LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

LUT School of Engineering Science

Degree Program in Chemical Engineering

Master's Thesis

Pulsed corona discharge and membrane filtration for purification of lettuce washing waters

Tommi Johansson

2016

TIIVISTELMÄ

LAPPEENRANNAN TEKNILLINEN YLIOPISTO
Teknillinen tiedekunta
Kemiantekniikan koulutusohjelma
Tommi Johansson

Pulssitettu koronapurkaus ja membraanisuodatus salaatin pesuvesien puhdistuksessa

Diplomityö, 2016
87 sivua, 49 kuvaa ja 22 taulukkoa
Työn ohjaajat: Professori Mika Mänttäri, Tutkijaopettaja Mari Kallioinen
Hakusanat: Pulssitettu koronapurkaus, nanosuodatus, hapetus, salaatin pesu, vedenpuhdistus

Pesuprosessit kuluttavat suurimman osan tuoretuoteteollisuudessa käytetystä vedestä. Tässä työssä tutkittiin hapetusta pulssitetulla koronapurkaustekniikalla ja membraanisuodatusta salaatin pesuvesien puhdistamiseen. Työn kirjallisuusosassa vertailtiin erilaisten hapetusmenetelmien soveltuvuutta prosessivesien käsittelyyn.

Pulssitetun koronapurkauksen tutkittiin hajottavan humushappoja ja pesuveden orgaanista ainesta. Hapen lisäys ja korkea lämpötila paransivat hapetusta. Veden UV-absorptio eri aaltopituuksilla väheni nopeasti käsittelyn seurauksena, kun taas orgaanisen aineksen täydellinen hajoaminen tapahtui hitaasti kokonaishiilipitoisuuden muutoksen perusteella. Veden johtokyky kasvoi oletettavasti nitraattien muodostumisen vuoksi. pH vuorostaan laski orgaanisten happojen muodostumisen seurauksena. Salaatin pesuvesissä oli paljon liuennutta orgaanista ainesta, josta 85 % oli riittävän pienikokoista läpäisemään 600 g/mol erotuskyvyn nanosuodatusmembraanin.

Testatuista membraaneista polymeerinen NF270 membraani antoi parhaan erotuskyvyn sekä orgaanisten (78 %) että epäorgaanisen (34 %) yhdisteiden suhteen ja myös hyvän permeabiliteetin. Lisäksi kyseinen membraani likaantui vähiten tutkituista membraaneista. Koronapurkauksella tehty hapetus laski permeabiliteettia yhdistetyssä kokeessa keraamisella membraanilla. Tulosten perusteella membraanisuodatus vaikutti lupaavammalta menetelmältä runsaasti orgaanista ainesta sisältävän salaatin pesuveden puhdistukseen kuin hapetus.

ABSTRACT

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

LUT School of Engineering Science

Degree Program in Chemical Engineering

Tommi Johansson

Pulsed corona discharge and membrane filtration for purification of lettuce washing waters

Master's thesis, 2016

87 pages, 49 figures and 22 tables

Supervisors: Prof. Mika Mänttäri, Ass. Prof. Mari Kallioinen

Keywords: Pulsed corona discharge, nanofiltration, oxidation, salad washing, water treatment

Washing processes constitute most of the water used in fresh-cut industry. Pulsed corona discharge (PCD) as an advanced oxidation process and membrane filtration were studied as possible treatment methods for lettuce washing waters. In the literature part, usability of different oxidation methods for treatment of process water was compared.

PCD effectively degraded humic acids and organic material found in the washing water. Oxygen injection and increase in temperature improved the oxidation efficiency. Total mineralization of organic material was not achieved. Conductivity of water increased, likely due to formation of nitrates. pH decreased when organic compounds were presumably degraded into organic acids. Washing water was measured to contain high amount of dissolved organic material, 85 % of it was small enough to penetrate the nanofiltration membrane with molecular weight cut-off of 600 g/mol.

Among tested membranes, polymeric nanofiltration NF270 membrane showed best retention for organic (78 %) and inorganic (34 %) compounds, good permeability and least fouling. PCD decreased permeability in combined experiment with a ceramic membrane. Nanofiltration seemed to be more promising method to purify lettuce washing waters having high concentration of organic compounds than oxidation.

ACKNOWLEDGEMENTS

I have spent awesome five years in Lappeenranta and met people, who have given me motivation to go on with my life and studies without severe problems. I would like to thank all the friends who are today standing next to me. One can only imagine what the future looks like.

I would like to express my gratitude towards my supervisors Mika and Mari, who helped and trusted me, while giving me relatively free hands with the research plan. I have learned many things about research process during this thesis work. I also want to thank the laboratory engineer Tuomas for helping me with various tasks and building the experimental setups, and Liisa with issues related to analysis equipment.

Finally, warm thanks for my parents for always supporting me, and my sisters for inevitable life-long relationship. Without the countless sage advice I have got from my father during the years, I might not be in this situation today.

Tommi Johansson

Lappeenranta, 28.12.2016

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

AOP	Advanced oxidation process
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
FS	Fixed solids
HA	Humic acid
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural organic matter
NTP	Non-thermal plasma
NTU	Nephelometric turbidity units
PCD	Pulsed corona discharge
SUVA	Specific ultraviolet absorption
TDS	Total dissolved solids
TMP	Transmembrane pressure
TOC	Total organic carbon
TS	Total solids
TSS	Total suspended solids
VRF	Volume reduction factor
UF	Ultrafiltration
UVA	Ultraviolet absorption

LIST OF SYMBOLS

C	Concentration	mg/l, ppm, ppb
E	Energy	J
f	Frequency	Hz
J	Flux	$kg/(m^2h)$
k	Permeability	$kg/(m^2hbar)$
M	Molar mass	g/mol
P	Power	W
p	Pressure	bar
Q	Volumetric flow rate	l/min
U	Voltage	V
V	Volume	l, m^3
T	Temperature	ºC
t	Time	h, min
λ	Conductivity	mS/cm
η	Dynamic viscosity	kg/(ms)

INTRODUCTION

Vegetables are washed to remove dirt, pesticide residues, microorganisms and bacteria. Fresh-cut products, especially lettuce, are one of the most common sources of food-borne diseases due to insufficient washing and disinfection. In typical fresh-cut industry operations, washing water constitutes almost 90% of the total water usage. Total water consumption is between 2 – 11 m^3 per ton of fresh-cut produce. Minimization of water consumption and wastewater discharges is nowadays one of the mayor challenges of food industry. Water usage adds expenses and producing high amount of wastewater impairs the public image of company. Water use and energy requirements could be decreased by recycling the waters used for washing. To make re-use possible, microbes and bacteria have to be removed and organic load decreased. Sedimentation, flotation, granular filtration, activated sludge treatment, chemical disinfection and several other techniques are traditionally used to clean wastewaters from food industry. [1, 2]

The purpose of this work is to evaluate, if pulsed corona discharge (PCD) oxidation and membrane filtration are suitable modern processes for cleaning of lettuce washing waters. Theoretical part gives an introduction to fresh-cut industry washing waters and water quality analysis. It also summarizes different advanced oxidation processes and their effects for treatment of different water samples, especially those containing organic material and bacteria. Principles of membrane filtration and PCD oxidation, as well as general performance of combined oxidation – filtration process are also presented.

In the experimental part of this thesis, effect of pulsed corona discharge oxidation in pure water, tap water and humic acids solutions is first evaluated. Formation of ozone during PCD treatment is monitored, and effect of different conditions like temperature and oxygen injection for treatment is studied. PCD is combined with ceramic membrane nanofilter to measure effects of oxidation for permeate flux and quality. Water quality parameters like ultraviolet absorption, total organic carbon, conductivity and pH are used to analyze, how composition of solution changes during the PCD treatment. Later on, two batches of lettuce washing water are obtained from a production plant and filtrated with several nano- and ultrafilters. Permeate flux during the filtrations is measured and quality of filtrated water is analyzed. PCD is used in direct treatment of washing water. PCD treatment is also combined with membrane filtration and it is applied as a post-treatment of membrane permeates. Objectives are to find suitable membrane, conditions and sequence for cleaning of the washing waters.

I THEORETICAL PART

1. Fresh-cut industry washing waters

The typical process flow diagram of fresh-cut industry is presented in Figure 1. Raw lettuce is first washed to prevent gross contamination, cut, washed again, rinsed and dried. Finally, the product is packed and stored. Water is mainly used for primary washing, main washing and rinsing of the product [1]. Washing is the final cleaning process of a fresh-cut product, and therefore maintaining the quality of washing water is highly important. [3]

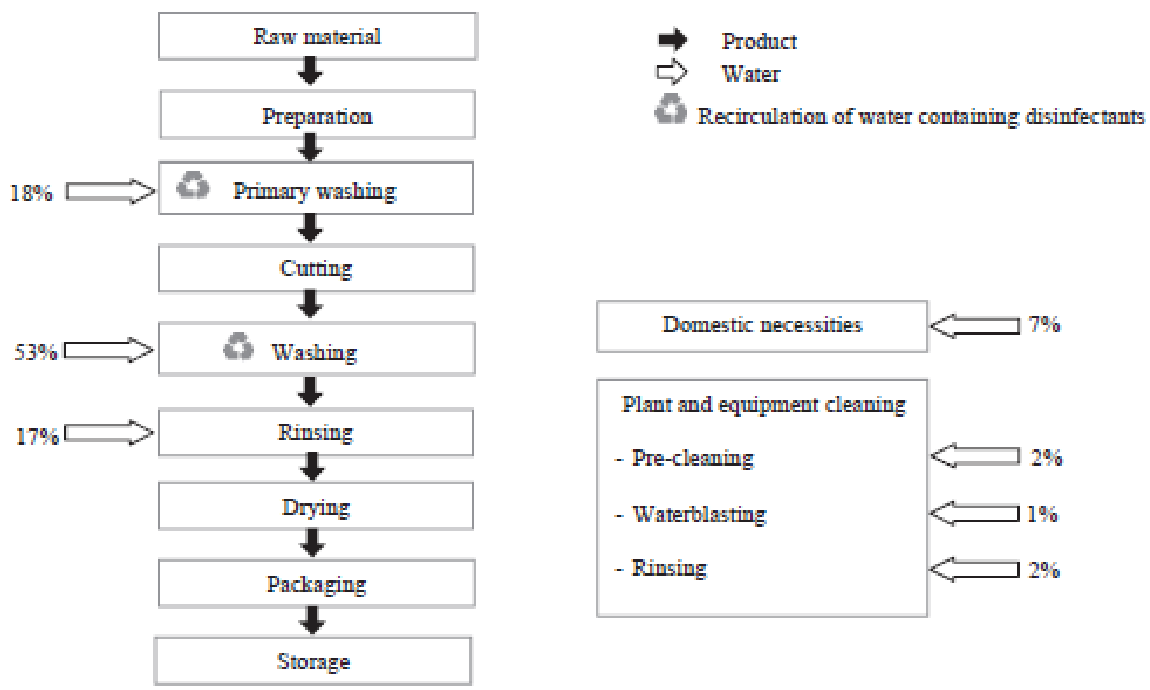


Figure 1: Typical process flow diagram of fresh-cut salad production. Water needed per step is shown with arrows and expressed as volume percentage of total water required in the process. [1]

The main objective of washing water purification is to remove bacteria and other microorganisms. Fresh-cut products itself are also commonly disinfected in addition of washing waters. Most common bacteria causing infections are Salmonella and Escherichia Coli. Cross-contamination is one of the mayor risks in processing facility, that occurs when active bacteria and microorganisms spread in the water from one production line to another [2]. Bacterial disinfection is traditionally performed with chemicals like chlorine, iodine and hydrogen peroxide. Microorganisms are sensitive to heat, which can be used directly to kill them or to enhance other treatments. [4]

Another target of washing water purification is to decrease the amount of organic compounds in water, which is high due to presence of dissolved soil and plant residues. Exact organic composition of lettuce washing water is difficult to predict for a certain water batch. Schmidt et al. [5] analyzed the quality of various leafy greens, like iceberg and romaine lettuce. Dry iceberg lettuce consisted of 13.1% cellulose, 16.9% hemicelluloses, 12.2% starch, 21.9% protein, 6.3% fat and 33.8% free sugars (fructose, glucose, sucrose). They also found trace amounts of organic acids, fructan and pectin. These components can get to washing water as plant residues. The pesticides used in the production plant are also transferred to washing waters, increasing the amount of harmful organic compounds.

1.1. Organic material in surface waters

Natural organic matter (NOM) comprises a mixture of organic material, like humic substances, polysaccharides, proteins, small organic acids, peptides etc. NOM can be classified into two groups: autochtonous NOM which origins mainly from extracellular parts of microorganisms, and allochthonous NOM which comes from decay of plant and animal residues. The latter is usually referred to as humic substances, and is the most common part of NOM. Humic material represent almost 80% of the total organic carbon (TOC) in the natural waters. It is divided to humic acids and fulvic acids. Humic acids have a molecular mass of 2000-5000 g/mol and fulvic acids 500-2000 g/mol, respectively. [6, 7]

Humic acids (HA) have aromatic structure and consist mainly of carboxyl, phenolic, carbonyl and hydroxyl groups. They are not dangerous for humans, but affect the color, taste and smell of water. They can also work as a substrate for the growth of microorganisms. They have strong bonding ability with many heavy metals and organic pollutants, which can make these harmful compounds more difficult to remove. Furthermore, humic acids are important precursors in formation of disinfection by-products (DBP). [8]

1.2. Water quality analysis

Several analysis techniques are used to determine the composition of waters containing organic material and bacteria. The most common methods are presented in Table I.

Table I: Analysis methods for different constituents present in water

What is analyzed	Method	Abbreviation
Amount of bacteria	Growth of culture	FC
Amount of organic substances	Total organic carbon	TOC
	Dissolved organic carbon	DOC
	Chemical oxygen demand	COD
Amount of solids	Total solids	TS
	Total dissolved solids	TDS
	Total suspended solids	TSS
	Fixed solids	FS
	Volatile solids	VS
Identification of organic and inorganic substances	Chromatography	HPLC, GC
	Spectrometry	MS, IR, UV-Vis

Amount of bacteria is typically calculated in colony forming units, so called fecal coliforms (FC) in a certain volume. Bacterial reduction is expressed in logarithmic scale. According to Manzocco et al. [1], 5 Log reduction of pathogenic bacteria is generally considered to fulfil the requirement for safe water disinfection and its possible recycling. Reduction of 5 Log means that the amount of bacteria would be 100 000 times smaller. According to standard, the analysis is performed using culture based methods. Water sample is placed onto a petri dish containing a growth medium for bacteria, usually agar. The agar plate is then incubated for one to three days in specific temperature (usually around 35^{o}C) to allow bacterial growth. The growth medium has to be suitable for the microorganism to be studied, since some bacteria can only grow on certain agars [9]. Bacteria can also be filtrated prior to analysis through 0.45 µm membrane filters. The filters containing bacteria are placed on absorbent pads or petri dishes containing for example membrane lauryl sulphate or membrane lactose glucuronide agar. After incubating, number of bacteria colonies on the dish is counted and reduction is calculated [10]. Prior to analysis, the residual oxidants can be neutralized by chemicals for example sodium thiosulphate. Samples are diluted if there would be too many colonies growing on the plate to allow manual counting. [3]

Amount of organic material in a sample can be determined by organic carbon or chemical oxygen demand analysis. According to European standard, total organic carbon (TOC) is “a measure of the carbon content of dissolved and undissolved organic matter present in the water.

It does not give information on the nature of the organic substance". All carbon in the sample is oxidized to carbon dioxide and the amount of CO_2 is measured by for example infrared spectrometry. Inorganic carbon is removed by acidification, which finally gives the TOC value. To measure the dissolved organic carbon (DOC), the water sample has to be first passed through a 0.45 µm filter to remove the suspended matter, but otherwise the procedure is similar. In chemical oxygen demand analysis, organic matter is converted to CO_2 and H_2O in reaction with dichromate in an acidic solution. The amount of organic compounds is proportional to the consumed dichromate [11]. Automatic analyzers are commonly used to determine these parameters. [12]

Total solids (TS) is determined by drying a liquid sample in oven at 100-105^{o}C for several hours using a suitable aluminum or ceramic dish. The residual contains all the suspended and dissolved solids of the sample. Total suspended solids (TSS) are measured by filtrating the sample through a glass microfiber filter, typically 0.45 µm, which is dried and weighted. Total dissolved solids (TDS) can be calculated by subtracting TSS from TS. For more detailed analysis, sample is heated at high temperature 550^{o}C furnace. The residue after heating is called fixed solids (FS) and contains inorganic substances, while organic substances are combusted (evaporated) as volatile solids (VS). [13, 14]

Several chromatographic and spectrometric techniques are used for detailed structural analysis and identification of organic and inorganic compounds. Mass spectroscopy (MS), infrared spectroscopy (IR), ultraviolet-visible spectroscopy (UV-Vis), high pressure liquid chromatography (HPLC) and gas chromatography (GC) are the most commonly applied methods. In chromatography, functional groups can be detected based on their retention time in columns. Optical spectrometry is based on light absorption of different wavelengths of the solution. In mass spectrometry, species are ionized and sorted based on their mass to charge ratio. [15]

Spectroscopy in ultraviolet wavelengths is commonly used to measure degradation of organic compounds. Wavelengths 254 nm (UVA_{254}) and 280 nm (UVA_{280}) are typical for analyzing of aromatic and unsaturated groups present in sample. Aromatic and unsaturated bonds are primarily broken, when organic compounds are oxidized [16]. Specific UV absorbance (SUVA) is calculated by UVA_{254} (absorbance per meter) divided by TOC (mg/l). SUVA value describes the ratio of hydrophilic to hydrophobic substances in the sample. SUVA values higher than 4 correspond to mainly hydrophobic, especially aromatic compounds. UV_{254}/UV_{365} absorbance ratio can be used to compare the amount of organic small molecular weight substances to large molecular weight ones. [17]

2. Oxidation processes

Oxidants cause other substances to lose electrons and become oxidized. Oxidation can be used as purifying method to degrade and reduce organic matter and/or to disinfect water by destroying the structure of microorganisms. Several processes are presented in this chapter, while main attention is paid into radical based and ozone containing methods. Oxidation primarily degrades organic matter into smaller molecular weight fractions. Complete mineralization of organic compounds into CO_2 and H_2O can be difficult to achieve. [18]

Advanced oxidation processes (AOP) are nowadays widely used and studied [2]. AOPs are based on production of highly reactive radicals like OH·, H· and O·. Hydroxyl radical (OH·) is the most important and has a high oxidation potential 2.8 V, which makes it the second strongest oxidant after fluorine. Oxidation is non-selective, which means that the radicals react with most functional groups in the organic and inorganic material. The lifetime of hydroxyl radical is only few nanoseconds at lowest, so the generation of radicals has to be performed in-situ of treatment [19]. [6]

Many species present in wastewaters work as scavengers of the radicals, reacting with them before they can attack to microorganisms or organic contaminants. As a result of these reactions, harmful disinfection by-products (DBP) can be formed. Scavengers can be organic or inorganic substances, like humic acids, proteins, carbohydrates, chlorides, sulfites, bicarbonates and carbonates [20]. For example, when both chloride and hydroxyl radicals are present in the water, undesired chlorate and perchlorate may form [21].

2.1. Oxidation with ozone

Ozone (O_3) is a strong, selective oxidant with an oxidation reduction potential 2.07 V. Ozone also initiates formation of hydroxyl radicals in presence of OH^- ions, as shown in reactions (1) and (2). These reactions are highly favorable in alkaline conditions, namely pH values over 7. [22]

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (1)$$

$$O_3 + HO_2^- \rightarrow \mathrm{OH} \cdot + \cdot O_2^- + O_2 \quad (2)$$

Ozone can be generated in-situ for example by ultraviolet irradiation, electrochemical methods or corona discharge. Many researchers have used oxygen generators, which produce ozone via corona discharge method [21, 23]. Ozone has a moderate solubility in water, which can be improved by turbulence, mixing, bubbling, increasing the pressure or lowering the temperature [24, 25].

