatment options for the wastewater and storm-water generated by these wood-based industries.

LIST OF PUBLICATIONS

I.   **Hansson H.**, Marques M., Laohaprapanon S., Hogland, W., 2013. Electrocoagulation coupled to activated carbon sorption/filtration for treatment of cleaning wastewaters from wood-based industry. Desalination and Water Treatment, doi: 10.1080/19443994.2013.808582.

II.   **Hansson H.**, Kaczala F., Marques M., Hogland, W., 2014. Photo-Fenton and Fenton oxidation of recalcitrant wastewater from the wooden floor industry. Water Environment Research, *Accepted.*

III. **Hansson H.**, Kaczala F., Marques M., Hogland, W., 2012. Photo-Fenton and Fenton oxidation of recalcitrant industrial wastewater using nanoscale zero-valent iron. International Journal of Photoenergy, doi: 10.1155/2012/531076.

IV. **Hansson H**., Kaczala F., Alexandre A., Marques M., Hogland, W. Advanced oxidation treatment of recalcitrant wastewater from a wood-based industry: a comparative study of O_3 and O_3/UV. *Submitted*

V. Svensson H., **Hansson H**., Hogland, W., 2014. Combined ozone and biological treatment of oak wood leachate. CLEAN – Soil, Air, Water. doi: 10.1002/clen.201400141

Related Publications

VI. Svensson H., **Hansson H**., Hogland, W., 2014. Determination of Nutrient Deficiency in Stormwater from the Wood Industry for Biological Treatment. CLEAN –Soil, Air, Water, doi: 10.1002/clen.201300621.

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Contribution of the author to the papers

Paper I: The author was responsible for the experimental design together with the supervisors. The author carried out the EC parts of the laboratory experiments and Dr Laohaprapanon conducted the activated carbon experiments. Data interpretation and writing was shared with the co-authors.

Paper II-III: The author was responsible for the experimental design together with the supervisors. The author carried out all the laboratory experiments. Data interpretation and writing was shared with the co-authors.

Paper IV: The author was responsible for the experimental design together with supervisor and the MSc student Alexandre Amaro. Mr Amaro conducted the treatability experiments and the author conducted the respirometry assays. Data interpretation and writing was shared with the co-authors.

Paper V. The author and Dr Svensson shared all work in the paper.

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ACKNOWLEDGEMENTS

The one thing I was sure of when I started my MSc studies was that I did not want to continue with PhD studies, so I want to thank my supervisors Professor William Hogland and Professor Marcia Marques, because without them, I would never have decided to develop the present thesis.

Besides my supervisors, during all my years in Kalmar, one more person has always been available to help me both in the lab and in the field; he has always been available to discuss whatever has been on my mind, something that is often necessary during PhD studies. Because of this, I would like to thank Henric Svensson, my colleague and friend, for everything.

Furthermore, I want to thank Fabio Kaczala and Sawanya Laophaprapanon for all the help in producing and interpreting data, making it appropriate for publication, Alexandre Amaro for the countless hours running the ozone equipment in the basement lab, Åke Erlandsson for making it possible to translate our combined ideas into full-scale working machines, Joacim Rosenlund for input on the small but important details of this

ABBREVIATIONS

AC   Activated Carbon

AOP   Advanced Oxidation Process

AOS   Average Oxidation State

BOD_5 Biochemical Oxygen Demand (5 days)

COD   Chemical Oxygen Demand

EC   ElectroCoagulation

MWWTP   Municipal Wastewater Treatment Plant

nZVI   Nano scale ZeroValent Iron powder

·OH   Hydroxyl radical

O_3/pH_{low} Ozone treatment at acid pH

O_3/pH_{adj} Ozone treatment at adjusted pH

O_3/UV Ozone treatment at adjusted pH with UV light

OUR   Oxygen Uptake Rate

pH_0 Initial pH

PP   Poly-Phenols

TOC   Total Organic Carbon

W/W   Weight/Weight

x

1. INTRODUCTION

1.1 Overview of the thesis

This thesis investigated an integrated approach to industrial wastewater management within the wood-based industries, which often do not have water as part of their production process (named wood-based dry industries), even though these industries produce highly polluted wastewaters (named cleaning wastewaters) in relatively low volumes with COD values of up to 30,000 mg/L, because of cleaning/washing procedures. The waters are often from multiple sources, and a viable management option would need to integrate multiple wastewaters into a single system. These types of industries also often create high volumes of storm-water because large areas are used for storage of wood and wood residuals; a secondary integration would be to integrate the management of these two very different water types.

From 2009 to 2014, the author worked as a member of the Environmental Science and Engineering Group (ESEG) of Linnaeus University on two R&D projects entitled "Development of an Integrated Approach from Industrial Wastewater and Stormwater Management in the Wood-Industry Sector" (with support from KK-Stiftelsen) and "Triple Helix Collaboration on Industrial Water Conservation in Småland and the Islands" (with support from the Knowledge Foundation and the European Regional Development Fund). The aims of the first project were to provide scientific knowledge and develop technical and sustainable solutions for water pollution control in the wood-floor industries and wood supply chains in order to minimize the impact of their activities on the environment. These aims were expanded with the

second project to also include a Triple Helix platform including a laboratory, a pilot, and demonstration and full-scale treatment plants. To achieve these objectives, six PhD students were involved in both projects. Previous work (Figure 1) in the project has included the physico-chemical characterization and initial treatability studies for both the storm-water and cleaning wastewater and were addressed by Kaczala (2011). Svensson (2014) studied toxicity and treatment options for storm and irrigation water. The cleaning wastewaters were studied by Laohaprapanon (2013), when the main focus was the characterization and treatment based on biological and adsorption processes. Joacim Rosenlund is currently studying inter sector environmental collaboration (Figure 1).

The project seeks co-production through cooperation between academia (Linnaeus University) and the industrial sector, including three industries that take part in the wood-floor production process (AB Gustaf Kähr, AkzoNobel, and Becker Acroma), a company that produces energy from wood waste (Kalmar Energi Värme AB), and a company that develops treatment plants for different kinds of wastewater (Revatec AB). AB Gustaf Kähr, a wood-floor industry in Nybro, Sweden, was used as a case study throughout both projects.

In the present thesis, the investigation focused first on single and combined treatment options for cleaning wastewaters, and second on the treatment of storm-water generated by the wood-floor industry.

A combination of treatments is essential for these types of wastewaters because finding a single treatment that could achieve pollutants reduction sufficiently well to make the wastewater safe for discharge is unlikely.

The treatment options investigated were mostly based on chemical processes, combined with biological treatment in some cases.
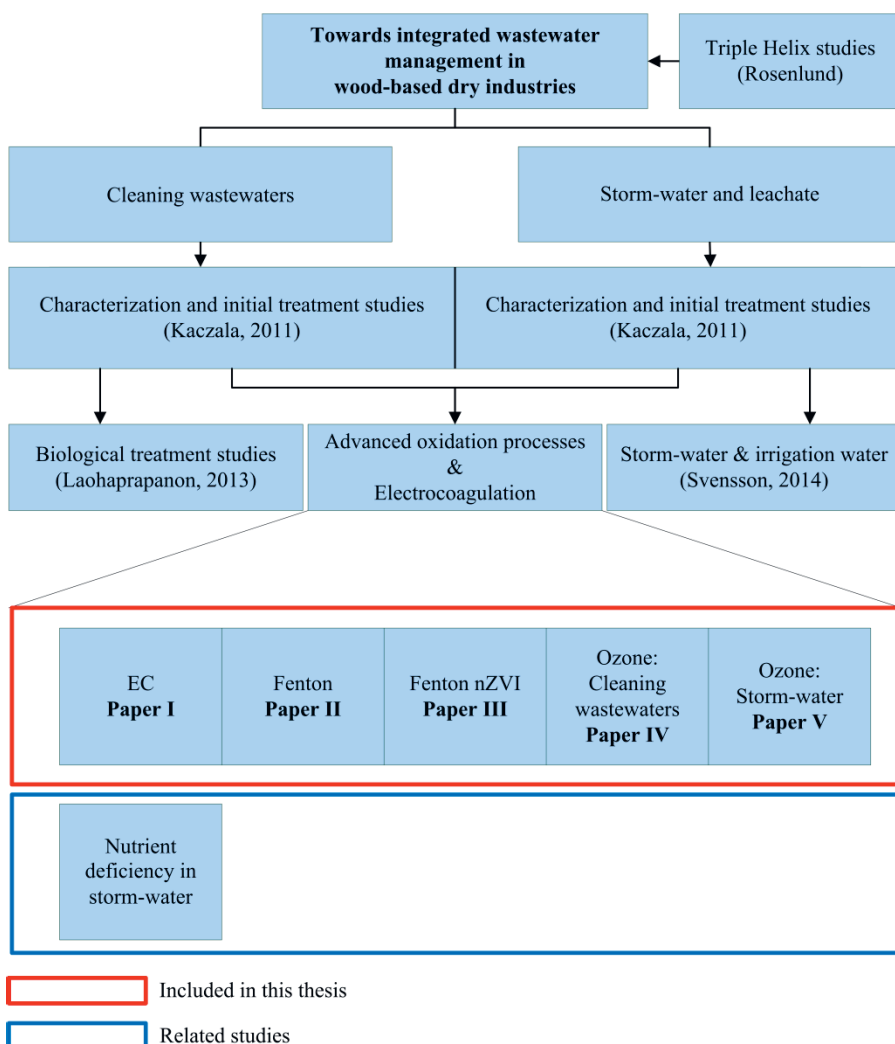
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Figure 1. Previous and current work within the projects supported by Knowledge Foundation and the European Regional Development Fund.