2.1.1. Ozone decomposition and oxidation kinetics

Immediate ozone demand is the maximum amount of ozone consumed in the reactions with water components immediately. Therefore, immediate demand is the point when ozone starts to concentrate in the water in continuous addition. High amount of residual ozone should be avoided to keep the costs low and save processing equipment. Ozone can be removed after the oxidation by so called ozone trappers, aeration step, or sufficient mixing within some time. However, this increases expenses due to installation of additional equipment. Suitable ozone dosage depends on many factors, like properties of the treatable water, contact time and contact surface area between ozone and water [17]. [27]

Decomposition time of ozone depends on the temperature, pH, water characteristics and ozone concentration. Increasing temperature and pH of water generally accelerates the decomposition. Since ozone reacts with various water components, the decomposition time is faster in wastewaters than in pure water. Decomposition time is difficult to predict due to variety between different water samples. Half-life time of ozone in water has been measured to vary between microseconds to several hours. [26, 27]

Sotelo et al. [27] investigated the influence of temperature and pH for ozone decomposition in distilled water pH-adjusted with disodium phosphate and potassium phosphate. Their results can be seen in Figure 2 and Figure 3. At temperature of 40°C, almost 80% ozone was decomposed after 13 minutes. At temperature of 10°C, only 15% ozone was decomposed in the same time. At temperature of 30°C and pH 9, over 80% of ozone had been decomposed in 4 minutes, while the decomposition was only 10% if pH was 7. The half-life of ozone in 20°C was measured as 9 min in pH 9 and as 70 min in pH 5.

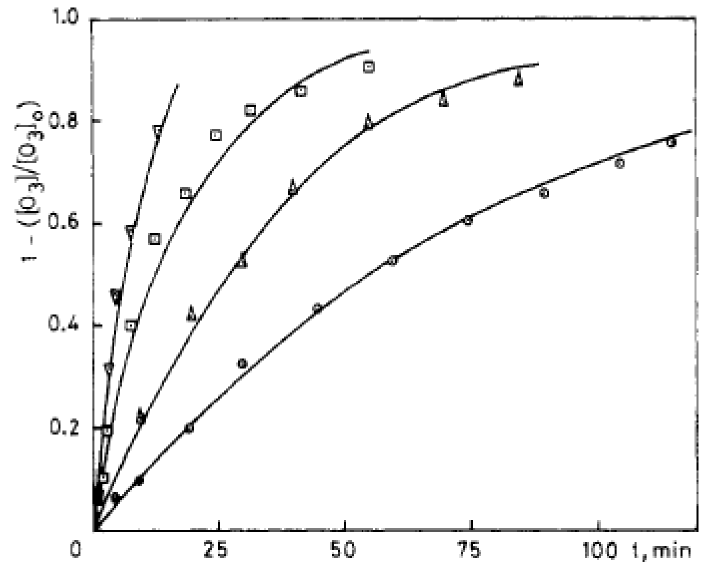


Figure 2: Decomposition time of ozone in water and its dependency on temperature. pH 7, agitation speed 100 rpm. Temperature: (o) 10°C (Δ) 20°C (□) 30°C (∇) 40°C. [27]

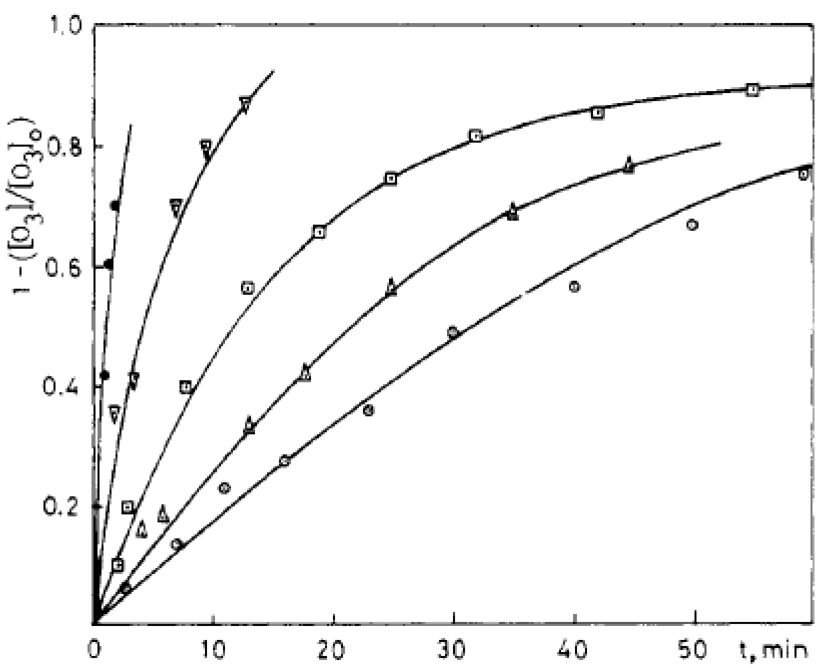


Figure 3: Decomposition time of ozone in water and its dependency on pH. Temperature 30°C, agitation speed 100 rpm. pH: (o) 2,5 (Δ) 5 (□) 7 (∇) 8 (·) 9. [27]

Kinetics of ozonation reactions are different in acidic and basic conditions. Increase in pH-value increases the amount of hydroxyl radicals due to faster decomposition of ozone [18]. In acidic conditions, ozone itself reacts selectively with unsaturated and aromatic groups in organic material [28]. Oxidation is usually more efficient in alkaline conditions. Turhan et al. [29] achieved COD removal of 23% at pH 6.5 and 65% at pH 12, when they treated dyes (400 mg/l) in a wastewater with ozonation for 120 min. Buyn et al. [23] used ozone in treatment of humic acid solutions. Ozonation decreased TOC when pH was between 7-11.4. At low pH 2.8, no change in TOC nor structure of humic acids was noted. This was explained by poor reactivity of ozone with saturated bonds in HA structure. At pH 11.4, indirect radical pathway was dominating and led up to 62% decrease in TOC.

2.1.2. Oxidation of organic matter

When organic material is degraded by ozone oxidation, products typically contain aldehydic, ketonic and carboxylic groups [30]. Ozonation can decrease the pH of solution when organic matter is degraded into organic acids. Byun et al. [23] noted that pH of humic acids solution decreased to 5.2 or less from initial pH of 7, when the solution was ozonated. Ozone is often combined with catalysts, hydrogen peroxide and/or ultraviolet light to increase the formation rate of radicals and performance of oxidation [18, 22].

As a result of oxidation in samples containing organic matter, significant reduction of UV-absorbance can be measured, while decrease in total organic carbon is low or even zero. Explanation for this is the degradation of organic compounds to smaller molecular weights substances, which does not significantly affect the amount of carbon measured [31, 17]. Examples of differences in reduction of DOC and UV absorption in different water samples are shown in Table II.

Table II: Results obtained with ozone oxidation in various water samples

Water type (source)	Water characteristics	Ozone dose, contact time	DOC removal	Reduction of UVA_{254}
River water [32]	DOC 5.1-6.6 mg/l, NTU 13.7-75	1.5 mg/l, 10 min	9.6 %	43 %
		3 mg/l, 10 min	10 %	71 %
Surface water [30]	COD 44 mg/l	3 mg/l, 30 min	25%	68 % (UVA_{275})
Secondary effluent [31]	DOC 4.2 mg/l, NTU 0.4-1.8, alkalinity 140 mg/l	4 mg/l, single dose	0 %	47%

Change in oxidative effect is greatest, when low ozone concentrations are used. Geluwe et al [20] investigated the influence of ozone concentration to reduction of organic material. Figure 4 presents the effect of concentration for reduction of COD and UVA_{254}. With gas phase ozone concentrations higher than 17 mg/l, removal of organic matter did not increase significantly. Only 13% better UVA_{254} reduction was observed when ozone concentration was increased from 17 mg/l to 89 mg/l. Gas phase ozone concentration of 17 mg/l corresponded to 3 mg/l concentration in liquid phase.

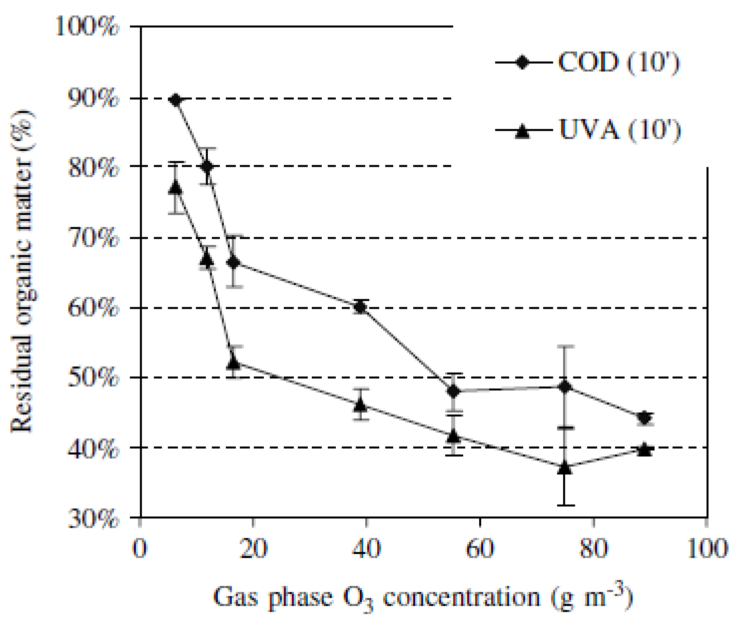


Figure 4: Effect of ozone concentration to residual COD and UVA_{254}. Treated sample was surface water from river (COD 83 mg/l). Ozone flow rate of 60 l/h during 10 min. [20]

2.1.3. Disinfection with ozone

Similarly than in oxidation of organic material, undirect radicals reactions with micro-organisms are increased when the pH and temperature of water are increased. High temperatures are favorable, because heat has a synergetic effect for inactivation of bacteria. Presence of organic content in water diminishes disinfection due to competitive reactions. Disinfection with ozone can be improved by combination of for example hydrogen peroxide, dimethyl dicarbonate (DMDC) or ultraviolet light [4].

Williams et al. [9] investigated the effect of ozone for disinfection of Esterechia Coli and Salmonella in cold (4°C) juices (pH 3.8) containing organic material. They showed, that disinfection of bacteria continues during storage at low temperature. 0.8 Log bacteria reduction was achieved after 60 min ozone (9 g/l) treatment and 24 h storage at 4°C. Combination of ozone treatment with H_2O_2 or dimethyl dicarbonate (250-600 ppm) achieved as high as 5 Log reductions in same conditions. Without storage the disinfection resulted in 2 Log reduction in combined treatment and hardly any reduction in plain ozonation.

2.2. Chlorine oxidation

Chlorine is the most widely used disinfectant because of its availability, low cost and expected effectiveness. Usually sodium hypochlorite (NaClO), calcium hypochlorite ($Ca(ClO)_2$), hypochlorous acid (HClO) and chlorine dioxide (ClO_2) are used as chlorine sources. Recently, outbreaks connected to pathogen contaminated fresh-cut vegetables has raised questions about disinfection efficiency of chlorine. Reactions of chlorine with natural organic matter (NOM) may also result in formation of harmful disinfection byproducts, like trihalomethanes and haloacetic acids. Moreover, disinfection with chlorine can produce high amount of wastewater. Chlorine dioxide is considered as more environmental chlorine source than the others. [1, 33]

Bacteria can develop resistance to common chlorine based sanitizers. As a result of that and differences between bacteria and water samples, various disinfection results have been reported. In study by Lee et al. [34], chlorine dioxide (4.3 mg/l) applied directly to lettuce surface reduced E. coli by 3.4 Log, Salmonella by 4.3 Log and L. monocytogenes by 5.0 Log after 30 min treatment. Manzocco et al. [1] reported that concentration of 50-200 mg/l free chlorine is able to achieve 6 log reduction of bacterial load. However, Mukhopadhyay et al. [4] claimed that with concentrations 50-125 mg/l of chlorine, its disinfection efficiency is limited to 1-2 Log reductions. In general, high chlorine doses are needed for effective disinfection compared to for example ozone.

Chlorine has been used in oxidation limitedly. Jin et al. [35] studied UV light and chlorine as a combined advanced oxidation process. When aqueous chlorine is exposed to UV light, hydroxyl radicals are formed. The production rate of radicals was shown to be only half of the rate with UV/H_2O_2 process, and so the degradation of organic compounds significantly less effective.

2.3. Hydrogen peroxide oxidation

Hydrogen peroxide is a good oxidant with a redox potential of 1.8 V. It is often used in combination with ozone or ultraviolet light oxidation. It is also a key component in the Fenton processes. H_2O_2 decomposes to form highly reactive hydroxyl radicals in the presence of ozone (reaction 3), light (reaction 4) or ferric ions (Fenton process). [17, 6, 8]

$$H_2O_2 + O_3 \rightarrow OH^- + \mathrm{OH}\cdot + O_2 \tag{3}$$

$$H_2O_2 + hv \rightarrow \mathrm{OH}\cdot + \mathrm{OH}\cdot \tag{4}$$

Hydrogen peroxide is produced commercially by oxidation of anthrahydroquinone. Alternative methods have been developed, because the production costs are high and the formed product has to be concentrated. Hydrogen peroxide can be produced in direct reaction of hydrogen and oxygen in the presence of a catalyst, but the process presents some challenges like side reactions and decomposition of the product. Transportation, handling and storage of high quantities of hydrogen peroxide is also challenging. Oxidation methods like ozonation, photocatalysis, electrochemical oxidation and pulsed corona discharge can be used to produce H_2O_2 in-situ of the treatment. Produced radical species in water can form H_2O_2 and in turn decompose it, as shown in reactions 5-7. [28]

$$\mathrm{OH}\cdot + \mathrm{OH}\cdot \rightarrow H_2O_2 \tag{5}$$

$$\mathrm{OH}\cdot + H_2O_2 \rightarrow H_2\mathrm{O} + \mathrm{H}O_2\cdot \tag{6}$$

$$\mathrm{H}O_2\cdot + H_2O_2 \rightarrow H_2\mathrm{O} + O_2 + \mathrm{OH}\cdot \tag{7}$$

H_2O_2 improves the oxidation efficiency in combined $O3/H_2O_2$ (perozonation) process, when compared to ozonation only. Optimal ratio of hydrogen peroxide to ozone dosage has been reported to be between 0.2 to 1. Removal rate of DOC from surface water improved from 53% to 61%, when 0.7 mg/l hydrogen peroxide was added prior to 2 mg/l ozone. Geluwe et al. [30] discovered that reduction of UVA_{280} in solution of humic acids increased from 42% to 54%, when 0.25 mol H_2O_2 was added per one mol of ozone. Low amount of H_2O_2 (less than 1 mol H_2O_2/mol O_3) is usually most practical, because excessive amount of hydrogen peroxide acts as a scavenger of OH· radicals. Hydrogen peroxide enhances the oxidation especially when organic matter content in water is low (less than 3 mg/l DOC). In high concentrations of organic compounds, ozone decomposition is accelerated by certain functional groups in the organic matter. [6]

Perozonation, like ozonation, is usually more effective in basic condition. Chen et al. [36] studied a catalytic perozonation process for removal of acetic acid in low pH values. The reactor contained 0.6 l solution of acetic acid in room temperature, and ozone was added in a flow rate of 41 mg/min. Ozone or $O3/H_2O_2$ oxidation could reduce the concentration of acid by maximum of 5.6% in 30 min, when pH of the solution was 3. When catalyst TS-1 was added to the solution, removal rate of acid increased to 29%. Deprotonation reaction of H_2O_2 (formation of HO_2^-) is difficult to proceed in pH values lower than 5. Increasing concentration of H_2O_2 from 100 mg/l to 300 mg/l improved the production rate of radicals and removal of acetic acid to 39%.

2.4. Oxidation with ultraviolet light and photocatalysis

Ultraviolet (UV) light can be used to degrade many different organic contaminants within a wide concentration range. It can be used either for direct oxidation, disinfection of bacteria or to enhance other oxidation technologies. Irradiation time is typically from seconds to one minute within wavelength range of 220 – 280 nm. Sometimes pulsed light is used, which includes flashes ranging from micro- to milliseconds and utilizes wide (100-1100 nm) wavelength range. [1, 4]

UV light is commonly used to break hydrogen peroxide and ozone into reactive radicals. Elevated temperature improves the production rate of radicals and synergetic effect of light and H_2O_2. Mukhopadhyay et al. [4] revealed that UV/H_2O_2 treatment with light intensity 0.63

mW/cm^2 and H_2O_2 (1.5%) achieved over 4 Log reduction of Salmonella attached in lettuce at temperature of 50°C. Jeirani et al. [37] compared an oxidation process, which was based on the combination of UV light and O_3, to ozonation and UV irradiation processes. Application of UV light reduced hardly any DOC, while UV light combined with ozone treatment could lead to high DOC reduction (89%). Efficiency of this treatment improved with increasing ozone dosage up to 15 mg/l. Koutahzadeh et al. [38] compared UV light treatment with various AOP:s in the degradation of synthetic dye. UV light alone enabled 83% degradation, but only 17% mineralization of dye in 45 minutes irradiation. Combined processes, including UV light combined with either H_2O_2 or TiO_2, achieved 99.9% degradation and 83% mineralization. These studies support the deduction that UV light is insufficient oxidation method when used alone.

Photocatalysis utilizes a light source and a semiconductor photocatalyst to initiate chemical reactions. First photocatalyst absorbs radiation and excites valence band electrons (e^-) and holes (h^+). Holes generate hydroxyl radicals in reactions with water, as seen in the reactions 8-9, or react directly with the organic substances.

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + H^+ + OH^{\cdot} \tag{8}$$

$$TiO_2(h^+) + OH^- \rightarrow TiO_2 + OH^{\cdot} \tag{9}$$

Valence band electrons reduce dissolved oxygen to superoxide radicals and further to hydroxyl radicals. Properties of a photocatalyst, like photoactivity, non-toxicity, inertness and expenses are important factors. TiO_2 is the most popular photocatalyst, as it has high activity, low toxicity, good stability and low production costs. Light source can be for example UV or solar light. Most photocatalysts need UV light wavelengths to activate, and because only 5% of solar light reaching the earth is UV light, sun light is not an efficient source. However, photocatalysts can be modified to utilize visible light wavelengths. [18, 39]

Photocatalysis is considered as environmental friendly oxidation process. However, it can be energy-intensive and the catalysts have to be separated from the solutions and recycled. Photodegradation of organic material is affected by many factors, like wastewater constituents, light intensity, selected photocatalyst and its amount, water pH, etc. Photocatalyst can be difficult to separate from the mixture. Another problem is that electrons and holes may recombine, decreasing the efficiency of treatment. [28, 39]

2.5. Oxidation with Fenton processes

Fenton processes can be used to degrade wide range of contaminants and formed by-products are usually harmless. The classical Fenton process utilizes mixture of H_2O_2 and Fe^{2+}-ions as reagents. Iron catalyst is decomposing the hydrogen peroxide into hydroxyl radicals like in the reaction 10. [18]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO\cdot \tag{10}$$

Advantages of Fenton process are possibility to use ambient temperature and pressure, relatively low cost reagents and simple operation procedure. Furthermore, no additional energy is needed to decompose the H_2O_2 molecules into radicals. Iron and hydrogen peroxide are both rather abundantly available and non-toxic chemicals. However, the amount of required raw materials can be high and the process is dependent on pH. For example, Bahmani et al. [40] used Fenton process to remove synthetic dye reactive black 5 (250 mg/l**)** from a solution. 300 mg/l H_2O_2 and 50 mg/l $FeSO_4$ was needed to achieve a removal of 59% COD and 97% color from the water in optimum conditions, pH 3 and temperature 40°C, after 30 min treatment. Optimal pH of Fenton process is typically between 2.5-4. Some iron species can be precipitated from the solution, forming iron sludge during the process. Optimization of iron and H_2O_2 doses has to be well controlled to minimize waste reactions. [18, 22]

There exists various Fenton-like processes utilizing different ferric ions, light and electricity. For example, Fe^{3+}-ions can be used instead of Fe^{2+} and reactions products include $HO_2^{\cdot}$ radicals. In photo-Fenton process, ultraviolet light is used to speed up the regeneration rate of Fe^{2+} from the formed Fe^{3+} complexes and ferric carboxylates. Energy requirements are increased due to UV-light supply, but lower amount of catalyst is needed and less sludge is produced. Furthermore, UV-light speeds up the formation of radicals. Photo-Fenton process is even more dependent on pH, optimal value being 2.8 [39]. Fenton process can also be assisted electrically, where electrolysis is used to supply H_2O_2 continuously by two-electron oxygen reduction in reactor. Iron powder is added normally to the reactor, or Fe^{2+}-ions are produced by iron anodes to decrease costs of chemicals. Energy consumption is increased due to electricity, but less catalyst is required and decreased amount of sludge is formed compared to classical Fenton. [18]

Murray et al. [41] removed NOM from natural water (DOC 7.5 mg/l) by Fenton and photo-Fenton processes. When 28 mg/l H_2O_2 and 5.6 mg/l Fe^{2+} was added in pH 4, Fenton process resulted in 78% UV_{254} and 93% DOC removal in 5 minutes. UV light (5 W) alone was not effective to reduce UVA and DOC, and purification effect of UV/H_2O_2 was also not comparable to Fenton methods. Maximum 95% reduction of UV_{254} absorption was achieved in 30 min by Fenton and in 5 min by photo-Fenton process. It can be concluded that under suitable conditions (pH and Fe^{2+}/H_2O_2 addition), Fenton processes are effective in degrading organic compounds.