1.2 Aim and Scope

The overall aim of this thesis was to increase the knowledge about on-site treatment options based mostly on chemical processes for treating single and mixed cleaning wastewaters and storm-water generated by the wood-floor and similar industries, and also to investigate individual and coupled/combined treatment steps.

Because of the complex composition of the cleaning wastewaters streams, global parameters such as COD and TOC were used as proxy indicators for assessing the degree of wastewater pollution and treatment efficiency. Besides proxy indicators, in some treatability studies the investigations included specific parameters, such as polyphenol levels. The biodegradability of the wastewater before and after treatment was addressed in some experiments because remaining compounds that result mostly from chemical treatment can pose even higher toxicity than the parent compounds.

All laboratory experiments were carried out at the Department of Biology and Environmental Science, Linnaeus University, Kalmar, Sweden. Wastewaters used in experiments described in **Papers I–V** were collected at AB Gustaf Kähr in Nybro, Sweden.

In the first treatability study (**Paper I**), EC was investigated because this method is known to produce good results on a wide variety of industrial wastewaters (Chou et al., 2010). EC coupled with sorption with activated carbon aimed at increasing the overall efficiency and making more wastewaters available for EC treatment.

To investigate the possibility of achieving mineralization of the pollutants instead of transferring them to a solid phase (as in the case of EC), the Fenton treatment was selected as the first option (**Papers II and III**), because it requires no electrical power, making it easier and possibly cheaper than some of the other options. To reduce the amount of sludge and at the same time try to improve the efficiency, nZVI replaced iron chloride (FeCl) in **Paper III**. For both **Papers II and III**, photo-Fenton was also studied to determine whether the addition of UV light could sufficiently increase treatment results to justify the power consumption.

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To eliminate the need for handling a solid phase, ozone-based AOP:s were studied (**Paper IV**). **Paper V** addressed the treatment of storm-water by coupling ozone and biological treatment, as a future combined treatment of cleaning wastewater and storm-water could possibly produces some advantages.

2. WASTEWATER TREATMENT

The complex urban water system is made up of many components (Figure 2) and in a modern society all streams must be handled in an appropriate way because potable water is becoming scarcer, particularly in large urban centres. While low volumes of cleaning wastewaters are generated by industries that do not use water in the production line, such as the one studied in this thesis, this does not diminish the importance of on-site treatment. These wastewaters are highly polluted with organic and inorganic compounds (Kaczala, 2011, Laohaprapanon, 2013). The MWWTPs in Sweden and most of Europe have similar set-ups and are built and optimized for treating household wastewater through different systems including mechanical, chemical, and aerobic/anaerobic biological treatment steps (Swedish EPA, 2008). These treatment systems are not designed to deal with wastewaters highly polluted with recalcitrant compounds released by industries. Low volumes of wastewater that have high organic contents can seriously disturb the biological processes in a MWWTP. It is not uncommon for a small and medium-sized MWWTP to present a large negative disturbance on their treatment efficiency because of industrial wastewater discharges, as in the case observed in the Kalmar region in 2013 (Steinvall, 2013). These disturbances can lead to large short-term problems, but in the longer-term perspective, a more serious problem might occur. In a worst-case scenario, the pollutants can be magnified in the food chain after passing through the MWWTP. Another major problem with the limited treatment that the industrial wastewater gets in MWWTP is sludge handling, as the sludge becomes hazardous because of

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the accumulation of contaminants. Reuse of the highly nutritious municipal wastewater sludge is something that in a sustainable society must by high on the agenda (Dolgen et al., 2007) and the fact that it is a very effective and attractive product for the agricultural sector once the quality is assured is well known (Kidd et al., 2007, Singh and Agrawal, 2008). To be able to recommend the use of sludge in agriculture as fertilizer, its composition must be kept under control and if, for instance, the sludge contains toxic organic compounds and heavy metals, there will be an increased resistance towards using it on crops (Levlin et al., 2001).

The literature contains several reports of successful application of AOPs with complete mineralization of a wide range of pollutants, and has provided encouraging results when AOPs are combined with other treatments (Lafi et al., 2010, Moussavi et al., 2012, Merayo et al., 2013).

For the sake of the urban water system (Figure 2) in principle, on-site treatment solutions before discharging into MWWTPs must be available for all highly polluted and toxic industrial wastewaters, irrespective of the volume generated.
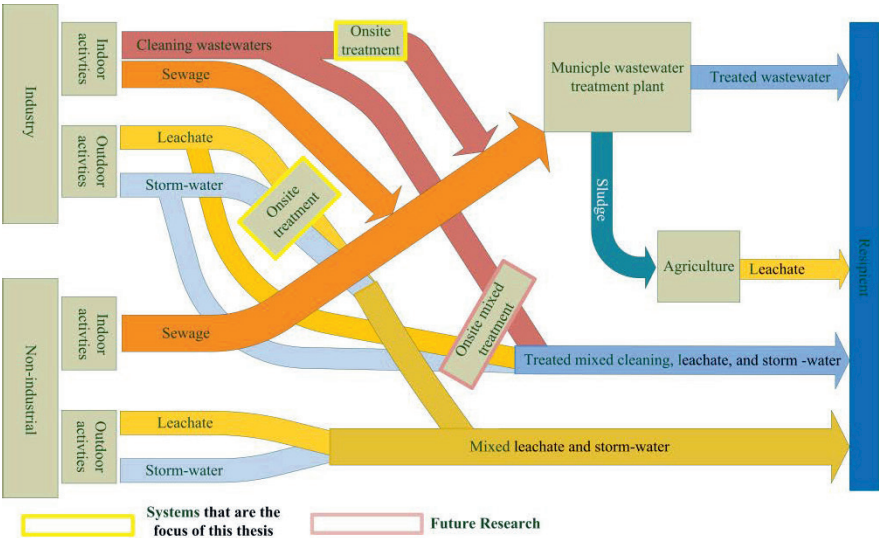

Figure 2. The urban water system, identifying those systems that are the focus of this thesis.

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2.1 Treatment systems

The treatment methods that were investigated separately or in combination are presented below.

2.1.1 Electrocoagulation

EC is a simple and efficient method, whereby the flocculating agent is generated *in situ* by the electro-oxidation of a sacrificial anode, generally made of iron (Fe) or aluminium (Al) that leads, at the appropriate pH, to insoluble metal hydroxides, which in turn remove pollutants by surface complexation or electrostatic attraction (Zaied and Bellakhal, 2009). The pH, together with the current density and the electrode material, are the most important parameters to be considered when using the EC treatment (Wang et al., 2009, Kobya et al., 2010).

2.1.2 Adsorption/filtration

Sorption (adsorption and/or absorption) mechanisms can be effective because of their high pollution-removal capacity. AC is the most common material for the reduction of organic and heavy metal pollutants. ACs, both powdered and granular, are made from a wide variety of carbonaceous starting materials: coals (anthracite, bituminous, lignite), wood, peat, coconut shells, among others. They are manufactured in such a way that they have a large network of internal pores, and the total surface area inside such carbons is typically 500 to 1500 m^2/g (Cooney, 1998). A treatment based on adsorption mechanisms is often of simple design and easy to operate and maintain. The downside is the relatively high cost (Singh et al., 2008, Gupta and Ali, 2012).

2.1.3 Advanced oxidation processes

AOP were defined by Glaze et al. (1987) as processes that "involve the generation of ·OH in sufficient quantity to promote water purification". Radicals are molecules that have an unpaired electron (Howe et al., 2012). Most radicals are highly unstable and immediately undergo a reaction with another molecule in order to obtain the missing electron.

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The hydroxyl radical is one of the strongest oxidants (E = 2.73 V) (Tunay et al., 2010), it is non-selective and capable of oxidizing a broad range of organic pollutants quickly (Torrades et al., 2011). In the present thesis, two main versions of AOPs were studied and applied: the Fenton reaction and ozone-based AOPs.

The Fenton reaction was first observed by H. J. Fenton in 1894 and is described as the enhanced oxidative power of hydrogen peroxide (H_2O_2) when using Fe as a catalyst under acidic conditions. It was later found that this enhancement was caused by the generation of ·OH (Tunay et al., 2010). The Fenton process is a relatively economical method, as it requires no additional energy when compared with many other AOP. Furthermore, both H_2O_2 and Fe are relatively cheap and safe. The Fenton oxidation can be assisted by UV light (photo-Fenton) and the latter oxidation is most effective in the presence of short UV light (UV-C, 180–290 nm) (Arslan-Alaton et al., 2010); it produces a more effective oxidation by hydrolysis of H_2O_2 contributing to ·OH formation (Tunay et al., 2010) and faster recycling of Fe^{3+} to Fe^{2+} (Tamimi et al., 2008) and photo-oxidation of Fe complexes (Safarzadeh-Amiri et al., 1997).

Another AOP uses ozone, which is produced naturally by lightning as well as artificially by the discharge of electricity in the presence of oxygen (O_2). It owes its name and discovery to its distinctive smell. The Dutch scientist van Marum described the "odour of electricity" in 1785 (Gottschalk et al., 2009). Pure ozone treatment at low pH is not considered as an AOP as it is not reliant on the ·OH reaction (Gottschalk et al., 2009), but all ozone experiments will be evaluated as AOP in the present thesis. Ozone is an unstable gas that has to be produced at the point of use. There are two main reaction pathways when using ozone: indirect and direct.