2.6. Oxidation with sonolysis

Sonolysis is a non-toxic disinfection and oxidation method utilizing ultrasound frequencies higher than 20 kHz. Ultrasound causes cavitation in water, forming rapidly alternating compression and decompression zones. Decompression zones generate small bubbles, which collapse and produce shock waves, free radicals (reaction 11) and hydrogen peroxide. Heat gradients (5500 °C) and rapidly increased pressure (50 MPa) are other results of cavitation [4]. Elevated heat and pressure are main reasons for destruction of microorganisms cells [42]. Around 80% of the produced radicals recombine back to water molecules after their formation, diminishing the efficiency of sonolysis compared to other radical based processes. [1, 28]

$$H_2O +)) \rightarrow OH \cdot + H \cdot \tag{11}$$

Several parameters affect the sonolysis treatment, like frequency, amplitude, volume and shape of the reactor and temperature [43, 44]. Sonolysis treatment is often combined with chlorine, oxygen, ozone, ultraviolet light or a chemical catalyst [28]. Sonolysis seems to be efficient mainly when combined with another oxidation process. Destaillats et al. [45] reported that sono-ozonation increased the demineralization rate of methyl orange from 40% to 80%, when compared to ozonation only. When ultrasounds where applied without ozone, mineralization degree was 35%. Sonolysis power was 50 kW and frequency 500 kHz, while voltage of ozone generator was 50 V. Treatment time was 80 min in pH 6 and temperature 15°C.

Seymour et al. [44] studied ultrasound disinfection of Salmonella on cut lettuce. Ultrasound waves (32-40 kHz) combined with chlorine (25 ppm) achieved 2.7 Log reduction of bacteria after 10 min treatment in a 40 l reactor. Separately used ultrasound treatment achieved 1.6 Log and chlorine 1.7 Log reductions. Cavitation effect of ultrasound detached the microbial cells from the lettuce, which improved the contact area of bacteria to be exposed to chlorine. Anese et al. [42] reported 5 Log reduction of Escherichia coli after only 5 min treatment with power ultrasound (572 W/l). Treated sample was 0.25 l lettuce washing water inoculated with various bacteria. Quick disinfection was the result of in-situ temperature rise from 30^{o}C to 65^{o}C. When heating only was used as a treatment, the inactivation results were similar than in ultrasound processing. If temperature was maintained under 35^{o}C, only 1 Log reduction of E. Coli was achieved in 5 min. Either long treatment time, high power or uncontrolled temperature has been usually needed to achieve adequate level of bacteria disinfection. [1]

2.7. Oxidation with electrochemical methods

Two oxidation mechanisms are involved in the electrochemical treatment: direct oxidation within the anode and indirect oxidation by oxidants produced in the electrolysis of water. Electrode material is one of the most important factors of electrochemical treatment. Electrodes should have high conductivity, chemical and mechanical durability, high surface area, good activity and they have to be inexpensive. Some common materials are graphite, platinum, boron-doped diamond (BDD) and PbO_2 [28]. Using boron-doped diamond electrodes has shown to result in the best formation rate of reactive oxygen species like hydroxyl radicals, hydrogen peroxide and ozone [21]. Efficiency of treatment can be usually improved by increasing current density and boron doping level. [3]

Another slightly different novel electrochemical oxidation method is so called electrolyzed oxidizing (EO) water. It is a solution generated with water and salt in an electrolytic cell. Produced ions (reaction 12) are separated and combined to form acidic electrolyzed water with hypochlorous acid (HOCl) and hydrochloric acid (HCl) in low pH (2-3). Alkaline electrolyzed water with sodium hydroxide (NaOH) is formed in high pH values between 6-12. [4]

$$H_2O + NaCl \rightarrow Na^+ + Cl^- + H^+ + OH^- \qquad (12)$$

Electrochemical oxidation is able to provide high degradation rate of organic compounds and even complete mineralization of them. Increase in current density usually results in improved disinfection efficiency, but it also increases the energy requirements [28]. Gomez-Lopez et al.

[46] investigated the efficacy of boron-doped diamond electrodes to treat lettuce washing water with high amount of organic material (COD 725 mg/l) and inoculated strains of Escherichia coli. 5 Log reduction could be achieved with 180 mA/cm^2 current density and 800 μmol/mol boron doping level during 35 min treatment time at 10°C. When current density was 30 mA/cm^2, 2.5 Log reduction of bacteria was obtained. Change in current density from 30 to 180 mA/cm^2 also improved COD removal rate by 40%. However, the change in current density increased energy consumption significantly, from 7 to 80 Wh/l when target COD removal was 20%. This relationship is shown in Figure 5.

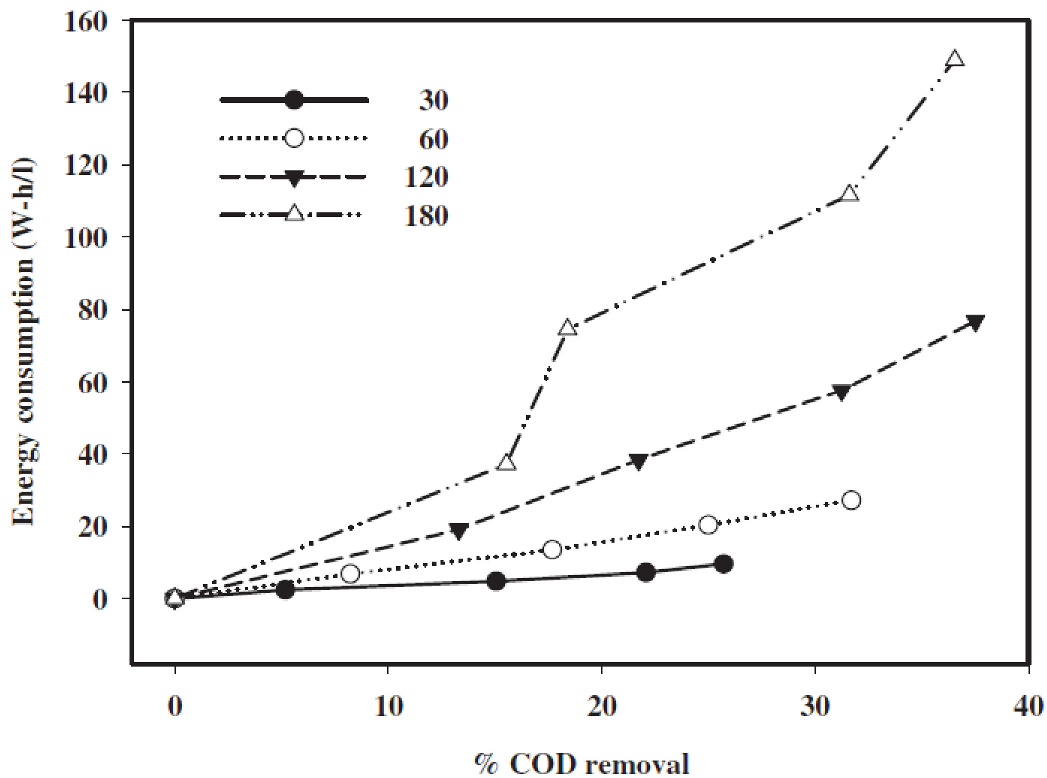


Figure 5: Electrochemical oxidation of lettuce wash water inoculated with bacteria. Effect of current density (mA/cm^2) for energy consumption as a function of COD removal. [46]

Rajab et al. [21] showed that synergetic effect of ozone and chloride formed in-situ of electrochemical oxidation enhanced the disinfection. They used BDD electrodes in treatment of solutions containing P. aeruginosa bacteria (10^7–10^8 FC/ml) at temperature of 25°C. Better inactivation rate was observed in solutions, where more ozone and/or chlorine was present. Density of 167 mA/cm^2 resulted in 6 Log inactivation of bacteria after 5 min treatment. In contrary, same reduction was achieved in 60 min when current density was 42 mA/cm^2. Energy consumption for 6 Log reduction was therefore higher with low current density.

3. Pulsed corona discharge

Pulsed corona discharge (PCD) produces electrical discharges to form oxidizing species in water. It is characterized as one of non-thermal plasma technologies, differing from high temperature thermal plasma systems. Dielectric barrier discharge, glow discharge, spark discharge and gliding arc discharge are among the other non-thermal plasma types. Oxidizing species include radicals like H·, O·, OH·, and HO_2 ·, molecules such as H_2, O_2, H_2O_2 and O_3, ions, shockwaves, UV-light and electrohydraulic cavitation. The most important reactions occurring by dissociation of water, ozone, oxygen and hydrogen peroxide molecules are presented in reactions (13-17). [19]

$$H_2O + e^- \rightarrow OH \cdot H^+ \cdot + e^- \tag{13}$$

$$O \cdot + H_2O \rightarrow 2\ OH \cdot \tag{14}$$

$$H_2O_2 \rightarrow> H^+ + HO_2^- \tag{15}$$

$$O_3 + HO_2^- \rightarrow \cdot O_2^- + OH \cdot + O_2 \tag{16}$$

$$\cdot O_2^- + H^+ \rightarrow HO_2 \cdot \tag{17}$$

Compounds can degrade directly by the discharge (for example pyrolysis due to high temperature gradients) or in reactions with oxidizing species. UV-light liberated by relaxation of excited species can degrade organic compounds, inactivate bacteria and dissociate H_2O_2 and O_3 into radicals. UV-light also enhances the production of H_2O_2 [47]. Hydroxyl radicals can further recombine to form hydrogen peroxide again. Shockwaves produced in the water by electric field increase the production of OH· and H_2O_2 by decomposing water molecules. Furthermore, temperature and pressure gradients are formed at the discharge zones. Among the produced species, hydroxyl radicals, hydrogen ions, ozone and hydrogen peroxide seem to achieve highest concentrations. Bacteria is mainly inactivated via two mechanisms: reactive oxygen species and UV light. Inactivation effect continues after treatment, if water is incubated for several hours. This has been connected to formation of certain long living species (for example H_2O_2) in water [48]. [19, 49]

PCD unit consists of asymmetric electrode pairs, where the discharge develops in the region near the anode and spreads out towards the cathode, but does not reach that [50]. Very sharp high voltage pulses are produced in the water with voltage rise times of some nanoseconds. Typical voltage is between 10-60 kV and frequency 30-1000 Hz. Free electrons gain high energy due to high electric field, forming plasma and streamer-like corona. Electrical discharges can be produced either in gas or liquid phase. Most common configurations consist of high-voltage point electrode and a grounded plate electrode on the other side of reactor. Figure 6 presents the typical electrode configuration in liquid phase. [19]

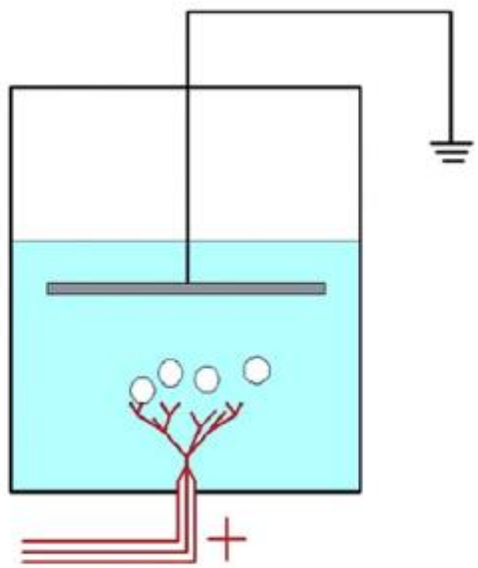


Figure 6: Pulsed corona discharge in liquid. Discharge is spreading from the high-voltage anode (bottom) towards cathode. Both the anode (point electrode) and cathode (grounded plate electrode) are installed in a liquid reactor medium. [19]

Advantages of PCD are optimizable conditions and no use of chemicals. When corona discharge reactor is built, the requirements for maintenance are also low and mainly include supervision of electrodes. Non-thermal plasma technologies require less electrical energy than thermal plasma systems. Corona discharge treatment provides in-situ production of different types of oxidizing species from water matrixes, without need to supply any chemicals and sources (like hydrogen peroxide and ozone). Reactions induced by oxidizing species are further accelerated by produced heat gradients, shockwaves and cavitation. However, pulsed corona discharge is still a novel technology and its efficiency in long-term full-scale water treatment plant has not yet been reported. Designing corona discharge reactors is complex because of many physical and chemical processes happening simultaneously. [19, 49, 50]

3.1. Reactor design and affecting parameters

High-voltage point electrode and grounded plate electrode are typically installed at the opposite sides of the reactor. Optimum electrode configuration is determined by suitable gap distance, material and phases where the electrodes are installed. Gap distance between electrodes is usually only few millimeters. Curvature electrodes (for example wires) made of stainless steel are typically chosen to be used as point electrodes because of high energy efficiency and low manufacturing costs. [19]

Discharge can be produced either in liquid or gas phase. Benefit of direct liquid discharge is that produced oxidants can directly react with target pollutants in water. Since radical species have a short lifetime of some nano- to microseconds, the reactor should be configured in a way that pollutants in water pass close to plasma discharges. Disadvantage of liquid discharge is slow transport rates in liquid, leading to recombination of active radicals near the discharge zones. Liquids have higher density and conductivity than gases, which means that higher electric current is needed to achieve the propagation of discharge. As a result of high electric field, erosion and wearing of electrodes may happen, which limits the duration of treatment and scale-up of PCD units. Using of multiple electrodes decreases the wearing and also improves energy efficiency [51]. [19]

Gas phase discharge enables achieving of higher ozone concentrations, because of high amount of source-oxygen in air. The energy requirement is also lower and wearing problems less susceptible than in liquid phase discharge. Liquid and gas discharge can be combined by for example installing point electrode in gas and asymmetric ground electrode in liquid phase (discharge above liquid or hybrid gas-liquid). Locke et al. [49] reported this configuration superior, because radicals and hydrogen peroxide are produced in liquid phase, while ozone and certain other active species are produced in gas phase and can dissolve into liquid phase. Sato [52] installed the electrodes vice versa: point electrode into liquid phase and ground electrode into gas phase. With this configuration, he achieved high concentrations of active oxidative species, UV light, hydrogen peroxide and ozone. Configuration where discharge is produced in bubbles has also been utilized. Discharge in bubbles has been measured to require lower energy for plasma generation and less electrode erosion problems than direct liquid discharge [51]. This configuration also produces high amount of different oxidative species. [19]

In addition to reactor design, several other factors are affecting the efficiency of PCD. Oxygen, air, argon or nitrogen can be induced in the discharge phase to enhance formation of oxidative species. Oxygen is an efficient and the most commonly used gas. Direct oxidation efficiency can be improved with catalysts. Removal of many target compounds have been improved by 15-60 % with catalysts like TiO_2 or activated carbon [53]. Fenton-like reactions can be induced by adding iron ions in the corona discharge cell. Energy input can be varied by changing either the voltage or frequency. Normally higher either of them, more reactive species are produced. High frequency is favorable for indirect oxidation with short-living radical species. In turn, low frequency allows more reactions between produced ozone and pollutants in water. Oxidation is usually more effective with high frequency, since radical pathway is more important. For example, Panorel et al. [54] reported 50% degradation of humic substances in water after 3 min of PCD treatment with frequency of 840 Hz, when it took 10 min to achieve the same result with frequency 200 Hz. When energy efficiency is the main target, low frequency has to be considered. Sequential discharge has been also claimed to be more effective than continuous discharge. Singh et al. [53] reported, that two minutes of discharge followed by one minute of no discharge achieved the same Log reduction of bacteria in half of the time needed with continuous discharge. This was explained by overly high concentration of hydroxyl radicals during continuous discharge, which scavenged themselves by forming hydrogen peroxide, a chemical that is not quite suitable for disinfection. [19]

pH of solution affects the production of hydroxyl radicals, which usually increases in neutral and alkaline conditions. However, OH^- and HO_2^- -ions consume radicals in strongly alkaline solution [8]. Optimal pH therefore depends on the target pollutant. Singh et al. [8] achieved better disinfection of bacteria at low pH values. They suspected that in acidic conditions, more H· are generated (reaction 18), which subsequently convert to reactive oxygen species (reactions 19-21). In turn, removal efficiency of phenol improved at high pH, since basic form of phenol is more reactive than its acidic form. Optimal pH for removal of humic acids was semi-alkaline, around 9. Dobrin et al. [25] reported, that pH of water decreased significantly as a result of PCD treatment, when organic acids were formed as degradation products. [53]

$$e_{aq}^{-} + H^{+} \rightarrow \mathrm{H}\cdot + H_2O \tag{18}$$

$$\mathrm{H}\cdot + H_2O_2 \rightarrow H_2O + O\mathrm{H}\cdot \tag{19}$$

$$\mathrm{H}\cdot + H_2O \rightarrow H_2 + O\mathrm{H}\cdot \tag{20}$$

$$\mathrm{H}\cdot + O_2 \rightarrow \mathrm{H}O_2\cdot \tag{21}$$

Temperature of water affects the degradation rate, formation of radicals and absorption of ozone. High temperature increases the rate constants, which means that species like ozone and hydrogen peroxide decompose faster into reactive radicals. However, low temperature has been claimed to improve the degradation of certain pollutants, like phenol and methyl orange. Low temperature extends the lifetime of radicals and increases the absorption of oxygen in water. [19]

Naturally, the contents of treatable water affect the treatment as well. Increase in organic load and turbidity decreases disinfection and degradation efficiency as a result of competitive reactions. Clear water with low turbidity also allows better penetration of UV light, which improves the oxidation and disinfection [49]. The discharge is transferred by ions in water, and therefore high conductivity (high concentration of ions) leads to shorter pulse duration and length. On the other hand, increasing conductivity intensifies UV radiation and strength of PCD pulse. Short streamer length can be often favorable, as it also produces higher plasma temperature gradients and acoustic pressure waves. Shih et al. [51] studied the effect of water conductivity for the production rate of reactive species in pulsed corona treatment. Deionized water was adjusted with potassium chloride to conductivities between 150-3000 µS/cm. They found out that increasing conductivity decreased the formation rate of measured hydrogen peroxide and hydrogen gas. Gathering these results, relatively low conductivity is beneficial in many cases, if corona system is installed so that target compounds pass close to the streamer.

3.2. Water treatment with corona discharge

PCD has been studied extensively for degradation of organic material. Studies involving different reactor design and operational conditions for treatment of various organic compounds and bacteria are presented in this chapter. The section also shows typical degradation results obtained with corona discharge treatment, and development of concentration of oxidizing species.

Dobrin et al. [25] compared corona discharge to ozonation, photocatalysis and sonolysis treatments. They used above-liquid plasma reactor with 1 l/min oxygen feed to remove diclofenac (50 mg/l) from tap water. Power 24 W, voltage 18 kV and frequency 22 Hz were applied to solution volume of 55 ml. Mayor part of ozone (90%) formed in gas phase was reported to leave the reactor without solubilization into water. Diclofenac was completely degraded after 15 min treatment (measured by UVA_{276}-value), while only 30% TOC was removed. The researchers monitored hydrogen peroxide concentration to measure ability of PCD to produce oxidizing species. Development of H_2O_2 concentration as a function of PCD treatment time is presented in Figure 7. High H_2O_2 concentration could be reached rather quickly, especially in diclofenac solution.