The direct oxidation of organic components by ozone is a selective reaction with a slow reaction rate. The ozone molecule reacts with unsaturated bonds because of its bipolar structure and leads to splitting of the bonds (Gottschalk et al., 2009).

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The indirect way involves the production of radicals; the production of radicals by ozone can be done in different ways. Ozone at high pH and ozone combined with H_2O_2 or UV light are some examples.

2.1.4 Biological treatment

Biological treatment methods have two main pathways: aerobic—in the presence of oxygen, microorganisms convert organic substrates to carbon dioxide (CO_2) and water (H_2O); and anaerobic—when microorganisms convert the organic substrate to methane (CH_4) and CO_2 without the presence of oxygen. These processes can be sensitive to both the chemical and physical properties of some compounds (Orozco, 2008), which reduces the effectiveness of the treatment. In the present thesis, a pulse-flow headspace respirometer was used as a biological reactor to determine both the efficacy of biological treatment when applied to the cleaning wastewaters and the effect the chemical treatments had on the biodegradability of the wastewaters.

3. METHODS

This chapter presents a brief explanation of the methods investigated in the thesis. Detailed explanations are found in the scientific papers (**I-V**).

3.1 Case study

The cleaning wastewater streams selected for the studies presented in **Papers I–IV** were collected from a wood-floor manufacturing industry (AB Gustaf Kähr) in Nybro, Sweden. Being a "dry industry", it uses no water as part of the industrial processes and water is mainly used for cleaning/washing surfaces and machinery after use. Although the volumes of different wastewater streams generated are small, they are highly contaminated with organic and inorganic pollutants (Kaczala et al., 2009, Laohaprapanon et al., 2010) The high COD : BOD ratio (around 4 or higher) indicates moderate-to-low biodegradability of these wastewaters.

In **Paper V,** storm-water and leachate from the same industry were studied. Wood processing industries store large amounts of wood outdoors, which requires large areas for storage that generates contaminated storm-water when logs and wood residues come in contact with rainfall and when the wood is sprinkled with fresh water to maintain the quality. This contaminated water was shown to be hard to degrade and is toxic (Svensson, 2014).

3.1.1 Wastewater sampling

The cleaning wastewaters for **Paper I** were sampled as separate samples (named after the processes in which they are generated, Table 1) and mixed before some of the treatments. For **Papers II–IV,** the cleaning wastewater was sampled as one mixed sample after a full-scale sedimentation plant at the case-study site. A brief characterization can be found in Table 1.

Table 1. Characteristics of the cleaning wastewaters studied. The SD is given in brackets (N = 5 for glue, floor, filler, blade and hardener; N = 11 for O_3/pH_{low} and N = 17 for O_3/pH_{adj} and O_3/UV).

Wastewater	pH	Conductivity (µS/cm)	COD (mg/L)	TOC (mg/L)	BOD$_5$ (mg/L)
Glue	6.2 (1.1)	0.5 (0.2)	19,044 (12,238)	--	2,061 (1,019)
Floor	6.9 (0.3)	2.0 (0.4)	4,091 (839)	--	818 (273)
Filler	7.8 (1.7)	9.4 (1.7)	22,460 (9,180)	--	6,623 (3,969)
Blade	12.5 (0.1)	10.3 (1.4)	5,890 (2,746)	--	2,075 (804)
Hardener	1.5 (0.2)	19.8 (1.3)	30,600 (11,524)	--	12,896 (9,696)
Papers II and III	2.2*	5.9*	4,956*	2,730*	--
Paper IV, Water O_3/pH_{low}	2.5 (0.1)	--	3,460 (526)	1,647 (307)	--
Paper IV, Water AOPs	2.3*	--	4,034 (209)	1,365 (47)	--

*N = 1.

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3.1.2 Storm-water sampling

Storm-water was sampled from a pond in the storage area at the case-study site and characterized (Table 2). The pond collects storm-water and leachate from a large part of the storage area.

Table 2. Characteristics of the storm-water and a process water similar to storm-water studied in the thesis. SD is given in brackets (N = 3).

Wastewater	pH	Conductivity (mS/cm)	COD (mg/L)	TOC (mg/L)	PP (mg/L)
Paper V, Storm-water 1	6.2 (0.1)	0.6 (0.1)	860 (16)	350 (7)	170 (11)
Paper V, Storm-water 2	6.1 (0.1)	0.5 (0.03)	541 (1)	203 (5)	74 (14)
Veneer-water	3.8 (0.3)	810 (40)	6250 (850)	2660 (150)	2200 (440)

3.2 Analytical methods

3.2.1 Chemical analysis

The main parameters selected for following up the organic pollutants' reduction from each wastewater stream and from the mixtures were the proxy indicators COD and TOC. COD and TOC was analysed using the Hach Lange (Hach Lange, Düsseldorf, Germany) cuvette tests LCK 114, 386 and 387. Phenolic substances were quantified using the Folin–Ciocalteu reagent (George et al., 2005) and colour was measured according to Hach Lange method 8025 (Hach Lange, Düsseldorf, Germany). The measurements were carried out with a Hach Xion 500 (Hach Lange, Düsseldorf, Germany) spectrophotometer for **Paper I** or a Dr5000 spectrophotometer (Hach Lange, Düsseldorf, Germany) for **Papers II–V**.

The pH and electric conductivity were measured using a WTW Multi 340i (WTW, White Plains, USA) for **Paper I** and a Hach Lange HQd (Hach Lange, Düsseldorf, Germany) for **Papers II–V**.

3.2.2 Respirometry

A pulse-flow headspace respirometer was used (PF-8000; Respirometer Systems and Applications, Fayetteville, USA) for some studies in the present thesis to study biodegradation and biotreatability. It consists of a number of bottles or reactors. These reactors receive the wastewater and in some experiments, inoculum and nutrients. The headspace gas within the vessel was used as an oxygen supply for the microorganisms that grow in the wastewater. Potassium hydroxide (KOH) was kept within the headspace to absorb the CO_2 that is produced by the microorganisms. This reduces the pressure in the sample bottle. O_2 is added from a pressure bottle and these additions are monitored throughout the test. This can provide continuous high-resolution data about the biological activity in the sample.

3.2.3 Average oxidation state

The AOS value was calculated using the COD and TOC data from different experiments according to equation 1 (Sarria et al., 2003). The COD and TOC values are expressed in mol O_2/L and mol Carbon (C)/L, respectively.

$$AOS = \frac{4(TOC-COD)}{TOC} \qquad [1]$$

The AOS can attain values between +4 for CO_2, and −4 for CH_4, these being the most oxidized and the most reduced states of C, respectively. The AOS is a parameter used to roughly estimate the degree of oxidation in a mixed wastewater sample.

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4. EXPERIMENTAL SETUPS

A brief explanation of the materials and setups related to the thesis is given here. More detailed explanations can be found in **Papers I–V**.

4.1 Electrocoagulation treatment

4.1.1 Electrocoagulation setup

An EC reactor of my own design was constructed for **Paper I** according to the results obtained in a preliminary study. The setup included a monopolar electrode with parallel connections in an array of four Al electrodes (Figure 3), with a surface area of 93.2 cm², and a current density of 161 A/m². The distance between each anode and cathode was kept at 1 cm. Agitation was provided by a magnetic stirrer operating at 200 rpm.

Figure 3. Monopolar electrodes connected in parallel in an array of four electrodes.

The current density and the treatment duration were chosen based on other reported experiments (Kobya et al., 2006, He et al., 2007, Yetilmezsoy et al., 2008). The pH_0 is an important factor for EC performance, and based on that, four different pH_0 values were studied to assess their effect on the COD reduction. The different cleaning wastewater streams varied greatly in composition. Therefore, to study the effect on the treatment efficiency with EC, the treatability studies included four different mixtures of the wastewaters.

4.1.2 Electrocoagulation combined with sorption

The two columns of the sorption/filtration unit were made from polyvinyl chloride (PVC) with an inner diameter (i.d.) of 70 mm, height of 750 mm, and a bed depth of 570 mm. The columns were fed from the bottom up. The experiment was conducted using a coal-based activated carbon.

Four different sequencing strategies of the different cleaning wastewaters, sorption and EC were studied (Figure 4).
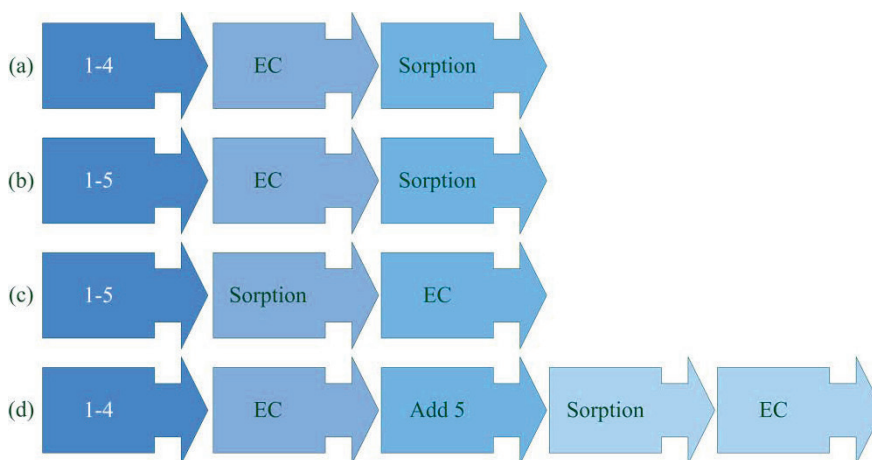

Figure 4. Different sequence strategies to treat mixtures of five cleaning wastewater streams. 1: Gluing, 2: Floor washing, 3: Filling, 4: Blade sharping, 5: Hardening.

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4.2 Advanced oxidation processeses

4.2.1 Fenton treatment

The dark-Fenton studies were conducted in 1 L glass beakers and the photo-Fenton studies were carried out in a glass-jacket immersion-type UV reactor with a volume of 0.7 L (LRS 2, UV-Consulting Peschl, Mainz, Germany) (Figure 5).
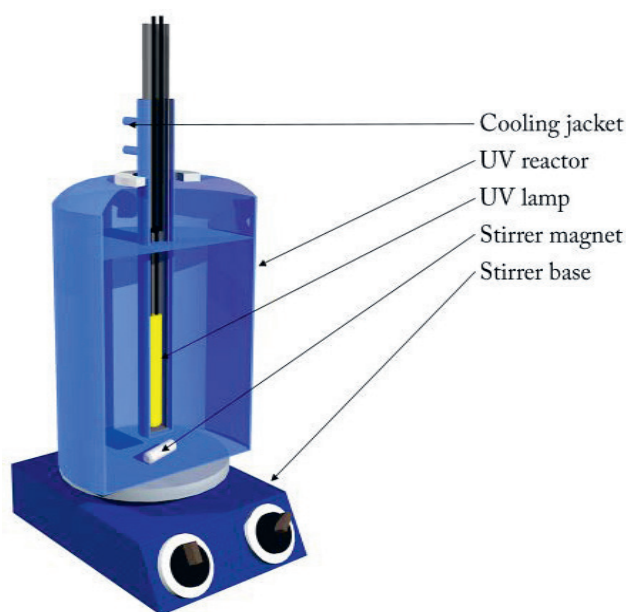
Figure 5. Cut-away drawing of the LRS2 UV reactor used in the photo-Fenton experiments.

All runs were conducted with a volume of 0.5 L of wastewater that was agitated for 120 min by a magnetic stirrer at 400 rpm. The pH was adjusted at the beginning of each run to be maintained between 2.95 and 3.05, because this pH range has been reported to be the optimum for Fenton oxidation (Padoley et al., 2011, Su et al., 2011). The pH was readjusted every 15 min throughout the 120 min of reaction time, if needed.

An excess of Fe can lead to scavenging of ·OH (Tamimi et al., 2008); to reduce this problem, in some experiments the reactants were added in equal aliquots during the treatment.

In the experiments described in **Paper II,** H_2O_2 and FeCl were used as reactants and in **Paper III,** the iron was changed to nZVI. The amounts of reactants for both studies were selected based on a preliminary study and a literature review. To have a better understanding of which independent variables play important roles in treatment efficiency, a two-level full-factorial design was applied, with triplicates of the central points. The independent variables were the H_2O_2 : COD ratio, the H_2O_2 : Fe ratio and the dosing mode; the levels of the variables are shown in Table 3.

Table 3. Variable levels applied in the 2-level factorial design.

Variables	Code	-1	0	+1
H_2O_2 : COD	χ_1	2 : 1	3.5 : 1	5 : 1
H_2O_2: Fe	χ_2	2 : 1	8.5 : 1	15 : 1
Dosing mode	χ_3	1	2	3

Notations: +1(high level); 0 (central point); -1 (lower level).

4.2.2 Ozone treatment

For both ozone studies **(Papers IV, V),** a tubular stainless steel ozone reactor of my own design with a volume of about 3 L was used. The ozone was generated from 99.5% pressurized O_2 by a water-cooled corona discharge ozone generator (ICT-10; Ozone Tech Systems, Stockholm, Sweden) and the ozone was passed through a stainless steel diffuser with a 20 μm pore size (SD-3; Ozone Solutions, Hull, USA). All remaining ozone was catalytically destroyed in an ozone destructor (OD-0100; Ozone Tech Systems, Stockholm, Sweden) and the ozone concentration was measured in the outflow from the ozone reactor by an ozone monitor (BMT 964; BMT Messtechnik GMBH, Berlin, Germany) (Figure 6).
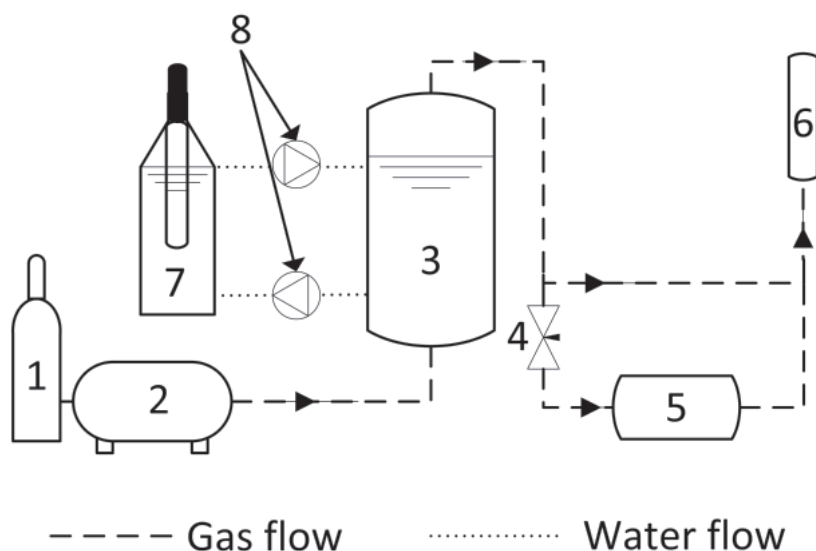
Figure 6. Ozone system (parts 7 and 8 were not included in Paper V). 1: O_2 pressure tank, 2: ozone generator, 3: ozone reactor, 4: needle valve, 5: ozone monitor, 6: ozone destructor, 7: UV reactor, 8: peristaltic pumps.

For **Paper IV**, a redesigned glass-jacket immersion-type UV reactor (LRS 2, UV-Consulting Peschl, Mainz, Germany) with a volume of about 1.9 L was attached to the ozone system via two peristaltic pumps (520SN, Watson-Marlow, Falmouth, United Kingdom) this setup gave the ability to alter the

retention time between the ozone reactor and the UV reactor. The UV light was emitted at a 150 W.

4.2.2.1 Ozone treatment of cleaning wastewater

Paper IV describes three different ozone treatments: ozone at the natural low pH of the cleaning wastewater (O_3/pH_{low}), ozone treatment with adjusted pH_0 (O_3/pH_{adj}) and with adjusted pH_0 and exposure to UV light (O_3/UV).

For O_3/pH_{low}, the ozone was added in five different concentrations within the range of $40 - 115$ g/Nm^3. The total amount of ozone added was based on the initial COD value of the cleaning wastewater. The maximum amount was at a ratio of 2 : 1 ozone : COD. The O_3/pH_{low} experiments were performed to find a baseline of degradation of COD and TOC that ozone could achieve for cleaning the wastewater. These results were used as a base for optimizing the range of the parameters for the treatment with ozone-based AOP.

For the O_3/pH_{adj} and O_3/UV, the range was narrowed to $40 - 90$ g/Nm^3, based on the results from the O_3/pH_{low} study. Recirculation flow was kept within the same range for all experiments and the pH_0 was adjusted to a range based on a literature review (Table 4).

To understand how important each independent variable was for treatment efficiency, a five-level full-factorial design with triplicates of the central points was applied. The independent variables for O_3/pH_{low} were input O_3 concentration and recirculation flow; for O_3/pH_{adj} and O_3/UV they were O_3 concentration, recirculation flow and pH_0 (Table 4).

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Table 4. Full-factorial design, two or three variables with five-levels in each. Numbers presented between [ ] are the levels used for the treatment O_3/pH_{adj} and O_3/UV.

Variables	Code	Values of coded levels				
		-1,41 [-1,68]	-1	0	1	+1.41 [+1.68]
O_3 (g/Nm^3)	χ_1	40	51 [50]	78 [65]	104 [80]	115 [90]
Recirculation flow (L/min)	χ_2	0.3	0.7 [0.9]	1.65	2.6 [2.5]	3
pH_0	χ_3	[3.0]	[4.6]	[7.0]	[9.4]	[11.0]

The highest % COD and TOC reduction for each treatment was also analysed using headspace respirometry in order to study remaining toxicity and biodegradability after treatment with ozone and ozone-based AOPs. Activated sludge was therefore exposed to untreated and treated cleaning wastewater (effluents from O_3/pH_{low}, O_3/pH_{adj} and O_3/UV treatments) and the oxygen uptake and uptake rate were monitored as an indication of biological aerobic activity. For the respirometry analysis, activated sludge from Kalmar MWWTP was collected and used as inoculum. The amounts of 320 mL wastewater, 90 mL activated sludge and predetermined volumes of macro- and micro-nutrients were added to each bottle according to Young and Cowan (2004). All wastewaters were diluted with tap-water to achieve a similar TOC concentration in all samples. All respirometry studies were conducted for 50 h. The conditions for the respirometry study were selected based on preliminary studies performed by the authors and a literature review.