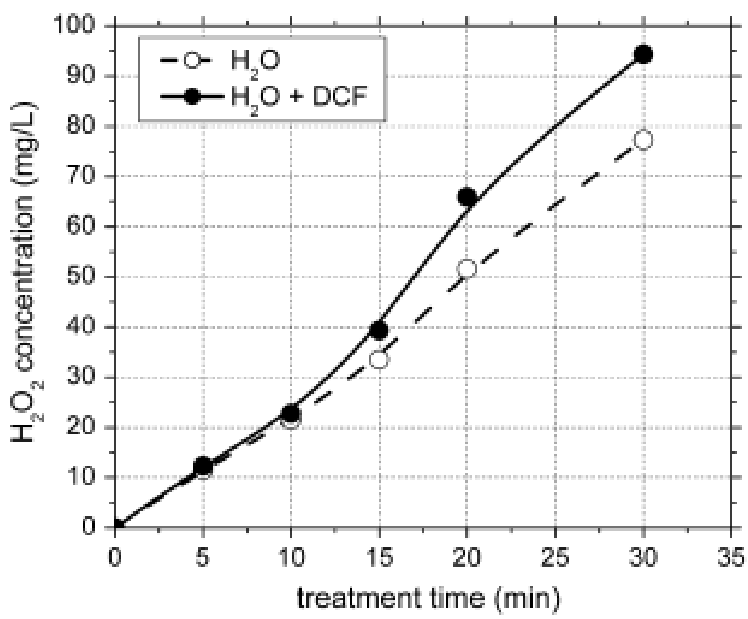
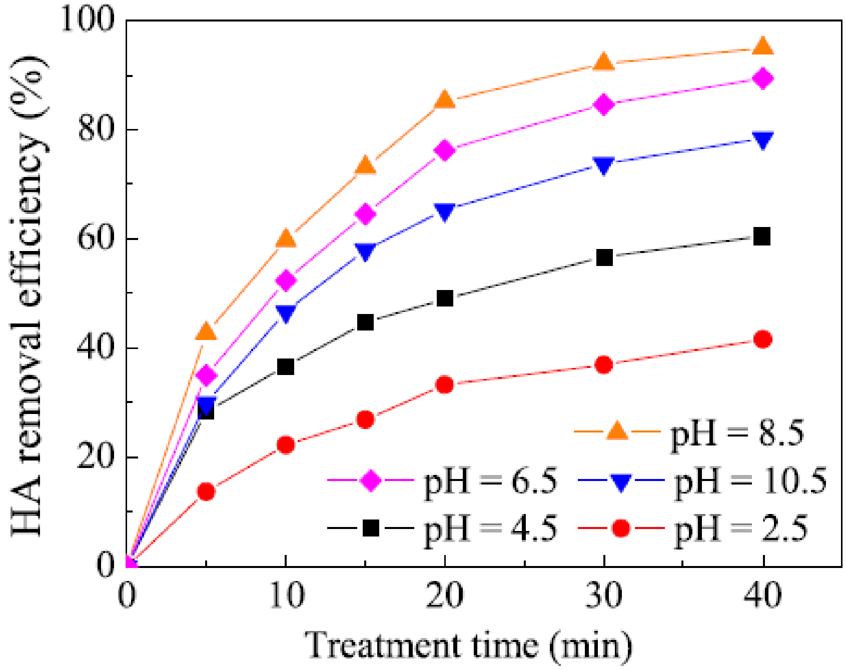


Figure 7: Hydrogen peroxide concentration development in water as a function of PCD treatment time. Black line represents development in a diclofenac (DFC) solution. Voltage 18 kV, frequency 22 Hz. 20ºC temperature and pH 6. [25]

PCD was the most effective compared to other AOPs to remove diclofenac. Especially complete mineralization was faster. Ozonation treatment degraded diclofenac (200 mg/l) almost completely after 30 min, but the mineralization was slow, resulting in only 24% decrease of TOC in 60 min. Oxygen/ozone gas flow rate was 50 l/h and the reactor contained 1 liter of solution [55]. Photocatalysis with TiO_2 could achieve 97% degradation of diclofenac (15 mg/l in 50 ml) after one hour of irradiation, while the TOC removal was 80%. Even though the initial diclofenac concentration was lower than in the PCD experiment and irradiation power was high (1500 W), degradation was four times slower in photocatalysis [56]. Sonolysis treatment degraded 90% of diclofenac (50 mg/l in 300 ml) in 60 min. TOC decreased only 15% during this period, however. Sonolysis was performed in the presence of catalysts and with power 90 W and frequency 216 kHz [57]. These experiments were performed in NTP conditions.

Wang et al. [8] investigated the efficiency of gas-phase pulsed corona discharge for removal humic acids (30 mg/l in 0.5 l). Degradation of humic acids was measured from change in absorption value. PCD (19.6 kV) treatment degraded 89% of humic acids in 40 min, while ozonation removed 62% of them, with equal generated ozone concentration. In addition of ozone, other chemical and physical processes thus participated in degradation of humic acids during PCD oxidation. DOC of the solution decreased by 52% from the initial value of 9.7 Lower discharge voltage 12 kV resulted only 48% degradation of humic acids in 40 min. pH solution affected the removal as shown in

Figure 8. Removal efficiency was highest in slightly alkaline conditions: within 30 min only 37% of HA was removed at pH 2.5, while the removal was 93% at pH 8.5. Increasing the pH to 10.5 decreased the removal to 74%, however. This was explained by OH^- and HO_2^--ions present in alkaline water, which reacted with the produced oxidative species. Lake water (DOC 9.4 mg/l) was treated in comparison and results were less effective: 41% of DOC and 68% UV_{254} were removed in same 40 min time period. The difference in results can be connected to more complex nature of substances in natural water than in model solutions. In-situ generated



ultraviolet light and hydrogen peroxide were reported to participate in ozone decomposition. Some disinfection by-products, like chloroform $CHCl_3$, were formed after 20 min plasma treatment. [8]

Figure 8: The effect of pH on the removal of humic acids in PCD treatment. Removal was measured by change in UVA_{254} of the sample. Voltage used was 19.6 kV and frequency 50 Hz. [8]

Koutahzadeh et al. [38] used PCD to remove acid black organic dye (10 mg/l in 2 l) and compared its energy efficiency to ultraviolet oxidation processes. Degradation was measured by the change in UV_{618} absorption and mineralization by the change of DOC of the solution. 45 min treatment with 15 kV voltage, 120 Hz frequency and 8 mm electrode distance resulted in 99.9% degradation of acid black. Changing the gap distance of electrodes in PCD from 8 to 2 mm decreased the degradation from 78% to 30%, when treatment time was 15 min. Addition of 80 mg/l TiO_2 catalyst improved degradation from 53% to 94% during 15 min PCD treatment. Adding more catalyst decreased the degradation rate, thus this was the optimal dose. In high catalyst concentrations, accumulation of TiO_2 nanoparticles increased turbidity and decreased the photocatalytic effect induced by UV-light. In comparison, ultraviolet light irradiation (450 W) was used together with H_2O_2 addition or TiO_2 catalyst. Mineralization of acid black with different processes is shown in Figure 9. UV light alone resulted in 84% degradation and 18% mineralization in 45 min, while addition of 1 ml H_2O_2 increased the degradation to 100% and mineralization to 84%. PCD degraded acid black slower than UV/ H_2O_2 or UV/TiO_2 processes, but mineralization was faster.

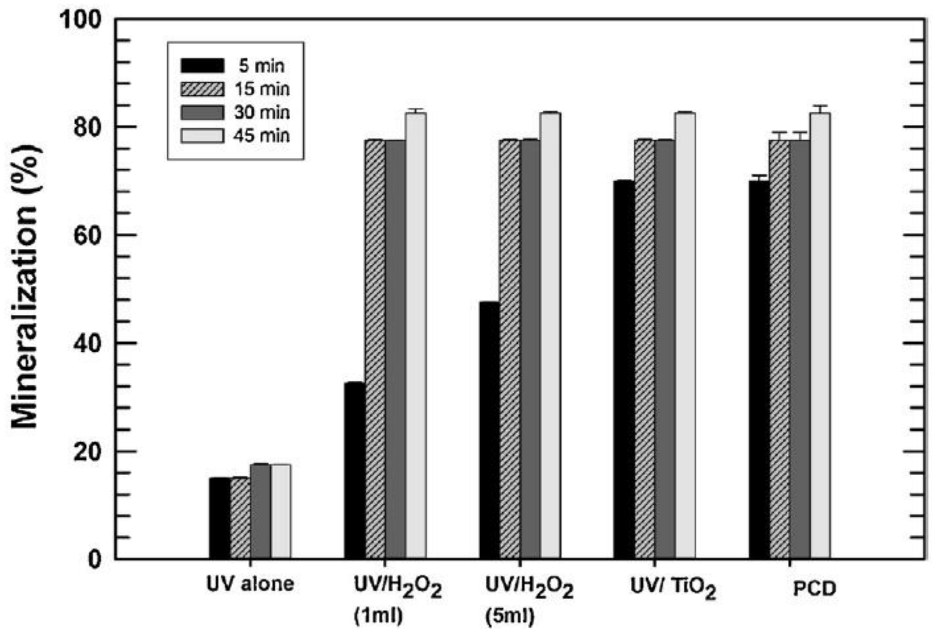


Figure 9: Mineralization of acid black (10 mg/l) with different UV oxidation processes and PCD. pH 5.2, T = 20°C. PCD voltage 15 kV, frequency 120 Hz and gap distance 8 mm. [38]

Singh et al. [53] examined the effect of different parameters affecting disinfection with non-thermal plasma (pulsed power) technology. Colonies of E. coli bacteria (10^7 FC/ml) were added to 50 ml of slightly saline (0.85% NaCl) water, which temperature was maintained between 30 to 40°C. Increasing voltage and frequency improved disinfection; 7 Log reduction of E. Coli was achieved in 4 min with 23 kV voltage, while same result took 8 min with 17 kV voltage. Frequency of 20 Hz led to 50% longer treatment time to achieve the same reduction than with 30 Hz. Acidic conditions were more effective: total disinfection time increased from 6 to 10 min, when pH was changed from 4 to 9. Production rate of hydroxyl radicals, hydrogen peroxide, ozone and superoxide radicals increased substantially when higher discharge voltage was used. Development of concentration of hydroxyl radicals is presented in Figure 10. Concentrations of hydroxyl radicals, ozone, hydrogen peroxide and superoxide radicals in distilled water were 56, 1, 17 and 18 mg/l, when pulsed power system was used for 12 min with voltage 23 kV and frequency 25 Hz. Ozone and hydrogen peroxide reached steady or decreasing concentrations after 5 minutes of discharge. It was explained, that radical species scavenge ozone and hydrogen peroxide in high concentrations.

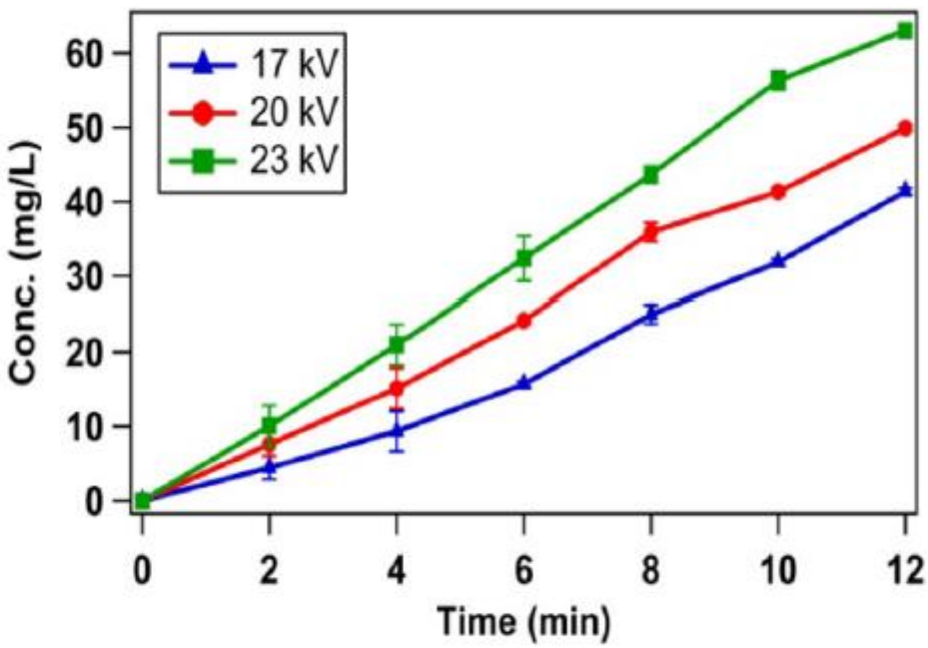


Figure 10: Concentration of hydroxyl radicals in function of time with different applied discharge voltage. Frequency: 25 Hz. [53]

Sato [52] studied concentrations of different radicals produced by pulsed electric field in tap water. He reported that without addition of oxygen gas, formation rate of H· was the highest compared to HO· and O· radicals. Relative radical intensities (concentrations) under oxygen bubbling are shown in Figure 11. When low amount of oxygen was added (49 ml/min), relative intensity of HO· greatly increased from 7 to 120. The intensities of other radicals also multiplied. Replacing oxygen with argon further increased the radical concentrations, but the degradation of phenol decreased from 100% to 75% when 10 min discharge was applied. The researchers stated that with oxygen addition, the produced O_3, O_2^- and O_2 also participated in the reactions. Reaction mechanisms are different, if gas like oxygen or argon is induced to the discharge shell.

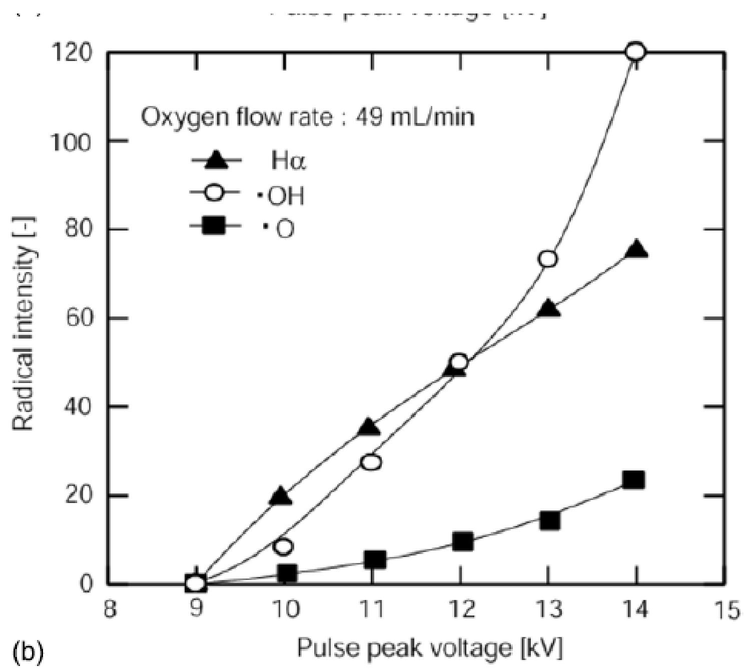


Figure 11: Relative intensity of H·, HO· and O· radicals produced by pulsed spark discharge. Voltage 17 kV, frequency 25 Hz. [52]

Lukes et al. [47] studied ultraviolet radiation produced by PCD oxidation. Conductivity of deionized water (1.15 l) was varied by adding dilute sulfuric acid. pH 2.8-3.0, temp 16°C. Water conductivity 500 µS/cm resulted in 7 times higher UV radiation than conductivity 100 µS/cm. Mean radiation power was measured as 240 W, being only 0.1% of the total power input 1.56 MW. Still UV light was analyzed to be responsible for 14% of the production of H_2O_2 and 30% of disinfection of Escherichia coli. Based on the studies by Lukes et al., role of ultraviolet light produced in PCD is especially important in disinfection.

4. Comparison of oxidation processes

Table III presents a short overview of some results achieved with different oxidation processes. In general, combined process is almost always more effective to degrade organic compounds and disinfect bacteria than oxidants used separately. For example, sonolysis can lead to increased temperature of the treated solution, which improves the inactivation rate of bacteria [42]. Sonolysis also causes cavitation, which can for example improve ozonation by increasing absorption of ozone into water [4]. Hydrogen peroxide addition and sonolysis enhance ozonation by increasing formation rate of radicals. H_2O_2 can also be broken into radicals by UV-light or ferric ions [17, 6, 8]. When treatment conditions are optimized, all the discussed processes, except plain UV-light [37], are viable options for oxidation of organic compounds and disinfection of bacteria. Energy efficiency of PCD is comparable to other advanced oxidation processes. It depends greatly on volume and nature of wastewater, as well as configuration of PCD unit and operational conditions. Degradation and even mineralization of organic material is usually fast, compared to for example ozonation and photocatalysis processes.

Table III: Overview of some results achieved with different oxidation processes in reference research articles

Method (ref)	Dose or power, time	Water sample	Results (change)
Ozone [32]	3 mg/l, 10 min	0.8 l of river water (DOC 5.1-6.6 mg/l, NTU 13.7-75)	$UVA_{254:}$ -71%, DOC: -10%
Ozone [30]	3 mg/l, 30 min	3 l of surface water (COD 44 mg/l)	UVA_{275}: -68%, COD: -25%
Ozone [31]	4 mg/l (single dose)	1.0 l of secondary effluent (DOC 4.2 mg/l, NTU 0.4-1.8)	UVA_{254}: -47%, DOC: -0%
Ozone [55]	50 l/h, 30 min	1.0 l solution containing diclofenac (200 mg/l)	UVA_{280}: -99%, TOC: -20%
Ozone [37]	6.2 mg/l, 20 min	0.7 l concentrate of reverse osmosis (2 mg/l manganese)	manganese: -97%, DOC: -38%
Ozone [9]	0.9 g/h O_3, 60 min + 24 h storage (4°C)	1.0 l of juice with strains of E. coli and Salmonella	0.8 Log reduction of bacteria. 0 Log reduction without storage
Ozone / H2O2 [30]	3 mg/l O_3 + 0.23 mol H_2O_2/ mol O_3, 30 min	3 l of surface water (COD 44 mg/l)	UVA_{275}: -75%, COD: -25%
Ozone / H2O2 [9]	0.9 g/h O_3 + 300 mg/l H_2O_2, 60 min + 24 h storage (4°C)	1.0 l of juice with strains of E. coli and Salmonella	5 log reduction of bacteria. 2 log reduction without storage.
UV light [37]	4400 µW/cm, 20 min	0.7 l concentrate of reverse osmosis (2 mg/l manganese)	manganese: -45%, DOC -2%
UV light [58]	450 W, 45 min	2 l acid black organic dye solution (10 mg/l)	acid black: -84%, DOC: -18%
UV / Ozone [37]	4400 µW/cm + 6.2 mg/l O_3, 20 min	0.7 l concentrate of reverse osmosis (2 mg/l manganese)	manganese: -63%, DOC -32%
Photocatalysis UV/TiO2 [58]	450 W, 45 min	2 l (10 mg/l) acid black organic dye solution	manganese: -99%, DOC: -83%

Photocatalysis UV/TiO2 [56]	1500 W, 60 min	0.05 l solution containing diclofenac (50 mg/l)	diclofenac: -97%, TOC: -80%
UV / H2O2 [41]	5 W + 2 mM H_2O_2, 60 min	0.5 l wastewater (DOC 7.5 mg/l)	DOC: -65 %
UV / H2O2 [58]	450 W + 1 ml H_2O_2, 45 min	2 l (10 mg/l) acid black organic dye solution	manganese: -99%, DOC: -83%
Fenton [41]	5.6 mg/l Fe^{2+} + 28 mg/l H_2O_2, 30 min	0.5 l wastewater (DOC 7.5 mg/l), pH 4	UVA_{254}: -95%, DOC: -83%
Fenton [40]	50 mg/l $FeSO_4$ + 300 mg/l H_2O_2, 30 min	2 l solution of reactive black dye (250 mg/l), pH 3	COD: -59%, color: -97%
Sonolysis / TiO_2 [57]	90 W, 60 min	0.3 l solution containing diclofenac (50 mg/l)	diclofenac: -90%, TOC: -15%
Sonolysis [42]	572 W/l, 20 min	0.25 l lettuce wash water inoculated with bacteria (T=31ºC)	4 log reduction of E. coli.
Electrochemical [3]	24 mA/cm^2, 25 W, 25 min	5 l water with E. coli (COD 300 mg/l, T=5ºC)	5 log reduction of bacteria, COD: -13%
Electrochemical [46]	180 mA/cm^2, 35 min	5 l lettuce wash water (COD 725 mg/l) with E. coli (T=10ºC)	5 log reduction
Electrochemical [21]	167 mA/cm^2 or 42 mA/cm^2, 30 min	10 l water with P. aeruginosa bacteria (7 Log FC/ml)	6 log reduction of bacteria in 5 min or 60 min
PCD [25]	24 W, 18 kV, 22 Hz, 15 min	0.055 l solution containing diclofenac (50 mg/l)	UVA_{276}: -100%, TOC: -30%
PCD [58]	15 kV, 120 Hz, 45 min	2 l solution containing acid black dye (10 mg/l)	acid black: -99%, DOC: -84%
PCD [8]	19.6 kV, 50 Hz, 40 min	0.5 l solution containing humic acids (30 mg/l)	UVA_{254}: -89%, DOC: -52%
PCD [8]	19.6 kV, 50 Hz, 40 min	0.5 l surface water (DOC 9.4 mg/l, NTU 2.5)	UVA_{254}: -68%, DOC: -41%
PCD [54]	20 kV, 840 Hz, 15 min	50 l solution containing humic acids (23 mg/l)	UVA_{455}: -88%, TOC: -38%
Pulsed power technique [53]	17 kV, 30 Hz, 8 min	0.05 l saline water with E.coli (conductivity 400 mg/l, T= 30-40ºC)	7 log reduction of bacteria

5. Membrane filtration

Membrane filtration technologies are separation processes utilizing thin, selective, semi-permeable filters. Feed solution passes through small pores in membrane and produces permeate, while retained substances form concentrate on the other side. Main pressure-driven technologies are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Classification is done based on operating transmembrane pressure (TMP), pore size and retention characteristics, as shown in Table IV. When tight membranes with small pore size are used, pressure difference across membrane has to be high to achieve liquid flow through membrane. UF and NF membranes are usually classified by molecular weight cut-off (MWCO) of rejected substances. RO membranes are basically non-porous. [59]

Table IV: Classification of membrane filtration systems. Data collected from [60]. The transmembrane pressure values are merely guidelines, while pressure in microfiltration can go as low as 0.1 bar and pressure up to 40 bar can be utilized in nanofiltration. Macromolecules include large molecules, like proteins, with thousands of atoms.

	Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
Transmembrane pressure (bar)	0.7-1.7	2-10	7-14	14-70
Pore size (µm)	0.1-10	0.001-0.1	< 0.1	
MWCO (g/mol)		300-500000	200-1000	
Retention:				
Suspended particles	+	+	+	+
Microorganisms	+	+	+	+
Macromolecules	-	+	+	+
Small organic molecules	-	-	most	+
Multivalent salts	-	-	+	+
Monovalent salts	-	-	some	+

MF is commonly used to remove suspended particles, turbidity and microorganisms. UF is also able to remove viruses and macromolecules like proteins. NF can reject various organic molecules like monosaccharides, dyes, pesticides and pharmaceuticals that have MWCO greater than 300-1000 g/mol. NF also rejects 50-100% of the divalent ions and usually less than 40%

of the monovalent ions. RO can be used to remove all the ions and is generally used for desalination. [6, 60]

Common requirements for membranes are good selectivity for the desired substances, mechanical strength and high permeate flux. Narrow pore size distribution is attributed to selectivity, while high porosity and thin membrane is needed to achieve high permeability. [60]

Membranes are manufactured from organic polymers or inorganic materials like ceramics and glass. Some criteria for selection of material include high mechanical and chemical strength, temperature resistance, hydrophilicity, permeability and cost of the material. Most commonly polymeric materials are cellulose acetate, polysulfone, polyvinylidene difluoride, polyethylene, polypropylene and different polyamides. Ceramic membranes are usually more expensive than polymeric membranes, but they have better chemical and mechanical resistance [31]. Membrane material or structure can also be modified to improve the performance. Some of the most common modification methods include surface coating, heat or solvent treatment, cross-linking and pyrolysis. [60]

Different membrane configurations include hollow fiber, tubular, spiral wound, and plate-and-frame. Hollow fiber configuration consists of thousands of thin (diameter from 0.5 to 1.5 mm) fibers packed in a module. Solution flows through the bore of the hollow fiber, and permeate is collected from the outside of the fiber. The filtration can also be operated in reverse mode, where water flows from outside to inside of the fibers. Tubular configuration is similar to hollow fiber, but diameter of the tubes is larger. Principle of filtration in tubular type configuration is shown in Figure 12. Plate-and-frame system is a simple one, consisting of sets of two flat membranes, with the feed sides facing each other. Spiral configuration is basically a plate-and-frame system wrapped around a central pipe, forming a leaf-like construction. Selection of the membrane model is based on separation problem, cleaning requirements, ease of maintenance and operation, compactness of the system and costs. [59, 60]

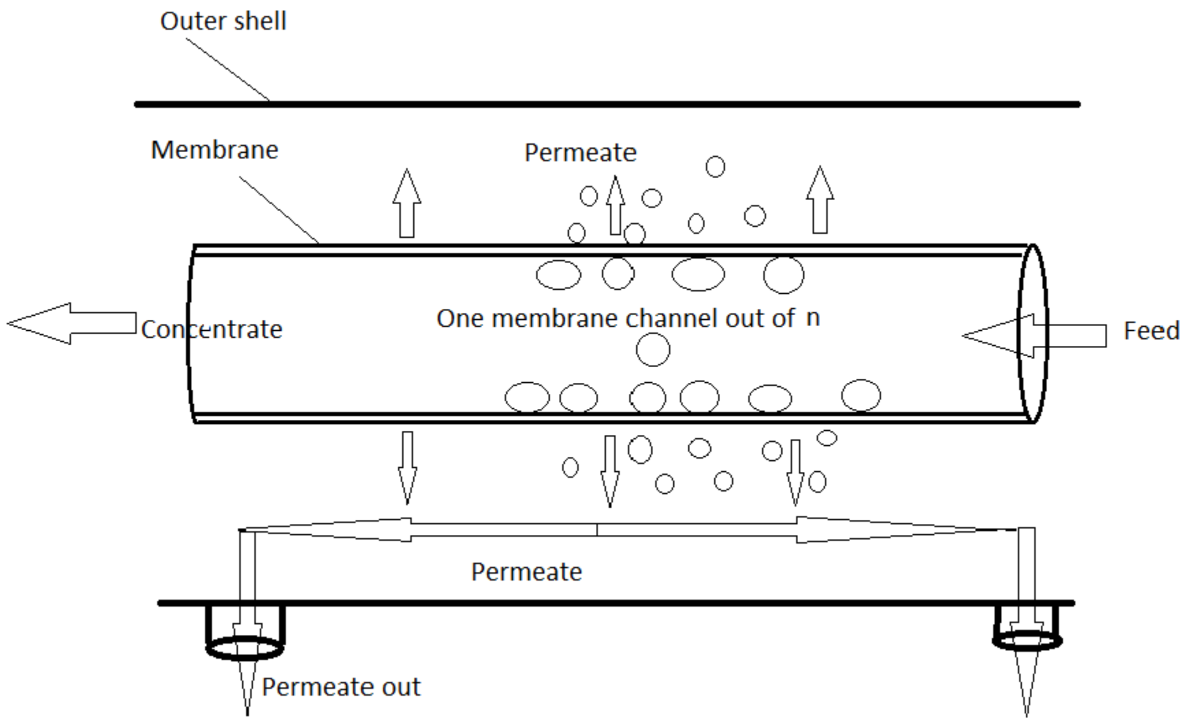


Figure 12: Principle of membrane filtration in tubular configuration.

There exists two membrane filtration modes: cross-flow and dead-end. In cross-flow filtration, the feed water is pumped tangentially to the membrane and the concentrate is recirculated. In the dead-end mode, entire solution is forced horizontally through the membrane. Dead-end filtration is mostly used in rather clean water, as thick layer (cake) of retained substances can be formed if feed solution is heavily contaminated. [59]

5.1. Fouling of membranes

Fouling can reduce the permeate flux through the membrane and lead to an increased energy demand, due to elevated pressure needed to maintain the flux. It also increases cleaning needs and may result in shorter membrane life. Fouling can be reduced by appropriate pretreatment of feed water, suitable selection and modification of membranes and optimization of operational conditions. Fouling of the membrane can be detected by changes in transmembrane pressure (TMP) and/or flux through the membrane. If TMP increases or flux decreases significantly, while all the other filtration conditions are constant, some fouling is likely to be happening. [7, 60]

There exists several possible fouling mechanisms. Colloidal fouling occurs, when particles and molecules accumulate to the membrane surface and form a cake or gel layer. Particles can also partly penetrate the pores of membrane, which causes so-called pore blocking. Organic matter may adsorb to the membrane surface or pores. This can be caused for instance by charged functional groups in the organic compounds, which attach to charged membrane surfaces. Organic foulants also interact with colloidal foulants. Inorganic fouling (scaling) is caused by precipitation of ions from solution and deposition of them to the membrane surface and pores. Inorganic fouling is mainly caused by iron, silica, calcium, aluminum, sulfate and phosphorus. Biofouling is the attachment of microorganisms to the membrane surface and growth of biofilm. Biofilm is composed of macromolecules and microorganisms and can cause degradation of the membrane surface, reducing the lifetime of membrane. [60]

Substances close to the size of membrane pores are prone to cause pore blocking, while particles larger than pores mainly lead to cake layer formation. Cake formation can be favorable form of fouling, because it is often quite easily removed. Inert cake can also act as a prefilter, which prevents attachment of material with high fouling potential on the membrane surface. Inorganic fouling may aid organic fouling, when ions bridge organic molecules with membrane surface or link multiple molecules together. Fouling caused by natural organic matter (NOM) adsorption has been claimed to be a major problem limiting the use of membrane processes in treatment of surface waters. [7]

Membranes can be cleaned with backwash washing or chemical cleaning methods. Backwash washing is typically used frequently, while chemical cleaning only daily or weekly. Reversible fouling means that foulants are not strongly adhered to membrane and they can be removed by normal cleaning processes. Performance of membranes fouled by irreversible fouling is difficult to restore. Basic chemical cleaning is typically used when foulants are organic compounds, whereas acidic cleaning is normally used for inorganic foulants. Hydrophobic membranes are generally more prone to fouling than hydrophilic ones. [59]

Surface of membrane is typically charged, which affects the rejection by electrostatic interactions between charged molecules and membrane. If the charge of solute is the same than that of the membrane, the electrostatic repulsion increases rejection. Nanofiltration membranes are normally negatively charged at neutral pH. Isoelectric point, where the NF membrane does not have charge, is typically between pH of 3-4. [22, 30]

6. Hybrid oxidation - membrane filtration processes

Previous chapters discussed different oxidation processes and membrane filtration separately. Combined process is assumed to reduce the fouling of membranes, by oxidizing foulants before or after they attach to membrane surfaces. Several parameters, like optimal pH of water and dosage of oxidants are discussed here. Based on the available literature, ozone and ozone based processes are the most widely studied oxidation technologies combined with membrane separations.

Degradation of NOM due to oxidation can cause small fractions of organic matter to plug the pores of membrane. If degradation propagates further, fractions might become so small that they pass the pores, deteriorating permeate quality. Geluwe et al. [20, 30] investigated the problem with five different nanofiltration membranes, and there was no concern that low molecular mass compounds would penetrate the membrane. There was a decrease in UVA_{275} of the permeate, but no change in COD. Feed solution was surface water from river (COD 44 mg/l), which was primarily passed through 2.5 µm cellulose filter. Kim et al. [24] revealed that NOM degraded by ozonation penetrated the ultrafiltration membranes, resulting in decreased TOC removal compared to UF only. They treated natural lake water (TOC 11.8 mg/l). Zouboulis et al. [17] reported deterioration of MF permeate quality, when ozonation was used prior to filtration. The sample solution was prepared by addition of humic acids and clay (TOC 8 mg/l). Probably small degraded organic fractions can pass loose MF and UF membranes but not tighter NF or RO membranes.

There exists only limited amount of studies where oxidation with pulsed corona discharge was performed prior to membrane filtration. Some research where plasma discharge and filtration units are installed in the same vessel can be found [50, 61]. Spark discharges can clean the membrane directly, if the discharge is applied close enough. The spark discharges generated from short electric pulses produce relatively strong shockwaves in water. Yang et al. [50] found out that the momentum transfer from a shock wave produced enough force to dislodge the deposited particles, mainly $CaCO_3$, from the filter surface. The energy consumption was really low compared to cleaning made by backwashing. Efficiency of corona discharge process for cleaning of filters is not clear, since the intensity of produced shockwaves is much weaker than in spark discharge. This is due to difference in energy input; corona discharge systems use discharges with energy 1 J per pulse, while arc and spark discharge processes utilize discharges one thousand times stronger. [61]

6.1. Ozone in the hybrid process

Ozonation has been shown in many studies to reduce fouling and increase permeability of membranes, if it has been performed before or in-situ of filtration [17, 20, 24, 23, 31]. Following paragraphs are presenting studies about hybrid processes: what conditions are applied and what effects ozonation has for membrane performance and water quality parameters.

Ozonation can transfer the hydrophobic organic substances into more hydrophilic ones, which are less prone to foul the membranes. Other structural changes, such as degradation to smaller compounds, can also have favorable results. If ozone concentration on the membrane surface increases, less fouling is usually measured. Therefore, oxidation is most useful to be performed close to membrane [6]. However, ozone resistance of most polymeric membrane materials is low and ozone can damage them. Ceramic membranes have been shown to be ozone resistant, as well as thermally, chemically and physically durable. [24]

Buyn et al. [23] performed multiple ozonation-nanofiltration experiments with different ozone dosage, pH and calcium concentrations. Model solutions (500 ml) containing humic acids (TOC 6.1 mg/l) were used as a feed water. Normalized permeate flux at different ozone dosages is presented in Figure 13. Flux decreased significantly during the first hours of the experiments. Fouling could not be prevented, but was reduced by pre-ozonation. This was connected to reduction of TOC in water due to ozone oxidation. Even low ozone dosage 0.6 mg(O_3)/mg(TOC) resulted in 35% higher flux after 72 hours filtration, than if no ozone oxidation was performed at all. 30% lower flux was observed in the presence of Ca^{2+} ions (1 mM), which was explained by calcium ions forming bridges between humic acids and membrane surfaces, causing them to attach to membrane more strongly. When ozonation was performed at pH of 11.4, slightly faster decline in permeate flux was observed than at pH of 2.8, which was connected to quicker degradation. When humic acids degraded due to ozonation, they caused more pore blocking, but the cake resistance was not so high. This means that increased hydrophilic repulsion between foulants and membrane caused less densely packed fouling layer and cake fouling reduced in high pH.

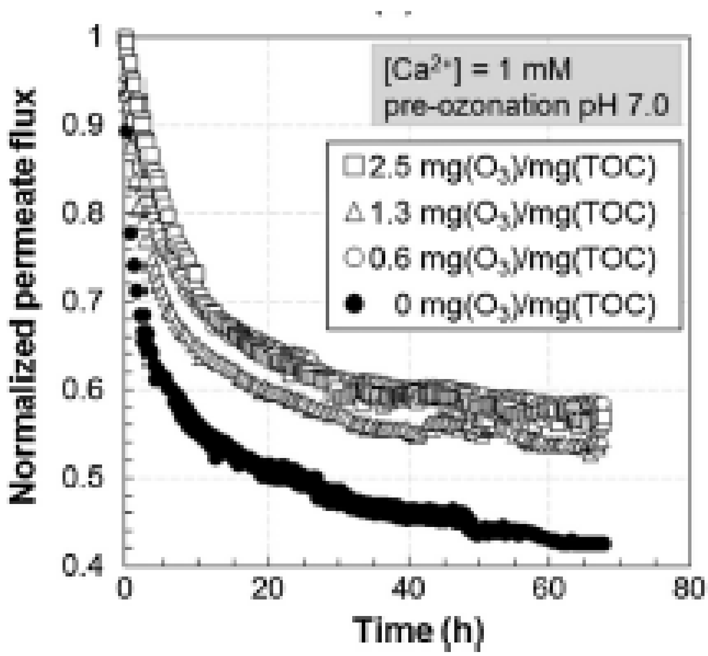


Figure 13: Normalized permeate flux as a function of filtration time, when pre-ozonation was performed in solution containing humic acids. Initial flux 84 l/m^{2}h^{-1}, temperature 23°C. [23]

Ozone/H_2O_2 treatment was combined with microfiltration by Zouboulis et al. [17] to mitigate fouling. Flat-sheet membrane was submerged in the same reactor (16 l) where ozone was induced as fine bubbles. The sample water used in the experiments was prepared by adding humic acids and clay into tap water (TOC 8 mg/l). Initial flux was 180 l/m^{2}h and TMP increased from 0.25 to 0.75 bar during 120 min microfiltration experiment. When ozone was dosed 0.2 l/min during the filtration period, TMP increased only by 50% during 120 min experiment, showing decreased fouling. Lower ozone dose of 0.1 l/min or addition of H_2O_2 did not have significant effect for TMP. Any dissolved ozone was not measured from the samples taken from the reactor and permeate, hence it was assumed to be consumed quickly. TOC in permeates increased by 30% due to degradation caused by O_3/H_2O_2 treatment. Decrease in fouling was connected to change in SUVA value of permeates from 6 to 3, which indicates increased hydrophilicity. Addition of H_2O_2 (molar ratio 0.05-0.2) resulted in better permeate quality, which was mentioned to be caused by higher production rate of hydroxyl radicals during the O_3/H_2O_2 oxidation.

Kim et al. [24] studied a hybrid ozone – UF process for treatment of natural lake water (TOC 11.8 mg/l). During ultrafiltration, permeate flux decreased by 60% from initial value 143 l/(m^{2}hbar) in less than a minute of filtration time. Addition of O_3 on the membrane surface with a gas flow rate of 0.2 l/min (concentration 9.5 g/m^3) and water cross-flow velocity of 0.88 m/s kept the permeate flux almost constant, with only 10% decline during first 20 s of filtration. Low ozone concentration of 1.5 mg/l or water cross-flow velocity of 0.11 m/s were insufficient to maintain constant flux. Increasing cross-flow velocity resulted in higher dissolved ozone concentrations. Turbulence created by high flow velocity broke ozone gas bubbles and improved the mass transfer. The study also revealed that a TMP of 0.68 bar resulted in higher permeate flux than pressures between 1.36 and 2.03 bar. Fouling layer on the membrane surface was thicker with higher TMP, which in turn could make fewer reactions between oxidants and foulants to occur.

Ozone oxidation and nanofiltration hybrid processes were studied extensively by Geluwe et al. [30]. They used surface water from river with initial COD of 44 mg/l. Ozone concentration in gas phase was constant being 12 mg/l, corresponding to liquid phase concentration of 2.7 mg/l in pure water. Increasing dose further did not have any effect on permeability. No dissolved ozone was detected for the first 28 min, hence all was consumed immediately. Permeability decreased by 40%, when water was filtered for 40 hours with a TMP of 8–10 bar. When ozone was induced, permeability decreased only by 20% during the same time period. UVA_{275} remained unchanged after half an hour oxidation, which indicated that unsaturated bonds were already oxidized in that time. UVA_{275} –value was then reduced by 70% and ozone concentration started to increase in liquid phase. O_3 concentration reached stable value of 1.45 mg/l in two hours.

II EXPERIMENTAL PART

7. Materials and methods

Experiments were conducted in a pilot hall of Lappeenranta University of Technology.

7.1. Membranes used in the experiments

Five different membranes were used in filtration experiments. Properties of the membranes are presented in Table V. Nanofiltration experiments were performed with two polyamide NF270 membranes in flat-sheet and spiral wound module, and a ceramic SG1485 membrane in tubular module. Ultrafiltration experiments were performed with the UC030 and RC70 membranes in flat-sheet Amicon Stirred Cell configuration, which allowed only small amount of water to be filtrated.

Table V: Properties of the used membranes and modules.

Type	Membrane	Module	Unit	Active area (m^2)	MWCO (g/mol)
nanofiltration membranes	SG1485	tubular	ceramic tube	0.102	600
	NF270	flat-sheet	CR250/2	0.090	200
	NF270	spiral wound	ceramic tube	2.600	200
ultrafiltration membranes	UC030	flat-sheet	Amicon	0.004	30000
	RC70	flat-sheet	Amicon	0.004	10000

Ultrafiltration membranes and the NF270 membrane in flat-sheet configuration were pretreated before experiments by submerging them into pure water for half an hour. SG1485 membrane was prepared by storing it in an ethanol solution overnight. It was tested to have MWCO of 600 g/mol (90% retention with polyethylene glucose solutions). The membrane had 19 channels with diameter of 3.5 mm and total surface area of 0.102 m^2. Supports of the membrane were made of Al_2O_3 and membrane layers of SiO_2 [62]. Figure 14 presents the configuration of the membrane SG1485.