4.2.2.2 Ozone treatment of storm-water

In **Paper V**, ozone and biodegradation studies were conducted for storm-water. Three different samples were analysed: two storm-water field samples (Storm-water 1 and Storm-water 2) and one steaming-water from a process similar to veneer production (veneer-water). The ozone was added at three different concentrations: 7, 50 and 100 g/Nm^3, at a flow of 1 L O$_2$/min. All wastewaters treated with ozone were analysed for COD, TOC, PP and colour. Based on the results from the ozonation study, new samples were then treated with ozone to 35% and 70% PP degradation to investigate the effect on biodegradability using headspace respirometry. For the respirometry analysis, wastewater from a pilot-scale wetland treating the same storm-water was collected and used as inoculum; 250 mL of treated water was added to 250 ml of inoculum. All wastewaters were diluted with tap-water to achieve a similar COD concentration in all samples. All respirometry studies were conducted for seven days. The conditions for the respirometry study were selected based on previous studies done by the authors (Svensson et al., 2014).

5. RESULTS AND DISCUSSION

5.1 Electrocoagulation treatment

5.1.1 Individual treatment

Paper I describes the results from the EC treatment and the combination of EC with sorption. Initially, the study focused on treating the individual cleaning wastewaters separately. These showed a large variation in the treatment effectiveness, measured as % COD reduction, from 2% (hardener wastewater) to over 75% (blade wastewater) as shown in Table 5. For both the individual and mixed wastewaters, pH 5 appeared to be the most effective pH_0. Based on the final organic load reduction, it was also found that there was no benefit in treating the waters individually. As no positive effect could be found by treating the waters separately, and because from an operational standpoint it would be advantageous to treat the waters as a mix, the study focused on the latter option.

5.1.2 Mixed treatment

When treating the mixed cleaning wastewater, the hardener wastewater appeared to have a large negative effect on the EC performance even when admixed at very low ratios compared with other wastewaters. Based on the treatment results with mixed wastewaters, the hardener wastewater stream was excluded from the EC treatment when EC was sequenced as a pretreatment to the sorption/filtration step (Figure 4). With this setup, a treatment by EC for 30 min produced a COD reduction of about 20%.

When EC was sequenced as a post-treatment to the AC sorption, an additional reduction of about 23% in the COD value was achieved. This secondary EC treatment included the hardener wastewater that had previously hindered effective EC treatment.

When these processes were combined in sequence, an overall average reduction of 71% of COD was achieved in a quick and consistent treatment process.

Table 5. COD reductions (%) for individual cleaning and mixed wastewaters in different sequences. The initial pH was 5. SD is shown in brackets.(N = 3).

	% COD reduction	
Glue wastewater	22	(0.8)
Hardener wastewater	2	(0.5)
Filler wastewater	15	(0.4)
Blade wastewater	77	(2.9)
Floor wastewater	44	(1.4)
Mix before sorption (all waters)	0	(0.5)
Mix before sorption (no hardener)	21	(0.2)
Mix after 50 % COD reduction by sorption	25	(0.3)

These results showed clearly that the different sequencing of treatments produced quite different results and that sorption/filtration can remove specific inhibiting pollutants, thereby allowing for effective treatment by EC. One possible inhibiting substance is acetic acid, which is a component of the hardener and is known to interfere with EC (Moreno-Casillas et al., 2007). The fact that the concentration of pollutants was not a major factor for the effectiveness of the EC treatment was investigated by diluting an untreated mix of all cleaning wastewaters and still very poor performance was achieved by EC, this supports the findings of an earlier study by Holt (2002).

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5.2 Advanced oxidation processes

The results from **Paper I** showed that the mixed cleaning wastewater was potentially hard to treat. With AOP there is the possibility of complete mineralization of a wide range of pollutants, as well as encouraging results from literature when AOP are combined with other treatments (Lafi et al., 2010, Moussavi et al., 2012, Merayo et al., 2013)

5.2.1 Fenton treatment

Papers II and III focused on the Fenton treatment, an AOP that does not require power. Next, the photo-Fenton process was included to investigate whether the power requirements by this treatment would produce sufficient enhancement when compared with the Fenton treatment.

In **Papers II and III,** only mixed cleaning wastewater was studied as an on-site pretreatment plant was installed at the Nybro site during the thesis development. This was based on sedimentation and all the streams mentioned in **Paper I** are mixed before treatment. Since this is the most likely scenario for future work at these types of industries, additional treatment should start with the effluent of a sedimentation step.

5.2.1.1 Dark Fenton

The effects of three independent variables (the H_2O_2 : COD ratio, the H_2O_2 : Fe ratio, and the dosing mode) and the effects of these variables on the COD and TOC reduction (in %) were assessed based on the data from the full-factorial design. For the Fenton treatment in **Paper III,** all the independent variables or factors studied had significant effects on the COD and TOC removal efficiency ($p < 0.05$). According to the treatability studies described in **Paper II,** the treatment efficiency was not affected by the dosing mode. In general, the independent variables that played the most important roles were the H_2O_2 : COD and H_2O_2 : Fe ratios in both **Papers II and III**. The dosing mode has been reported to both have (Yoo et al., 2001, Zhang et al., 2005) and not have an effect (Rivas et al., 2003), but the reason for this is unclear (Deng and Englehardt, 2006). No literature has been found where the dosing mode and the nZVI have been studied.

The results in **Papers II and III** showed that a high H_2O_2 : COD ratio and low H_2O_2 : Fe ratio promoted the highest reduction efficiencies for COD and TOC. However, there are some differences between using FeCl (**Paper II**) and nZVI (**Paper III**) as a catalyst (Table 6). FeCl produced a significantly higher reduction for both COD and TOC (paired t-test, $p<0.05$).

Table 6. Results from Fenton treatment of mixed cleaning wastewater (N = 11).

Reduction	Paper II (FeCl)		Paper III (nZVI)	
	COD	**TOC**	**COD**	**TOC**
Average (%)	62	40	43	25
Max (%)	78	66	78	50
Range (%)	47	54	43	33

The results obtained in both studies indicated that higher concentrations of the oxidizing agent and the catalyst were able to reduce higher amounts of COD and TOC, despite the fact that Fe in high concentrations was a potential scavenger of hydroxyl radicals.

When the efficiency of the treatment systems was evaluated based on the consumption of the oxidizing agent per unit of removed COD or TOC (H_2O_2/g of COD and TOC removed), it was found that the most effective combinations in the Fenton system were those that used relatively low concentrations of H_2O_2 and high concentrations of Fe. These results suggested that scavenging took place when higher concentrations of H_2O_2 were available; however, if scavenging actually occurred, it was not severe to the point of preventing an increase in COD and TOC reductions and this was true for the experiments described in both **Papers II and III.**

An important aspect regarding the Fenton treatment was the reduction of Fe^{3+} to Fe^{2+}, as Fe^{2+} is the active species in the Fenton reaction, which makes the presence of reaction intermediates able to reduce Fe^{3+} and regenerate the catalyst, to be crucial.

However, there are reaction intermediates that, instead of reducing the Fe^{3+}, remove it from the Fe^{2+} / Fe^{3+} cycle, because of the generation of Fe complexes, delaying and/or inhibiting the oxidation process (Safarzadeh-Amiri et al., 1997). The cleaning wastewater studied contained acetic acid (from the hardener used in the wood-gluing process) and formaldehyde (urea–formaldehyde-based glue) that can transform into formic acid during the Fenton process (Liu et al., 2011), with formation of ferric carboxylate complexes that are resistant to oxidation (Safarzadeh-Amiri et al., 1997). For both **Papers II and III,** the lower Fe concentration showed the largest differences between the COD and the TOC reduction, which supports this hypothesis. The effect was more pronounced in **Paper II**.

5.2.1.2 Photo-Fenton

The effects of independent variables and the effects of these variables on the COD and TOC reduction (%) were assessed for the photo-Fenton treatment as well, but no significant factors could be found, as mentioned in **Papers II and III**. The results showed that the levels applied to the studied factors did not affect significantly the results in the case of the photo-Fenton experiment ($p > 0.05$), suggesting that either the long UV exposure time has eliminated large differences in the results or that other variables might be involved more significantly in the performance of chemical oxidation combined with UV irradiation.

The results regarding COD and TOC reductions with photo-Fenton have shown that the addition of the UV light had a significant positive effect compared with Fenton in both cases (paired t-test, $p < 0.05$). Besides the increased maximum efficiency, there was also a substantial reduction in the range of the results (Table 7). This shows that the photo-Fenton process could effectively treat the cleaning wastewater with fluctuations in the COD and TOC values, something that would be very appropriate in a full-scale plant where loads vary from day to day, such as the cleaning wastewaters investigated in the present thesis.

Table 7. Results from photo-Fenton treatment of mixed cleaning wastewaters. (N = 11).

Reduction	Paper II (FeCl)		Paper III (nZVI)	
	COD	TOC	COD	TOC
Average (%)	74	57	74	52
Max (%)	82	62	79	62
Range (%)	21	12	12	18

There was also a significant difference in the magnitude of improvement in reduction, when comparing COD and TOC. The higher increase for TOC compared with that observed for COD (paired t-test, p<0.05) suggested that with the photo-Fenton process, besides a general improvement in reduction, there was also a larger improvement in the mineralization process. The two main reasons for these results are probably as follows: (i) the photo-Fenton process is known to assist the Fe^{3+}/Fe^{2+} cycle (Tamimi et al., 2008); and (ii) photochemical activation of ferric carboxylate complexes by UV irradiation occurs and the subsequent generation of ferrous ions has been reported in the literature (Safarzadeh-Amiri et al., 1997).