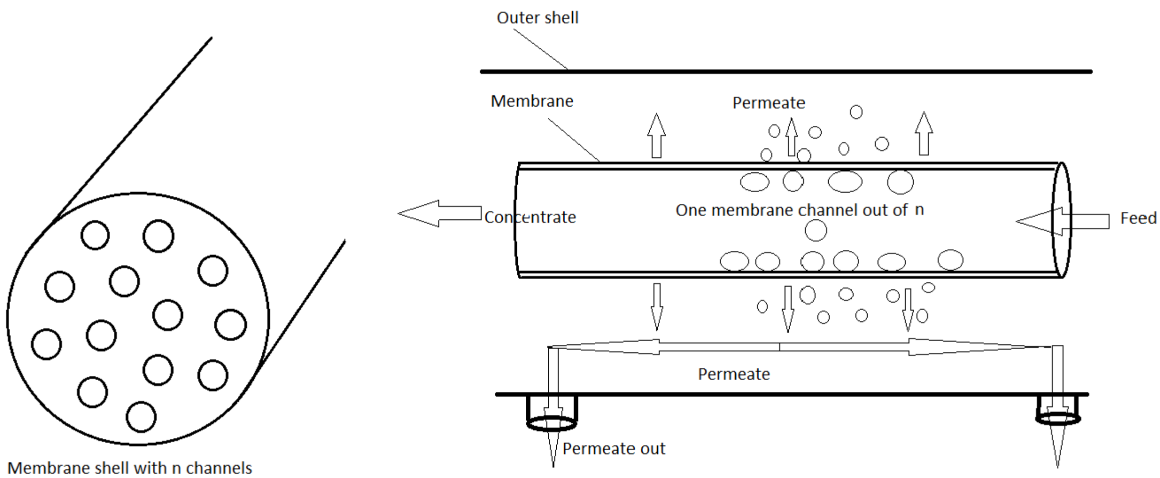


Figure 14: Nanofiltration membrane SG1485 used in the experiments. Left: membrane from the front side, right: schematic diagram of one membrane channel. n = 19 channels.

Alkaline chemical cleaning of the membranes was performed by circulating 1.5 vol-% Ultrasil110 solution in the membrane system for 20 minutes at temperature of 35^{o}C.

7.2. Pulsed corona discharge unit

The PCD unit consisted of multiple (total 64) wired electrodes installed horizontally. Schematic picture of the PCD unit is presented in Figure 15. Water was induced at the top of the unit and it formed droplets evenly to the reactor chamber when falling down to bottom. The unit was therefore operating in hybrid liquid-gas discharge mode. This type of system provides high water surface area for plasma and benefits of both liquid and gas phase discharges.

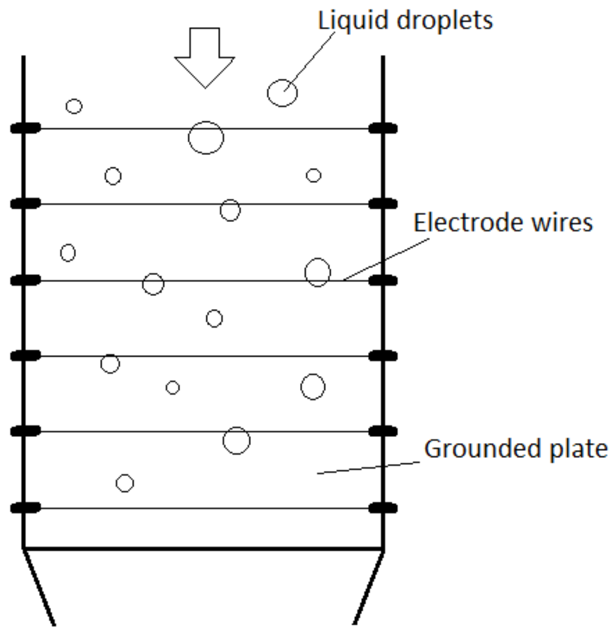


Figure 15: Schematic figure of the gas-liquid PCD unit used in the experiments

During the experiments with PCD, flow rate of water was maintained at 6 l/min. With higher flow rates the system would have been flooding. Voltage of PCD was 22 kV and the frequency could be changed between 300 – 833 Hz. Power with frequency 500 Hz was 60 W while energy of a single pulse was 0.12 J. Therefore, the delivered energy dose per hour was 2 kWh/m^3, when 30 l solution was treated with frequency of 500 Hz. Oxygen gas was induced into bottom of the PCD shell in some of the experiments. Amount of oxygen was calculated based on pressure drop in the gas bottle, while 1 bar of gas corresponds to volume of 0.0535 $m^{3.}$

7.3. Combined PCD – NF system

The experiments with pure water, deionized water and model humic acid solutions were performed in combined membrane filtration - pulsed corona discharge system. Flow diagram of the equipment is presented in Figure 16. The system was also used in two experiments with salad washing water. Amount of water circulated was 30 l in all of the experiments with this combined system. Ceramic nanofiltration membrane SG1485 in tubular configuration was used mainly because of ozone resistance.

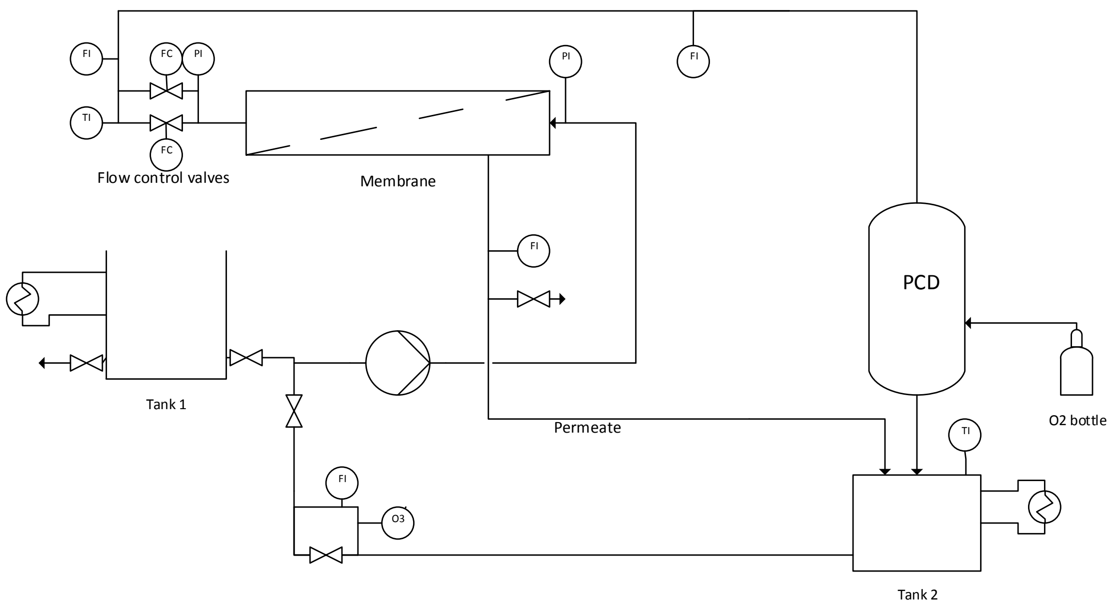


Figure 16: Process flow diagram of the combined PCD – NF system

Ozone concentration in water was measured through the experiments with combined PCD – NF system. Place of the used Orbisphere C1100 ozone sensor was changed between three points: just after the PCD, before the membrane (as in Figure 16) and after the membrane before the PCD. Sensor was placed before the membrane if not mentioned else. Measurement of concentrations of reactive radicals, hydrogen peroxide and UV light would have required various chemical addition methods or special equipment, so those were not determined in the study.

7.4. Analytical equipment

The analytical equipment included conductivity meter, pH meter, TOC analyzer, UVA analyzer and scanning electron microscope (SEM). Shimadzu Ordior TOC-L Analyzer was used for TOC and TIC analysis and Jasco V-670 Spectrophotometer for UV-absorption measurements. Used conductivity meter was Knick Konduktometer 703 and pH was measured using Methohm pH Meter 744. Inorganic substances in water were analyzed with Hitachi SU3500 SEM-device with X-ray microanalysis. Total solids and fixed solids were analyzed according to standard method SFS 3008 and suspended solids according to standard SFS-EN 872 [13, 14]. Volatile solids were calculated by subtracting the concentration of fixed solids from the concentration of total solids.

7.5. Properties of lettuce washing waters

Two batches of salad washing water were obtained from a vegetable processing plant in Finland. Water had been used for washing of fresh iceberg lettuce several times at a pre-rinsing step, and it was collected from a storage tank the same day. Water was stored outside in temperature between 0–10^{o}C and used in experiments within 10 days. While the first batch of the washing water was collected untreated, second one was pre-chlorinated in the vegetable processing factory and filtrated through 10 µm cartridge filter to remove possible salad particles.

Properties of the two water batches are presented in Table VI. Water contained high amount of organic material, alkalinity and dissolved solids. Based on amount of volatile solids (1400 mg/l), 78% of solids in the first batch water consisted of organic material. Inorganic analysis with scanning electron microscope (SEM) showed that water also contained significant amount of potassium, followed by natrium, chlorine, calcium and phosphorus. Potassium is an essential nutrient for growth of lettuce. Evidently, inorganic material also included salts like NaCl. Chlorine treatment of the second water batch removed part of the organic material and presumably inactivated bacteria. Cartridge filter also removed the suspended solids. Alkalinity of the water was higher due to chlorination. Based on the amount of volatile solids (350 mg/l), only 37% of the second batch water consisted of organic material.

Table VI: Characteristics of the lettuce washing water batches used in this study

Parameter	Batch 1	Batch 2
TOC (mg/l)	800	170
Conductivity (µS/cm)	640	1030
Total solids (mg/l)	1800	950
Suspended solids (mg/l)	35	3
Volatile solids (mg/l)	1400	350
pH	4.2-7.5	8.2-9.1

7.6. Conduction of experiments

Primarily, SG1485 membrane was used in combination with PCD. Effect of pulsed corona discharge treatment for permeability of SG1485 membrane, water quality parameters and ozone concentration was evaluated with tap water. Deionized water was used in comparison to see if ions in tap water had any effect for measured parameters. Changed parameters were water temperature (13 – 19^{o}C), oxygen injection to the PCD shell (0.5 – 0.8 m^{3}) and the frequency of

PCD (500 and 833 Hz). In further experiments, only a frequency of 500 Hz was used. Ozone decomposition in function of time was studied measuring ozone concentration just after PCD, before the membrane and after the membrane before PCD.

Humic acid experiments were also performed in combined PCD – NF system. HA solutions were prepared in laboratory using Sigma-Aldrich humic acid sodium salt technical grade with 39% carbon. Concentrations of HA solutions were measured by TOC analysis, based on carbon present in the structures. HA solutions (concentrations 65-130 mg/l) were first filtrated through the membrane to measure the fouling potential. During the combined PCD – NF experiments, permeate was not collected, but passed to the tank below PCD unit to avoid concentration of the feed stream. Oxygen was injected during the first 10 minutes in some of the experiments. No dissolved ozone over 15 ppb was detected during the experiments, which indicates that all the produced ozone was consumed in reactions. Degradation of humic acids (100-130 mg/l) during the PCD treatment was measured with TOC and ultraviolet absorption spectroscopy analysis. Effects of oxygen injection and different temperature for degradation were evaluated.

7.6.1. Conduction of the salad washing water experiments

First batch of the washing water was filtrated through SG1485 membrane in tubular configuration and NF270 membrane in flat-sheet configuration. Ultrafiltration membranes UC030 and RC70 were used as well for comparison. Permeate was collected during the filtration, while feed water continuously concentrated. Operational parameters in the filtrations are shown in Table VII.

Table VII: Parameters of the membrane filtration experiments of washing water. Temperature is presented at the beginning and end of filtration. N.A. = no data available. VRF = volume reduction factor.

<table>
<tr><th>Type</th><th>Membrane</th><th>Module</th><th>Water amount, l</th><th>VRF</th><th>T
(°C)</th><th>p
(bar)</th></tr>
<tr><td rowspan="4">nanofiltration membranes</td><td>SG1485</td><td>tubular</td><td>86</td><td>5</td><td>9.5 (30)</td><td>3.7</td></tr>
<tr><td>NF270</td><td>flat-sheet</td><td>29</td><td>6</td><td>16 (23)</td><td>4.2</td></tr>
<tr><td rowspan="2">NF270</td><td rowspan="2">spiral wound</td><td>600</td><td>10</td><td>7.5 (22)</td><td>4.5</td></tr>
<tr><td>500 (permeate)</td><td>10</td><td>13.5 (19)</td><td>4.5</td></tr>
<tr><td rowspan="2">ultrafiltration membranes</td><td>UC030</td><td>flat-sheet</td><td>0.3</td><td>4</td><td>13 (18)</td><td>1</td></tr>
<tr><td>RC70</td><td>flat-sheet</td><td>0.3</td><td>4</td><td>12 (18)</td><td>3</td></tr>
</table>

Volume reduction factor (VRF) describes the portion of permeate produced from feed water and was calculated by equation (22). Amount of produced permeate, and corresponding VRF after specific filtration time *t* was calculated based on flux values, which were measured frequently.

$$VRF = \frac{total\ volume\ of\ water\ to\ be\ filtrated}{volume\ of\ produced\ permeate\ at\ (t)} \tag{22}$$

During the experiments there were changes in temperature, which affects the viscosity of solution and thus permeability. Permeate flux values were therefore corrected to temperature of 20°C according to equation (23). Viscosity values were obtained for tap water at corresponding temperatures [63]. [64]

$$J_{corrected} = \frac{\eta(x\ °C)}{\eta\ (20\ °C} * J_x \tag{23}$$

Where J_x Measured flux at temperature of x, kg/(m^{2}h)

η Dynamic viscosity of a solution at a certain temperature, kg/ms

Parameters including UV absorption, TOC, conductivity, pH, total solids, suspended solids and fixed solids were used to evaluate the efficiency of filtration and PCD treatments. Changes of the parameters in filtration experiments are presented as a function of VRF. Temporary retention of certain parameters (for example TOC) after the filtration time *t* was calculated by equation (24). Samples from the concentrate and permeate streams were taken at the moment *t.*

$$TOC_{\%ret}(t) = \left(1 - \frac{TOC_{permeate}(t)}{TOC_{concentrate}(t)}\right) * 100\% \tag{24}$$

PCD treatment of the first batch lettuce washing water began by washing water and then permeate treatment from SG1485 membrane filtration. Because of prolonged effect of oxidants produced in water, water quality parameters were also measured for some time after PCD was turned off. Experimental conditions of the washing water treatments are shown in Table VIII.

Table VIII: Experimental conditions in PCD treatment of salad washing waters

Washing water batch	Sample	Treatment time	Frequency	Oxygen injection	Temperature
Batch 1 (untreated)	Washing water	2 hours	500 Hz	0.5 m^3 (first 7 min)	9°C
	SG1485 permeate	2 hours	500 Hz	0.5 m^3 (first 7 min)	9°C
Batch 2 (chlorinated and filtrated)	Washing water	4 hours	500 Hz	0.4 m^3 (first 7 min)	9°C
	NF270 permeate	4 hours	500 Hz	0.4 m^3 (first 7 min)	9°C

PCD was also combined with SG1485 membrane as in the initial experiments. No liquid phase ozone was detected. In the combination, PCD was used between 1.5 h – 2 h and 4 h – 4.5 h while filtration of washing water lasted for 25 hours. 0.5 m^3 oxygen was injected during the first treatment period. Temperature was 12.5°C and pressure 3.7 bar. During the combined experiment, permeate was collected and untreated washing water was continuously pumped into PCD tank (4% of the total volume per hour) to keep the amount of liquid constant.

Second washing water batch was filtrated with spiral wound module NF270 in conditions presented in Table V, as a comparison to experiments with flat-sheet module NF270. Part of the permeate (30 l) from filtration was afterwards treated with PCD, while the rest 500l was filtrated again. This was done to evaluate which method, nanofiltration or PCD treatment, better purified permeate. It was also measured if significant changes in composition of water happen in a long 4 h PCD treatment of salad washing water and NF270 permeate. Conditions of the PCD treatment of second water batch are presented in Table VIII.

8. Results of the experiments

8.1. Performance of the ceramic membrane SG1485

Tap water permeability of SG1485 membrane was evaluated frequently and the results are presented in Figure 17. Initial permeability was 7.2 kg/(m^2hbar), which increased to 16.4 kg/(m^2hbar) after the first alkaline chemical cleaning (experiment 8 in the figure). After first experiment with salad washing water (experiment 11), permeability decreased from 15.6 to 2.4

kg/(m^2hbar), which was restored to 13.4 kg/(m^2hbar) with alkaline cleaning. It can be deduced, that the membrane was initially not clean, and its function was fully restored with the first chemical cleaning.

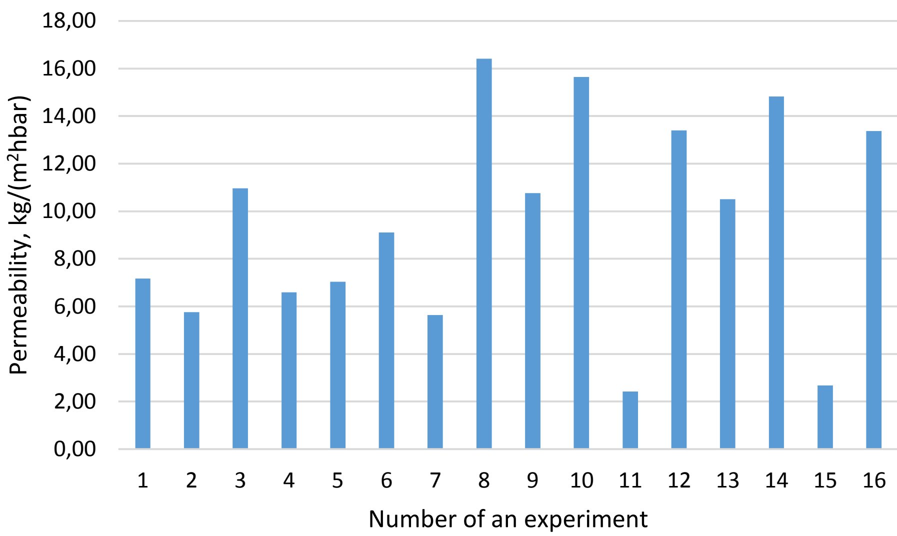


Figure 17: Permeability of tap water in pressures 1.9-12.5 bar. Temperature between 18-24°C. Experiments were performed in period of 20.1.2016 – 8.4.2016 and are shown in chronological order. Chemical cleaning was done prior to experiments 8, 10, 12, 14 and 16.

When humic acid solutions were filtrated, there was no change in permeability during 150 min and 400 min of experiments or in tap water permeability after the filtration. Therefore, humic acids were not presumably fouling the membrane further. Permeability was slightly lower with humic acids solutions than with tap water, 6.2 compared to 7 kg/(m^2hbar) with used TMP of 3.2 bar.

During PCD treatment, permeability increased in most of the initial experiments lasting longer than 60 min, which can be connected to oxidation of foulants on membrane. However, after the first chemical cleaning, permeability was stable during the further experiments with tap water and humic acids. Figure 18 shows examples in development of permeability during three different PCD – NF experiments with humic acid solutions.

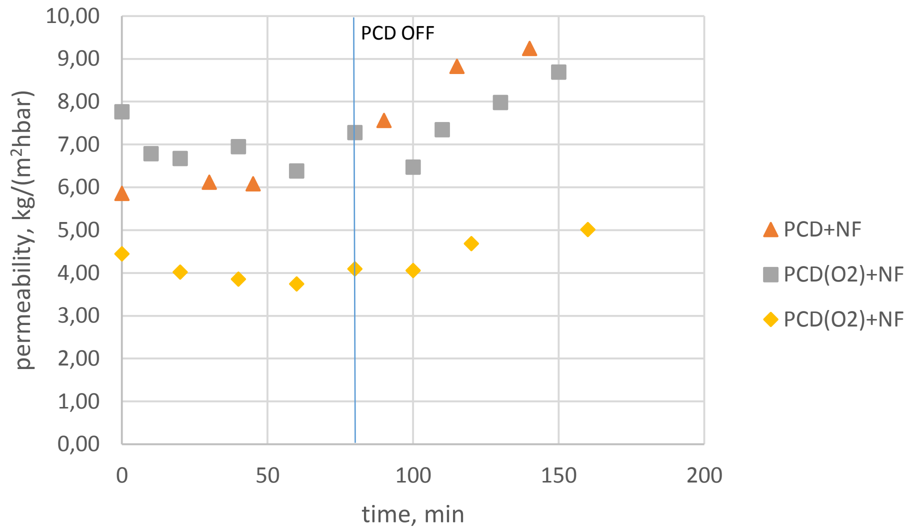


Figure 18: Permeability of SG1485 membrane during PCD treatment of humic acids solutions (120-130 mg/l). PCD on between 0-80 min. T=18-21°C.

8.2.Formation of ozone in PCD treatment

Ozone sensor was installed before the membrane and development of ozone concentration in liquid phase was monitored constantly. Sudden increase (40-70%) in ozone concentration was noted soon after the PCD was shut down. High electric field produced by PCD presumably caused interferences to the ozone monitor. As presented in Figure 19, ozone concentration is not shown to increase constantly as it should. Ozone concentration value was therefore unreliable until PCD was closed. Only ozone concentrations after PCD was turned off could be analyzed.

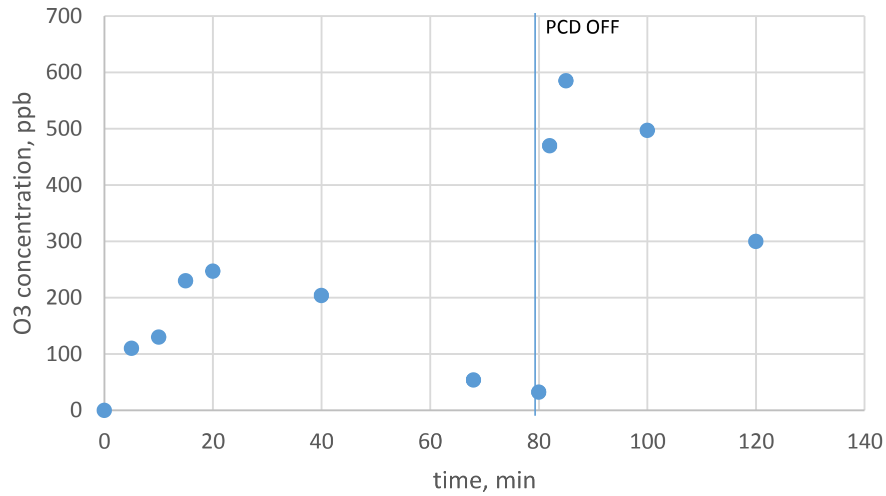


Figure 19: Ozone concentration development in function of treatment time. T = 19ºC. PCD on between 0-80 min. Figure demonstrates the problem with the used ozone sensor.

8.2.1. Effect of temperature and oxygen injection for ozone concentration

Ozone concentration in liquid phase was greatly dependent on temperature and oxygen addition. Concentration reached in tap water at 13ºC was over threefold compared to that at 19ºC. Oxygen addition of 0.5 to 0.8 m^3 into PCD shell reached fourfold to sevenfold concentrations compared to experiments in air atmosphere. Maximum ozone concentration with and without oxygen injection in two different temperatures is presented in Figure 20. Frequency of PCD did not affect the maximum achieved ozone concentration.

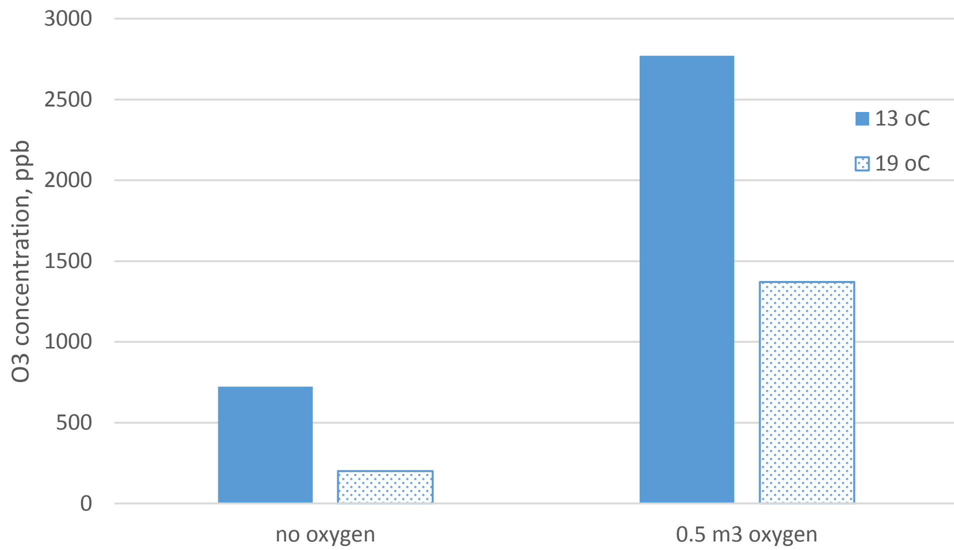


Figure 20: Ozone concentration dependency on temperature and oxygen injection. PCD on for 35 min. Oxygen induced during the first 15 minutes.

The injection of 0.8 m^3 oxygen enabled gas phase oxygen concentration of 96% in the PCD shell. In comparison, injection of 0.5 m^3 enabled gas phase concentration of 91%. Gas phase oxygen concentration decreased by speed of 5% in ten minutes due to small leakage. Amount of 0.4 – 0.5 m^3 oxygen was then injected in further experiments, as this achieved high enough gas phase oxygen concentrations for efficient production of ozone.

Overall, measured liquid phase ozone concentrations were relatively low in this work. Geluwe et al. [6] achieved ozone concentration 1450 ppb after only 6 minutes ozonation in pure water (20^{o}C). However, they used pure ozone and induced it directly to the liquid reactor medium as fine bubbles. Singh et al. [53] achieved steady 1000 ppb concentration in distilled water after 5 minutes of discharge in pulsed power system. Kornev et al. [65] measured gas phase ozone concentration of 6000 ppb in similar PCD configuration, while ozone concentration in liquid phase (distilled water) did not exceed 100 ppb (20^{o}C, no oxygen). The reactor system used in this work does not apparently allow high ozone mass transfer to liquid phase, because contact time between discharges and water droplets is short.

8.2.2. Decomposition time of ozone in PCD treatment

Ozone decomposition as a function of time was studied measuring ozone concentration just after PCD, before the membrane and after the membrane. There exists only limited amount of research about decomposition time of ozone in pulsed corona discharge treatment. Therefore, the results were compared to values found in literature for decomposition time of ozone in ozonation.

Ozone concentration just after PCD was notably higher than before the membrane, as shown in Figure 21. It should take 4 min for water to travel this distance of three meters, taken into account the residence time in the tank below PCD unit and liquid flow rate of 6 l/min. As shown by Sotelo et al. and Lenntech BV, 4-12% of ozone should decompose in that time, but the maximum concentration difference was 45% after the PCD was turned off [27, 66]. Ozone concentration before the membrane was also significantly higher than after the membrane, taken into account that it should take only 25 seconds for water to travel this distance. This difference could be accounted to fouled membrane: reaction of ozone with foulants on the membrane surfaces. However, fouled membrane does not explain the concentration difference between the measurement points before the membrane.

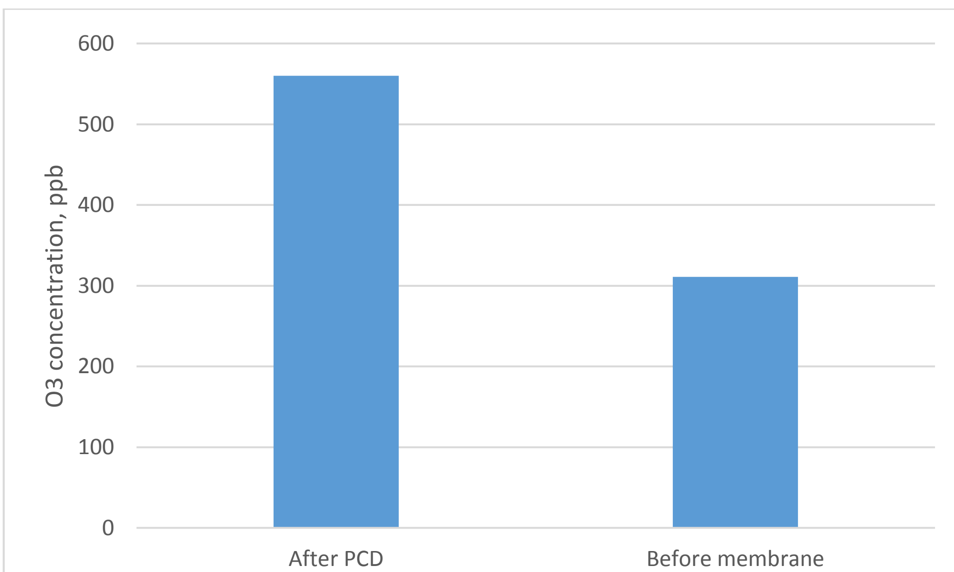


Figure 21: Ozone concentration after PCD unit and before membrane. T= 19°C. PCD on for 45 min.

The concentration differences could also be explained by ions in tap water. Ions and/or traces of organic material have been reported to result in faster decomposition of ozone [26]. Therefore, ozone decomposition was evaluated similarly in ultrapure deionized water. Even then, the ozone concentration was 585 ppb after the membrane, while it was only 217 ppb before the membrane in similar conditions when PCD was turned off (Figure 22). Magureanu et al.

[67] also evaluated the effect of ionic species (carbonate/bicarbonate) present in tap water during non-thermal plasma treatment. Pure water did not show difference in decomposition rate of ozone, compared to tap water in their study.

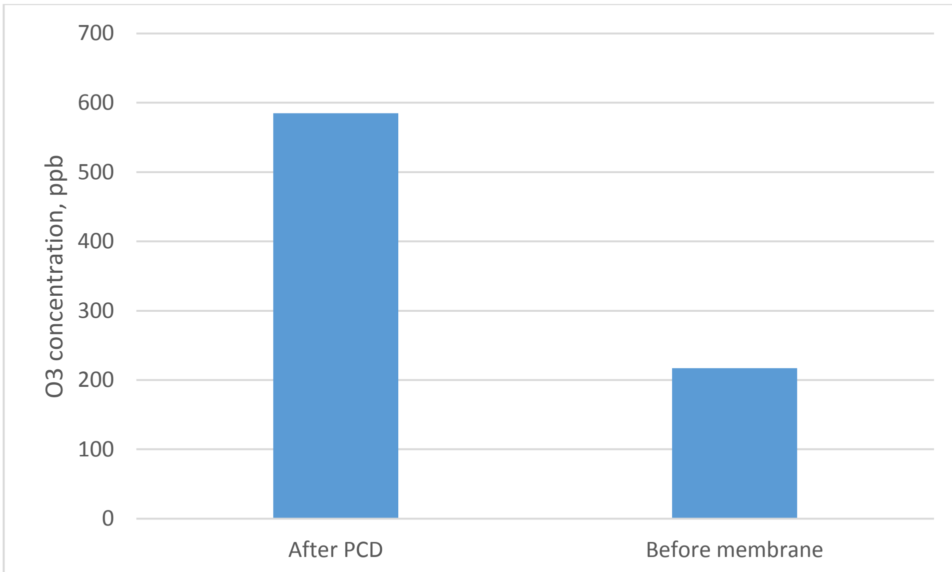


Figure 22: Maximum ozone concentration in pure water after PCD and before membrane. T=19^{o}C. PCD on for 80 min.

As a conclusion, decomposition time of ozone produced by pulsed corona discharge can not be compared to ozonation process and can be assumed to be merely affected by other oxidants in water. As stated in chapter 2 of this work, UV light and H_2O_2 accelerate the decomposition of ozone, both of which are also formed in pulsed corona discharge treatment. Additional studies are required to further evaluate the decomposition time of produced oxidants in pulsed corona discharge treatment.

8.3. Effect of PCD for conductivity of water

Conductivity increased significantly during PCD treatment, especially with deionized water. Only small increase was measured during filtration of deionized water, tap water and humic acids solutions, if PCD was not used. This change can not be due to ozone present in water either, since the conductivity was measured to be the same even after bottle filled with sample was left untouched for some hours after treatment. Table IX shows the conductivity values both in concentrate and permeate in different samples.

Table IX: Conductivity values prior/after PCD and NF experiments in different water samples.

Treatment method	Sample	Treatment time	Conductivity (µS/cm)	
			Feed water	Permeate
Nanofiltration (SG1485)	Humic acids (65 mg/l)	0 min	125	94
		150 min	130	98
		Change	4 %	4 %
PCD + NF treatment	Tap water	0 min	115	93
		90 min	139	121
		Change	21 %	30 %
PCD + NF treatment	Humic acids (125 mg/l)	0 min	125	101
		80 min	211	129
		Change	68 %	27 %
PCD + NF treatment with O_2 injection	Humic acids (125 mg/l)	0 min	123	77
		80 min	149	100
		Change	21 %	30 %
PCD + NF treatment	Pure water	0 min	7	8
		80 min	180	151
		Change	2471 %	1788 %

Nitrate formation might be the main reason for increased conductivity. Kornev et al. [65] showed in their studies, that PCD treatment produces nitrates (NO_3^-) and nitrites (NO_2^-) in oxygen-nitrogen atmosphere. Nitrites further oxidize to nitrates. Nitrate formation is increased in low conductivity solution, which explains the most significant change in pure water in this work. Increase was also lower when oxygen was injected, because this decreases the nitrogen content in gas. Nitrogen is naturally required for formation of nitrates.

Other degradation products including conductive ions (O^-, H^+, OH^-, H_3O^+), acids and aldehydes can also increase the conductivity [38]. In addition, it is possible that oxidants and discharges containing high energy corrode the pipes and equipment, detaching some metals (for example iron) from the surfaces.

8.4. Effect of PCD for degradation of humic acids

UVA_{254}, UVA_{280}, UVA_{250}/UVA_{365}-ratio, SUVA and TOC were used to evaluate the degradation of humic acids. The main results of the experiments are collected in Table X. Increase in treatment time gradually improved the degradation. 60 min usage of PCD corresponds to 2 kWh/m^3 energy use.

Table X: Influence of PCD treatment on degradation of humic acids. The table presents the treatment time of PCD with possible oxygen addition (0.5 m^3), total filtration time, concentration of humic acids, temperature, and change in measured water quality parameters in feed stream during the treatment. N.A. = no data available.

Experiment	PCD time	Total time	HA (mg/l)	T (°C)	UVA_{254} % left	UVA_{280} % left	$UVA_{250/365}$ % change	TOC % left	SUVA
#1 PCD	90 min	120 min	98	17.7	49	42	57	85	6.2 / 3.6
#2 PCD + O2	45 min	75 min	126	19.4	62	58	30	90	6.4 / 4.3
#3 PCD + O2	80 min	100 min	120	12.5	40	34	60	75	6.4 / 3.6
#4 PCD + O2	150 min	180 min	120	19.3	18	13	144	59	6.7 / 2.0
#5 PCD	115 min	120 min	115	20.3	48	41	53	N.A.	N.A.
#6 PCD + O2	80 min	160 min	123	19.7	30	23	92	67	6.2 / 2.6
#7 PCD	80 min	160 min	130	19.5	52	46	46	79	5.6 / 3.7

Degradation by destruction of double bonds and aromatic rings was much faster than demineralization. This can be seen in quick decrease of UVA_{254} and UVA_{280} values and slow decrease in TOC. Figure 23 presents an example of changes in UVA and TOC values during PCD treatment of humic acids. For instance, decrease in TOC was only 13% when 48 mg/l TOC solution (123 mg/l HA) was treated for 40 min (500 Hz) with oxygen addition at 19°C. UVA_{254} decreased by 39% and UVA_{280} by 43% in the same experiment. The difference is mainly explained by selective reactions of ozone with aromatic and unsaturated bonds of organic material. The amount of small molecular weight substances increased quickly: $UV_{250/365}$ absorbance ratio increased by 30% during 40 min PCD treatment.

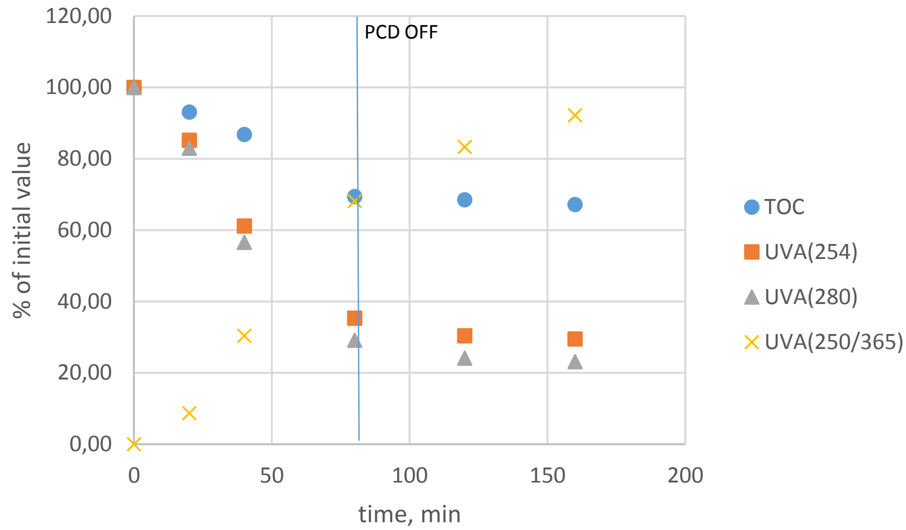


Figure 23: Changes in UVA and TOC values during PCD treatment of humic acids (123 mg/l). T=19ºC. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m^3. 0.5 m^3 oxygen injection between 1-8 min. UVA$_{250/365}$-ratio is expressed as a percentage change and other values as a percentage of the value in the untreated sample.

Degradation and mineralization degree of humic acids was higher when treatment time increased. Figure 24 presents changes of UV$_{254}$, TOC and UVA$_{250/365}$ –ratio in 150 min PCD treatment. Even this relatively long treatment did not degrade the humic acids completely, as there was still 18% UVA$_{254}$ and 59% TOC left in the end.

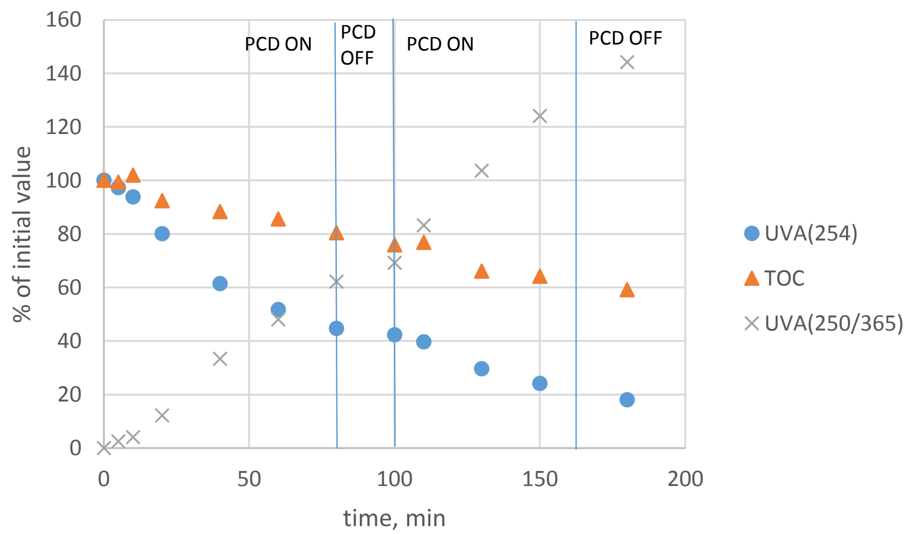


Figure 24: Long PCD treatment of humic acids solution (120 mg/l). T=19ºC. PCD on between 0-80 min and 100-170 min. Maximum delivered energy: 5 kWh/m^3. 0.5 m^3 oxygen injection between 1-8 min and 0.3 m^3 more between 105-110 min.

Degradation of humic acids continued after PCD was turned off, approximately for an hour. For example, 5% more UVA_{254} reduction, 2% more TOC reduction and 15% additional increase in $UVA_{250/365}$ –ratio was measured after 40 minutes of shutdown of PCD (19^{o}C). The results indicate, that some physical or chemical processes still occurred in water after PCD unit was turned off. Ozone concentrations higher than 15 ppb were not measured in the samples, but other long-living oxidative species (like hydrogen peroxide) might have been present in the water for prolonged time, inducing reactions with organic material.

Humic acids were transformed to be more hydrophilic due to PCD oxidation. This can be seen in SUVA values decreasing from average of 6.5 (hydrophobic) to 3.5 (slightly hydrophilic). Hydrophilic substances are significantly less susceptible to foul membranes than hydrophobic ones [6]. Since no fouling was observed in the HA experiments, the effect of increased hydrophilicity is difficult to evaluate.

TOC and UVA values increased in permeate as a result of PCD treatment. An example is presented in Figure 25. Initially humic acids did not penetrate pores of the membrane, since the values of TOC and UVA in permeate were similar than during the filtration of tap water. After 20-40 min of PCD treatment, these values started to increase gradually. This indicates that the degraded humic acid fractions penetrated the membranes. Even though percentage change was significant, final values were still low after 80 min treatment. For example, UVA_{254} of the produced permeate was only 5% and TOC only 13% of the value measured in feed stream.