All results for photo-Fenton were similar for both **Papers II and III,** suggesting that there was not much difference between using nZVI and FeCl in the photo-Fenton process.

5.2.1.3 AOS value

When both Fenton and photo-Fenton treatments reached high treatment efficiency, AOS values of approximately +3 were reached. The value of +3 suggests that most of the effective treatments reached a stable AOS value, as +4 is the maximum. In such cases, even with continued treatment, intermediate compounds with higher oxidation states are not formed. From the moment AOS stabilizes, the chemical treatment is about mineralizing organic contaminants with no partial oxidation (Sirtori et al., 2009). The increase in AOS as observed in this study, particularly in the photo-Fenton treatment, suggests the generation of an effluent with enhanced biodegradability (Sirtori et al., 2009) and reduced toxicity (Elmolla and Chaudhuri, 2009).

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5.2.1.4 Comparison of nZVI and FeCl

For dark Fenton, FeCl performed significantly better than nZVI in the reduction of both COD and TOC. However, for photo-Fenton, there was no significant difference between FeCl and nZVI regarding COD reduction. For TOC reduction, nZVI was significantly better than FeCl (paired t-test, $p < 0.05$). These results showed that when UV light was applied there was a larger improvement in the treatment with nZVI than in the treatment with FeCl, which could be because of the fact that UV irradiation improved nZVI solubility (Alizadeh Fard et al., 2013). These results demonstrated that it is possible to achieve at least the same efficacy using nZVI or FeCl. This would be in addition to the reduced amount of sludge generated when nZVI is applied, as previously reported (Babuponnusami and Muthukumar, 2012).

5.2.2 Ozone treatment

The Fenton process produced substantial reductions in COD and TOC and showed the possibilities of AOPs. The ozone treatment consumed some power but ozone is a powerful oxidant and is effective as a radical generator (Gottschalk et al., 2009).

5.2.2.1 Ozone treatment of cleaning wastewater

In **Paper IV,** mixed cleaning wastewaters continued to be the focus. Two samples were taken for this study; the sampling procedure was designed to minimize variations in the wastewater composition because of storage, as well as variations inside the industry.

5.2.2.1.1 The effects of the independent variables

The reduction in COD achieved with the O_3/pH_{low} treatment was significantly affected by the initial ozone concentration and the recirculation flow ($p < 0.05$). However, ozone concentration had a stronger influence on COD reduction than the recirculation flow (Figure 7a) and was the only factor that affected the reduction in TOC (Figure 7b). According to Figure 7a, the highest COD reduction (in %) was achieved with lower input concentrations of ozone combined with higher recirculation flows. This has likely occurred because of lower loss of ozone in the off-gas, when applying O_3 in lower

concentrations. For this reason, the range of the O_3 concentration input was narrowed for the later experiments.

In the treatment with O_3/pH_{adj}, the COD reduction was significantly affected by both recirculation flow and pH_0 ($p<0.05$). The effect of pH is illustrated in Figure 7c, which shows a 3D surface with a clear change within the different pH ranges, illustrating that at low and high pH_0 ranges, the treatment performance regarding COD reduction decreased. The results showed in this case that the middle ranges of pH_0 could achieve better reduction in COD. The fact that the performance at higher pH_0, which should lead to higher production of ·OH, did not increase could be caused by the fact that any beneficial increase in reaction rate was counteracted by the greater ozone requirement as a result of loss of oxidants by increased self-decomposition (Alvares et al., 2001) and the presence of ·OH scavengers.

TOC reduction for O_3/pH_{adj} treatment was only significantly affected by changes in the recirculation flow ($p<0.05$).Recirculation flow was likely to have a large effect on the dissolution of ozone in the water, which would affect the reduction of TOC. However, as concluded earlier, recirculation flow was not a significant factor for TOC reduction using O_3/pH_{low}. The effect of recirculation for O_3/pH_{adj} can be seen in Figure 7d; a higher recirculation flow is better until very high flows are reached. This is likely because at low flow the retention time in the UV reactor is too long (lamp off) and most of the ozone is consumed with no new ozone coming in. At high flow a high production of radicals is maintained in the UV reactor and the dissolution of new ozone in the ozone reactor is easy, but at very high flows the reaction time in the UV reactor is too low to promote easy dissolution of new ozone in the ozone reactor. This correlates with the O_3/pH_{low} results, where the lowest flow is still too high for easy dissolution of new ozone in the ozone reactor, and because of this, recirculation flow is not a significant factor for TOC reduction.

Also, for the O_3/UV treatment, the percentages of COD and TOC reductions were significantly affected only by recirculation flow ($p<0.05$). Figures 7e and 7f show clearly the effect of recirculation flow and how the effect of pH on the O_3/pH_{adj} treatment disappeared. The higher the recirculation flow, the higher

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were the COD and TOC reductions, regardless of the pH_0. This shows a reverse trend of the O_3/pH_{low}, where all flows were too high. Here, the O_3/UV radical production is so fast that it is likely that the dissolved O_3 is low even at the highest flow when the water enters the ozone reactor. This correlates well with O_3/UV having significantly lower ozone waste gas per g COD removed compared with O_3/pH_{adj}, (t-test, $p<0.05$).

The relationships between the independent variables and the dependent ones or the responses (% of COD and TOC reductions) are visualized through some 3D surface plots in Figure 7. Considering that there were no significant effects caused by different levels of ozone concentration input on the COD and TOC reductions ($p>0.05$) in the O_3/pH_{adj} or O_3/UV treatments, the 3D graphs for these experiments (Figures 7c–7f) are presented only for the significant independent variables (recirculation flow and pH_0).

The coefficient of determinations of the quadratic theoretical models describing the reduction variation as a function of the selected independent variables were as high as 0.88, 0.74, 0.84 for COD and 0.75, 0.70, 0.83 for TOC for the treatments O_3/pH_{low}, O_3/pH_{adj} and O_3/UV, respectively, suggesting high agreement between experimental and theoretical data.
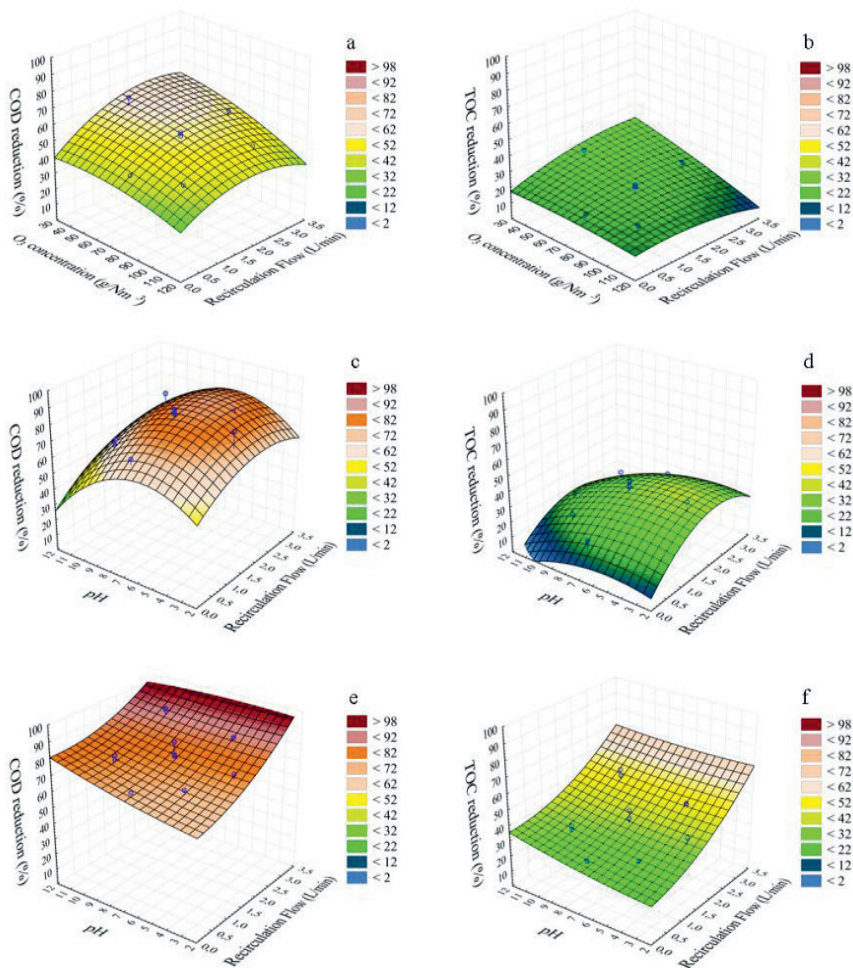
Figure 7. 3D surface plots of COD and TOC reduction (in %) as a function of the independent variables for O_3/pH_{low} (a, b), O_3/pH_{adj} (c, d) and O_3/UV (e,f). Graphs a, c and e show % COD reduction, b, d and f show % TOC reduction

5.2.2.1.2 Treatment efficiency – COD and TOC reductions

The COD and TOC values (Table 8), show substantial reductions. However, comparing the performance achieved by different treatments, the treatments with O_3/pH_{adj} and O_3/UV promoted significantly higher COD and TOC reductions than obtained with the treatment O_3/pH_{low} (one-way ANOVA, Tukey test, $p<0.05$).

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Regarding the TOC reduction, the O_3/UV treatment gave a significantly better performance (Table 8) than the other treatments (one-way ANOVA, Tukey test, $p<0.05$).

Table 8. COD and TOC reductions obtained with different ozone-based treatments (N = 11 for O_3/pH_{low} and N = 17 for O_3/pH_{adj} and O_3/UV).

Reduction	O_3/pHl_{ow}		O_3/pH_{adj}		O_3/UV	
	COD	TOC	COD	TOC	COD	TOC
Average (%)	53	22	77	30	81	40
Maximum (%)	65	31	86	43	94	56
SD	6.8	4.2	9.0	8.0	8.1	8.9

Such results suggest the complete mineralization of the organic contaminants when adding UV light to the ozone-based processes, as the TOC reduction indicates that the organic carbon was completely converted to CO_2 (Medley and Stover, 1983). A positive effect on the TOC reduction by ozone and UV has also been reported by Chin and Bérubé (2005).

5.2.2.1.3 AOS changes during the treatment

An increase in the AOS values was observed as the O_3 / COD ratio increased and a tendency to reach a plateau was observed (Figure 8). As previously stated, this suggests a cleaning wastewater with enhanced biodegradability and reduced toxicity (Figure 8).
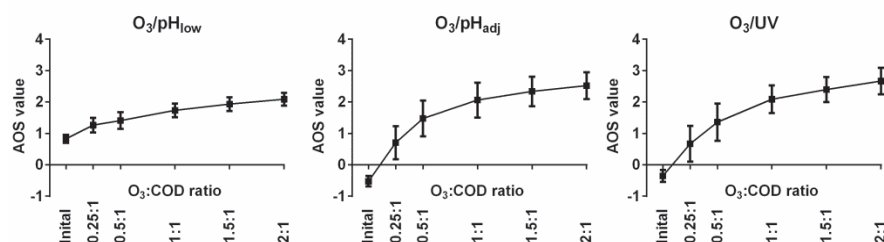

Figure 8. Average AOS values during treatment with O_3/pH_{low}, O_3/pH_{adj} and O_3/UV. Error bars show standard deviations.

5.2.2.1.4 Respirometric study

In order to combine the knowledge obtained from the AOS calculation and validate the results, some samples from the most effective runs in each treatment setup were used in further investigations with the respirometer. To enhance the effect of the plateau in the AOS value that can be seen in figure 8 the wastewaters where treated with 3:1 as well as 1:1 (ozone : COD) ratios before the biological treatment.

The experimental results from the respirometry assays showed that ozone treatment at low pH (O_3/pH_{low}) increased the inhibitory/toxic effects in comparison with the untreated cleaning wastewater. For both O_3/pH_{adj} and O_3/UV, however, the toxicity decreased in comparison with the untreated cleaning wastewater, as indicated by the higher oxygen uptake rates observed in Figure 9. The best results were produced by the cleaning wastewater treated with O_3/UV. The reduction in the inhibition/toxic effects in the effluent after treating the cleaning wastewater with O_3/pH_{adj} and O_3/UV confirmed the results obtained with the AOS calculations, which showed the highest increase for the previously mentioned treatment processes (Figure 9). Concerning the period that the activated sludge took to achieve the peak of oxygen uptake, a much longer period was observed in samples treated at low pH (O_3/pH_{low}) in comparison with those treated with O_3/pH_{adj} or O_3/UV. The peaks of oxygen uptake were reached after 39 h (1:1) and 25 h (3:1) in wastewater treated with O_3/pH_{low}. Nevertheless, it took less than 1 h for the microbial metabolic process to reach its peak in the effluent of O_3/pH_{adj} or O_3/UV treatments (Figure 9).
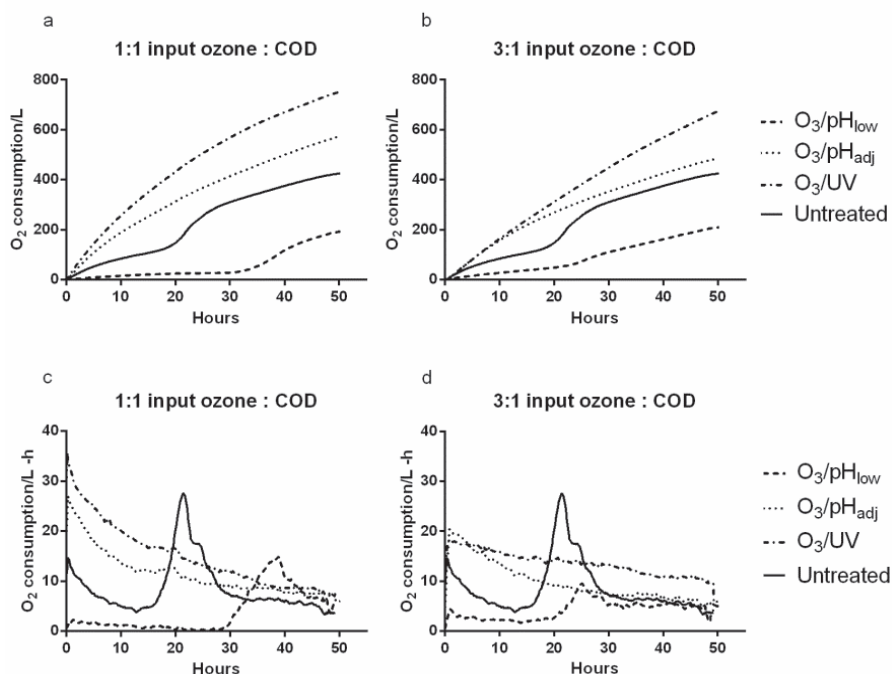
Figure 9. Cumulative oxygen consumption (a, b) and oxygen uptake rate (c, d) per L of untreated and treated cleaning wastewater by O_3/pH_{low}, O_3/pH_{adj} and O_3/UV.

All results suggested the formation of oxidation by-products after the treatment at low pH (O_3/pH_{low}), which were not easily biodegradable and/or were toxic in the activated sludge. It has been reported in the literature that formation of oxidation by-products is common when applying O_3 treatment at acid pH (Gottschalk et al., 2009). On the other hand, the O_2 consumption peaks reached in the initial stages of the biological treatment of the effluent generated by O_3/pH_{adj} and O_3/UV treatments indicated the potential use of these treatment configurations before the cleaning wastewaters are sent to the MWWTP or to an on-site biological treatment. The results showed that a substantial part of the pollutants in the cleaning wastewater could be readily available for microorganisms.

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After 50 h of biological treatment of the effluent obtained with the O_3/UV treatment, at a 3:1 ozone : COD ratio, an increase in the TOC reduction by more than 300% and 60% in comparison with the effluent obtained with O_3/pH$_{low}$ treatment and with the raw cleaning wastewater, respectively, was observed. The considerable improvement in biological activity can be explained by a more effective mineralization because of the reaction between ·OH and the pollutants in the cleaning wastewater, compared with the selective reaction between ozone and mainly double bonds (Gottschalk et al., 2009).

5.2.2.2 Ozone treatment of the storm-water

The encouraging results from the ozone treatment of cleaning wastewater (**Paper IV**) combined with indications that PP reduction could enhance the biological treatment of storm-water and leachate (Svensson et al., 2012) suggested that it would be possible to find a use for ozone also in the treatment of the storm-water, because PP has successfully been degraded by ozone (Zenaitis and Duff, 2002).

The treatment of the storm-water from the case-study site has been previously studied with wetlands and filters (Svensson, 2014). Because the pollutant reductions obtained in those studies was partial, ozone could be used as an initial treatment before wetland treatment to reduce the most harmful pollutants, such as PP (**Paper V**).

5.2.2.2.1 Ozone treatment

Ozonation of storm-water samples reduced the amount of organic matter (Table 9). Composition of wood leachate has been shown to vary considerably with the tree species (Svensson et al., 2013), and the results from this study showed a substantially higher reduction than previously reported, but similar reductions to the veneer-water, which was similar to the COD concentration found in previous studies (Zenaitis and Duff, 2002, Zenaitis et al., 2002).

Table 9. Total reduction after injecting 4 g/L ozone in the reactor. Range in brackets (N = 3).

Reduction	Storm-water 1	Storm-water 2	Veneer-water
COD reduction (mg/L)	620 (10)	350 (50)	1960 (720)
Reduction (%)	73 (2)	66 (8)	31 (12)
TOC reduction (mg/L)	220 (3)	120 (30)	630 (190)
Reduction (%)	62 (1)	50 (11)	24 (7)
PP reduction (mg/L)	150 (1)	60 (10)	1920 (60)
Reduction (%)	91 (1)	83 (7)	87 (3)

The ozonation results for veneer-water showed that during the first half of the experiment, the efficiency was below 1:1 regarding g O_3 / g COD removed. This indicates that a chain reaction occurred between the ozone and the phenols in the wastewater, as reported by Mvula and von Sonntag (2003). This seems likely because of the very high concentrations of PP and the low pH of the veneer-water. This high efficacy was only found at the start of the experiments; the amount of ozone needed to degrade organic molecules rose rapidly during the ozonation process. This happened when the target molecules were less vulnerable to ozone. In the end, as much as 11 g O_3/g COD was needed in Storm-water 2.

5.2.2.2.2 AOS value

The AOS values increased for all treatments. The largest change in AOS was observed in Storm-water 2, followed by Storm-water 1 and the veneer-water. As previously stated, this increase has been linked to effluent with enhanced biodegradability (Sirtori et al., 2009) and reduced toxicity (Elmolla and Chaudhuri, 2009). No plateau was reached for the AOS value in any of the samples. This was also discussed previously: when the AOS value stabilizes, the chemical treatment is only mineralizing organic contaminants, with no partial oxidation (Sirtori et al., 2009). Because complete mineralization was not the goal of this study, this was not considered to be a problem. However,

the AOS results indicated that more degradation could be achieved with ozone but this would be very costly when considering the amount of ozone per g of COD removed.

5.2.2.2.3 Biological treatment

PP was effectively degraded by ozone because ozone reacts faster with certain types of aromatic and aliphatic compounds, such as phenol, both in spiked solutions (Perkowski et al., 2003) and when treating wood leachate (Zenaitis and Duff, 2002). This was clearly shown in the present study, with the reduction reaching 80%–90% (Table 9). PP are often reported as being the main problem in wood leachate because of their toxicity, as well as their high colouring effect on the receiving waters (Svensson et al., 2012). When all wastewaters in the study were treated with ozone to reach 35% and 70% PP degradation the results showed that pretreatment of wood leachate with ozone followed by biological treatment would be a positive combination (figure 10). This differs from the results found by (Zenaitis et al., 2002), where no improvement in biodegradability by ozone pretreatment was found. The reason for this could lie in the difference in the wood species studied. The largest effect on biodegradability was seen in Storm-water 2, where a significant positive effect was found by removing 70% of PPs by ozone treatment. However, at 35% PP removal, this positive effect was not present; in fact, a significant toxic effect was observed (ANOVA, Tukey test, $p<0.05$) (figure 10).
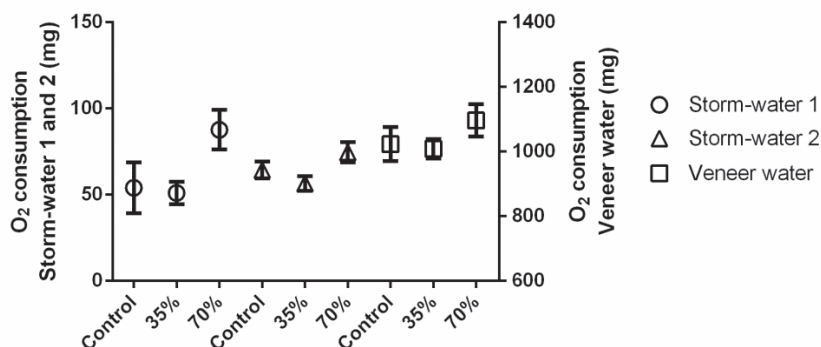
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Figure 10. Total O₂ consumption during the 7 day respirometry study.

This indicates that for ozone to be an effective treatment, it needs to be applied in a relatively large dose; this could be because of the formation of oxidation by-products when ozone is applied in low doses, as discussed earlier. For Storm-water 1, there were no significant effects compared with the control, but there were significant differences between the samples (ANOVA, Tukey test, $p<0.05$) (figure 10). This could also indicate a weak toxic effect in the 35% PP reduced sample. For the veneer-water sample, there were no significant effects. The AOS results correlated well with biodegradation results, as the smallest change was for the veneer-water, where no biodegradation effect was observed.

6. CONCLUSIONS

EC is a treatment option that has produced good results for different cleaning wastewaters. However, results presented in **Paper I** showed that despite this, some of the cleaning wastewaters investigated were completely resistant to the EC treatment. The problem was overcome by combing EC with sorption and the correct sequencing produced good treatment efficiency. EC was proved to be useful as a pretreatment and as a post-treatment, in a system coupled with AC sorption for treating cleaning wastewater. However, for the most effective result, one wastewater (hardener) had to be left out of the pretreatment. The main issue with EC and sorption was, however, that the pollutants are not destroyed: they are only transferred to a solid medium; additionally, the results in **Paper I** did not indicate that EC would generate an effluent clean enough for discharge, and therefore, a better treatment option is required.

AOPs could be that option and among them, the Fenton treatments (**Papers II and III**) give better results than the ones obtained with EC (**Paper I**). In general terms, high COD and TOC reductions were achieved (approximately 75% and 60%, respectively) in a single treatment. There were only small differences between using FeCl or nZVI as a catalyst and the photo-Fenton process appeared to be more effective than the dark-Fenton process. In particular, this was true when using nZVI as a catalyst, likely because UV light enhanced the solubility of nZVI; the fact that more similar results were found for FeCl and nZVI when using photo-Fenton would indicate that one of the main limiting factors when using nZVI is the solubility of the Fe powder. The Fenton treatments were an improvement over EC because the pollutants were

mineralized to the same or a higher degree than with EC. However, there was still a solid phase issue with the Fenton process, the handling of the iron sludge after the treatment has finished, even if nZVI has proved to reduce this problem.

To remove or to reduce the issue of handling solid by-products as much as possible, the present thesis included investigations with ozone-based treatments. Ozone treatment at the natural acidic pH of the studied cleaning wastewater substantially reduced COD and TOC in the wastewater (by about 65% and 30%, respectively). This was not quite as good as the best results with photo-Fenton, and the respirometry assays showed that the biodegradability of water was actually lowered as an effect of the treatment. It has previously been shown that the ozone treatment usually works better at high pH. When the pH_0 of the cleaning wastewater was raised to pH 7, the ozone treatment results were in the same range as the best results for photo-Fenton (roughly 85% and 40%, respectively, for COD and TOC). The combination with UV light produced significant improvement regarding TOC reduction (approximately 50%). No significant improvement was achieved for the COD reduction (approximately 90%), but the highest oxygen consumption during the respirometry study was found for the cleaning wastewater treated with O_3/UV. However, both O_3/pH_{adj} and O_3/UV produced an effluent that was significantly more biodegradable than the control and the effluent from the O_3/pH_{low} treatment.

The most important result to be applied in a future full-scale plant is the reduction of the time it took for the effluents from the O_3/pH_{adj} and O_3/UV treatments to reach the microbial metabolic rate peaks. This time was reduced from 24 h for untreated cleaning wastewater to less than 1 h for the treated cleaning wastewater, which is an important factor for an on-site biological post-treatment or at an MWWTP.

Another relevant aspect is that this type of on-site biological treatment could combine the treatment of storm-water and cleaning wastewater, because the storm-water from the case-study site proved to be treatable with ozone, with COD and TOC reductions of around 70% and 60%, respectively. However, the main goal of the ozone treatment for storm-water was not complete

mineralization, but to apply ozone to enhance the biodegradability of the storm-water. Because of this, a more important factor was the fact that around 85% of the PP was removed by the ozone treatment. When storm-water with 35% and 75% less PP than the control (PP was degraded by ozone treatment) was studied for the effect this had on the biodegradability of the storm-water, it was shown that for one sample (Storm-water 2) there was a positive effect when 70% of the PP was removed, but a toxic effect when only 35% was removed. No positive effect was seen for Storm-water 1. These results correlate with what was found for the cleaning wastewater, where more powerful ozone treatments were needed to achieve satisfactory results regarding improvements in biodegradation.

The conclusion from the ozone treatability studies was that for the cleaning wastewater, ozone AOPs can produce an effluent that could be suitable for biological treatment and that O_3/UV produces the largest improvement in biodegradability and the highest reduction in COD and TOC. For storm-water, ozone treatment has to be seen as a powerful treatment option for the reduction of COD, TOC and particularly PP, but the low increases in biodegradability reduces the suitability of this treatment for storm-water.

In general, the present thesis has shown a large range in treatment effectiveness for some treatments for wastewater from the same industry. It has also discussed how important it is to combine general parameters such as COD and TOC with toxicity and biodegradation studies, as even substantial reductions in COD and TOC have shown no improvement in biodegradation or in some cases, even a reduction in biodegradation after treatment. The AOS value has been shown (**Papers IV and V**) to be a good indicator of reduction in toxicity and enhanced biodegradation, which confirmed the findings of some previous studies (Elmolla and Chaudhuri, 2009, Sirtori et al., 2009).

Among all treatment approaches, the most successful one was the combination of O_3/UV, which promoted very high degradation of the pollutants and generated an effluent with high biodegradability with a minimal solid phase.

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7. RECOMMENDATION

In 1999, the Swedish parliament set 16 environmental quality objectives to be met by 2020. The Swedish Environmental Protection Agency has proposed an intermediate objective for the environmental objective system that is focused on stimulating increased resource economizing and recycling of nutrient materials that are free of hazardous materials to the extent possible (Swedish EPA, 2013). To increase resources economizing and the recycling of nutrient materials (MWTTP sludge), keeping it free from hazardous materials to the extent possible, industrial wastewaters need to be kept out of the MWTTP wherever possible. Because of this, the recommendation for industries with wastewaters similar to those addressed in the present thesis would be to aim for a complete on-site treatment system. Ozone-based AOPs have been shown to be effective for these types of cleaning wastewaters, and encouraging results indicated that combining ozone/UV with a biological treatment would generate an effluent that could safely be discharged to a recipient water body, possibly in combination with treated storm-water.

7.1 Future Research

Because of the recommendations, there is a need for more research assessing possible effects by combining storm-water and cleaning wastewater. Possible positive effects could be found by utilizing the high PP content of storm-water to enhance the treatment of the cleaning wastewater, as it is known that phenol enhances ·OH production during ozone treatment (Sang-Kuk, 2004). Future investigation should also include the possible effects the mixture of cleaning wastewater and storm-water could have on the biological treatment.

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