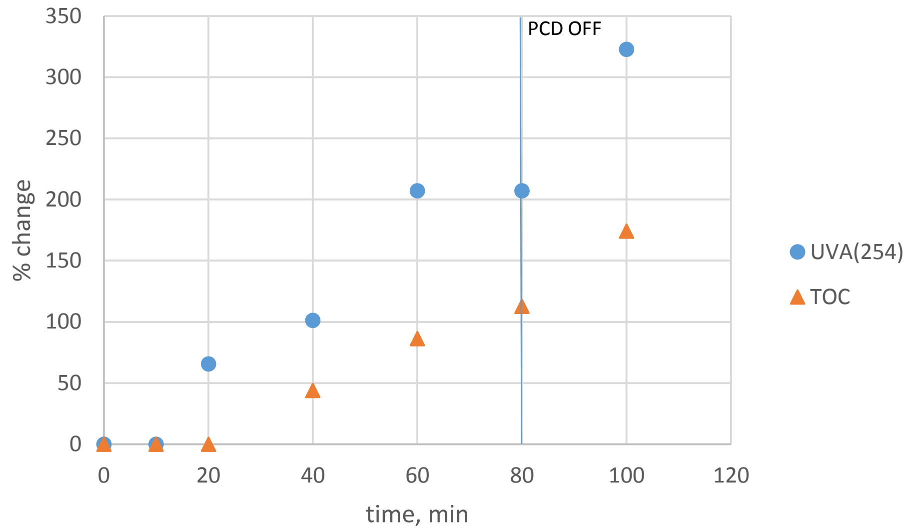


Figure 25: Changes in TOC and UVA(254) in permeate during PCD treatment. T=13ºC. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m^3. 0.5 m^3 oxygen injection between 1-8 min.

Retention of membrane SG1485 decreased due to degradation. Retention of TOC decreased from 95% to 82% during 100 min of experiment. Similarly, retention of UV_{254} decreased from 99% to 86% during same time. Initial retention can be assumed as 100% due to tap water interference. The development of retention are shown in Figure 26.

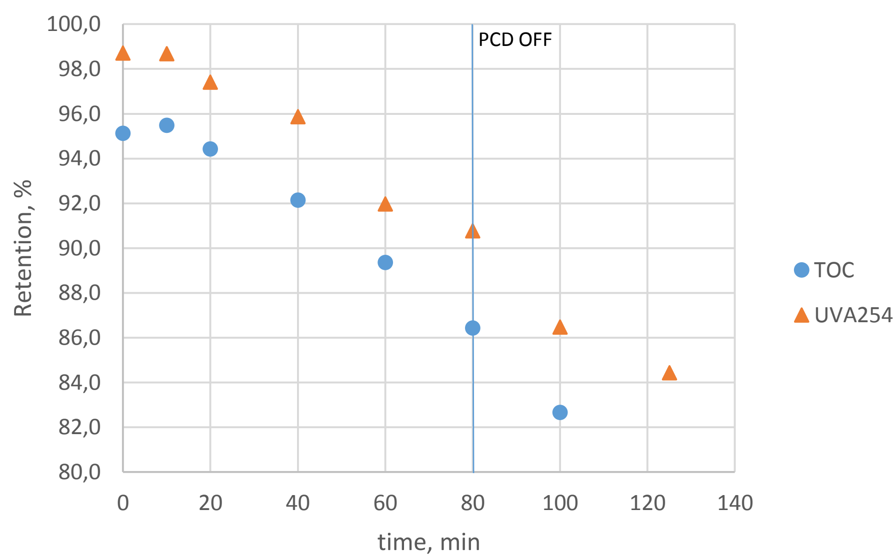


Figure 26: Retention of TOC and UV_{254} in filtration during combined PCD treatment. T = 13ºC. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m^3. 0.5 m^3 oxygen injection between 1-8min.

Inorganic carbon (IC) decreased rapidly both in concentrate and permeate during the PCD treatment. Figure 27 presents the changes of TOC and IC in the concentrate. Initial TOC was 46.8 mg/l and IC 7.5 mg/l. It is presumable that IC consists of tap water constituents like carbonate ions, since the IC concentration in the tap water is the same than the initial concentration in humic acid solutions. Most of the IC in feed also goes through the membrane, thus it has to contain small compounds, most possibly monovalent ions such as bicarbonate. Magureanu et al. [67] as well experienced decrease in inorganic carbon during non-thermal plasma treatment, but the reason was not explained. Formation of gases like CO_2 due to the PCD treatment can be one possible reason for decrease in inorganic carbon content. There exists only limited amount of research about change of inorganic carbon content in liquid sample during non-thermal plasma treatment.

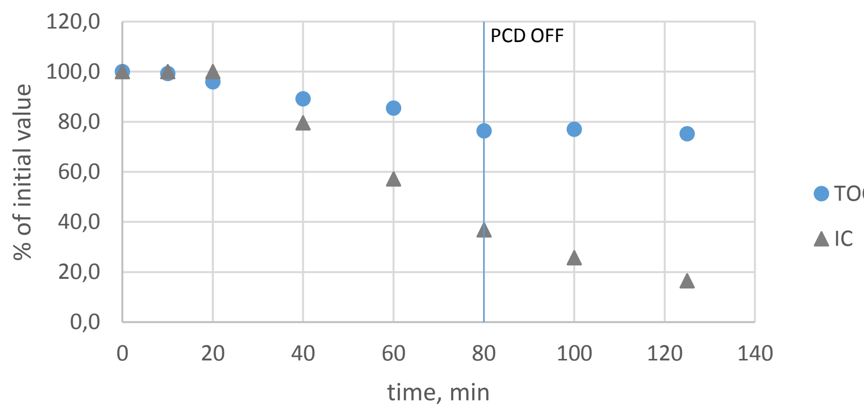


Figure 27: Example of change in TOC and IC values during PCD+NF experiment. T=13°C. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m³. 0.5 m³ oxygen injection between 1-8 min.

8.4.1. Effect of oxygen injection and temperature for degradation of humic acids

Oxygen addition and higher temperature improved the degradation of humic acids, measured by UVA and TOC values. As discussed in chapter 3, addition of oxygen increases the formation of oxidative species in water, especially ozone. Elevated temperature increases the formation rate of reactive radicals.

Change of TOC during treatment in three different conditions can be seen in Figure 28. Treatment at 19°C temperature and with oxygen addition (0.5 m^3) decreased TOC by 31% in 80 min. When oxygen was not used, the reduction of TOC was only 19% in the same conditions.

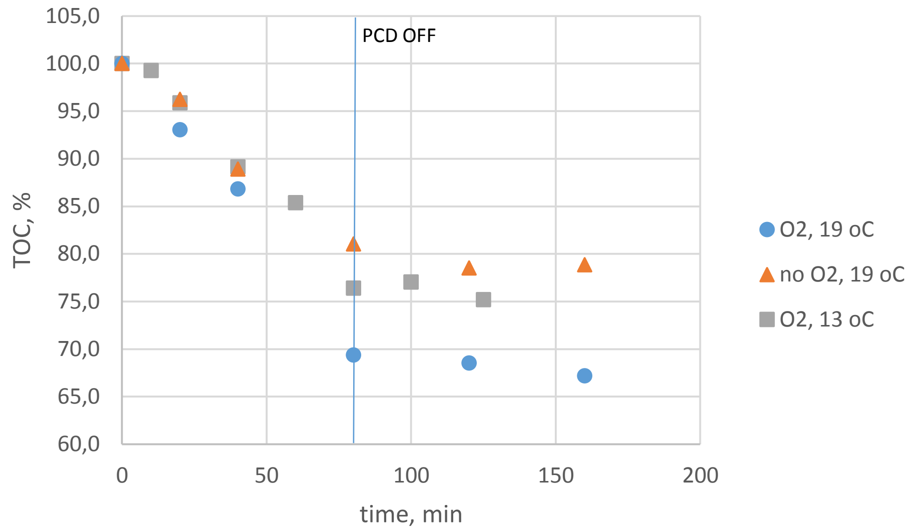


Figure 28: Effect of oxygen injection and temperature for TOC values. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m^3.

Effect of oxygen injection and temperature for reduction of UV_{254} absorbance is presented in Figure 29. While UVA_{254} reduced by 65% in 80 min when 0.5 m^3 oxygen was added, it reduced only by 44% when oxygen was not used (19^{o}C). Treatment in lower 13^{o}C temperature with oxygen addition resulted in faster reduction of UVA_{254} than the treatment at 19^{o}C without oxygen. This indicates, that oxygen injection is more important for degradation of humic acids than the temperature difference of 6^{o}C.

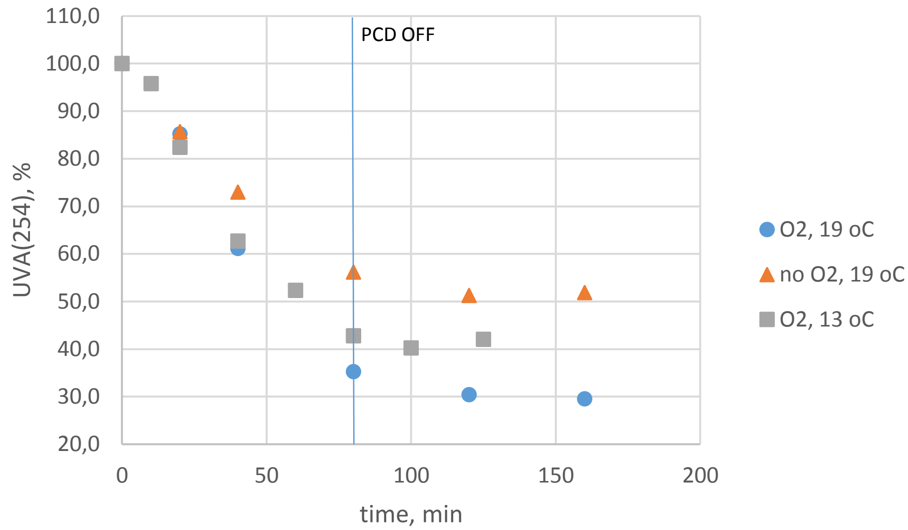


Figure 29: effect of oxygen injection and temperature for UV_{254} absorbance values. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m^3.

Respective change in $UVA_{250/365}$ –ratio in the three experiments is presented in Figure 30. The ratio represents the increase in amount of small molecular weight substances compared to large ones. PCD treatment with 0.5 m^3 oxygen injection achieved 68% increase in the ratio during 80 min, while change was 38% without oxygen.

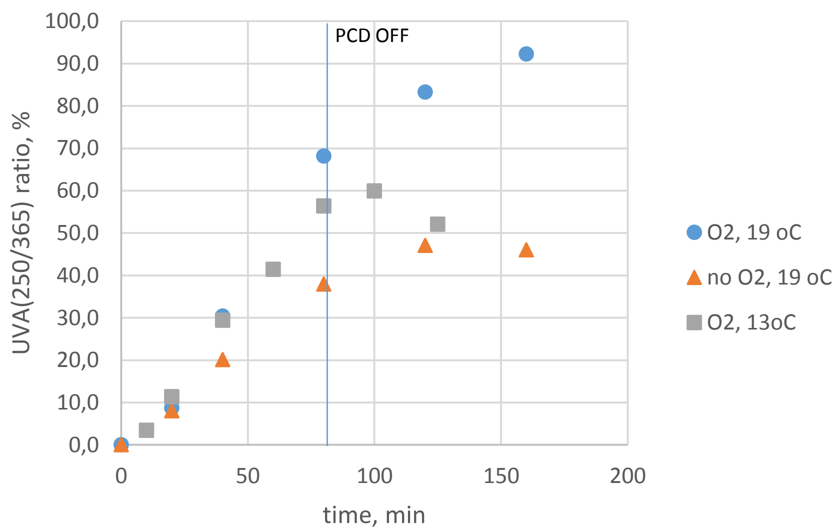


Figure 30: effect of oxygen injection and temperature for change in UVA(250/365)-ratio. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m^3.

Effect of temperature and added oxygen for SUVA values is shown in Figure 31. Oxygen injection showed enhanced SUVA reduction, 41% in 80 min compared to 31% without oxygen.

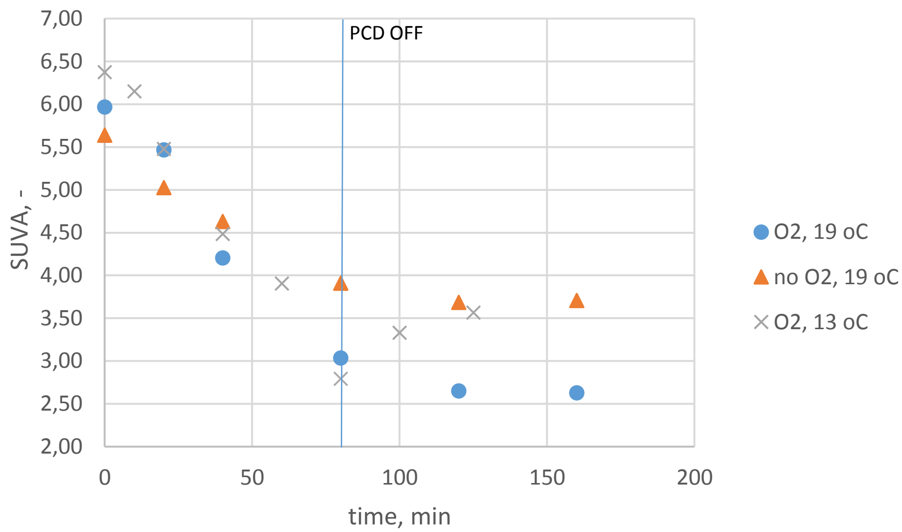


Figure 31: effect of oxygen injection and temperature for SUVA values. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m^3.

Temperature or oxygen injection had only small effect for changes in permeate composition. TOC and UVA_{254} change in permeate in different temperature is presented in Figure 32. Initial TOC was 5% of the feed values, which increased to 11% during 80 min PCD function. Corresponding change in UV_{254} was from 1% to 5%.

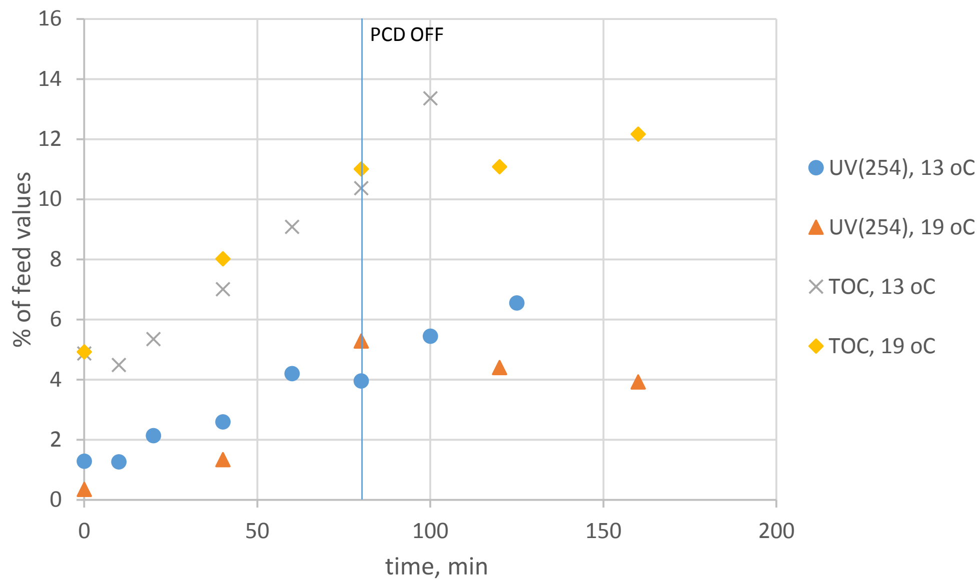


Figure 32: Effect of temperature for TOC and UVA(254) values in permeate. PCD on between 0-80 min. Maximum delivered energy: 2.67 kWh/m^3.

8.5. Purification of salad washing waters

8.5.1. Treatment by membrane filtration

Figure 33 shows the permeability of different membranes at the beginning and end of lettuce washing water filtration experiments. Filtration conditions are presented in Table V. Permeability decreased by 30-85% during the filtration depending on used membrane. There was also similar difference in tap water permeability before and after the experiment, as shown in Figure 34. Most fouling seemed to occur with OC030 membrane, which was followed by SG1485, RC70 and NF270 membranes.

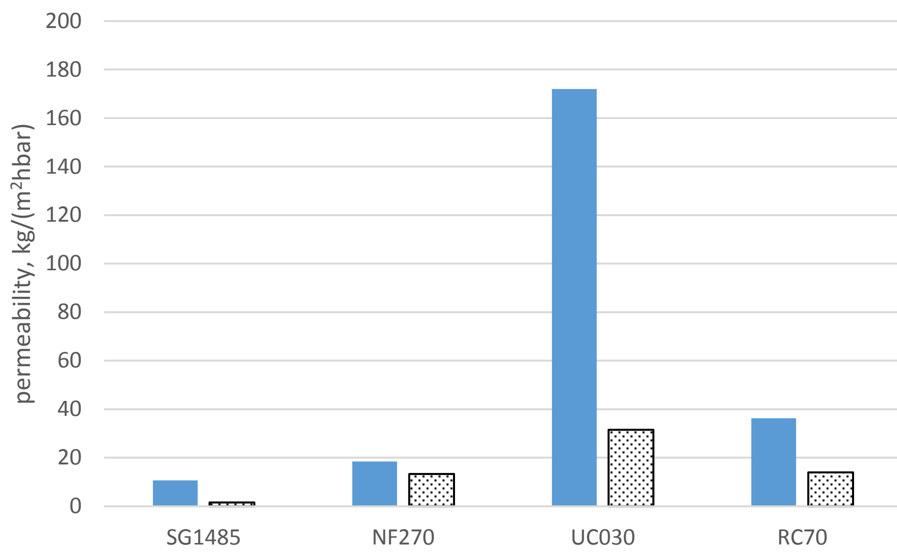


Figure 33: Permeability at the beginning and end of the lettuce washing filtration experiments with different membranes. Permeability is temperature corrected to 20ºC.

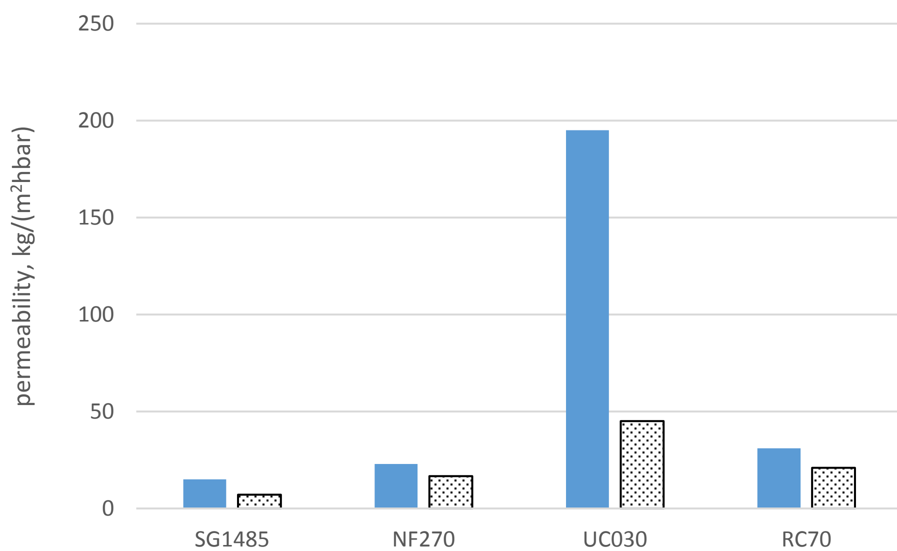


Figure 34: Tap water permeability before and after the lettuce water filtration experiments with different membranes. T=20ºC.

Chemical cleaning was required to clean the fouled membrane. For ceramic membrane, 85% of initial permeability was restored with one 20 min treatment with Ultrasil110 (1.5%) solution. Cleaning of NF270 achieved even 15% higher permeability than its initial permeability before the filtration experiments.

8.5.1.1. Treatment with nanofiltration membranes

Retention was definitely better with NF270 flat-sheet membrane when compared to SG1485 in tubular configuration. Figure 35 presents concentration of TOC as a function of volume reduction factor (VRF) with both membranes. The concentration of TOC was four times higher than the initial value at VRF of 5.6, when NF270 membrane was used, which indicates organic material concentrated well on the other side of membrane. At that VRF, the retention of TOC was also as high as 93%. With SG1485 membrane, retention of TOC was only 42% at VRF of 4.9.

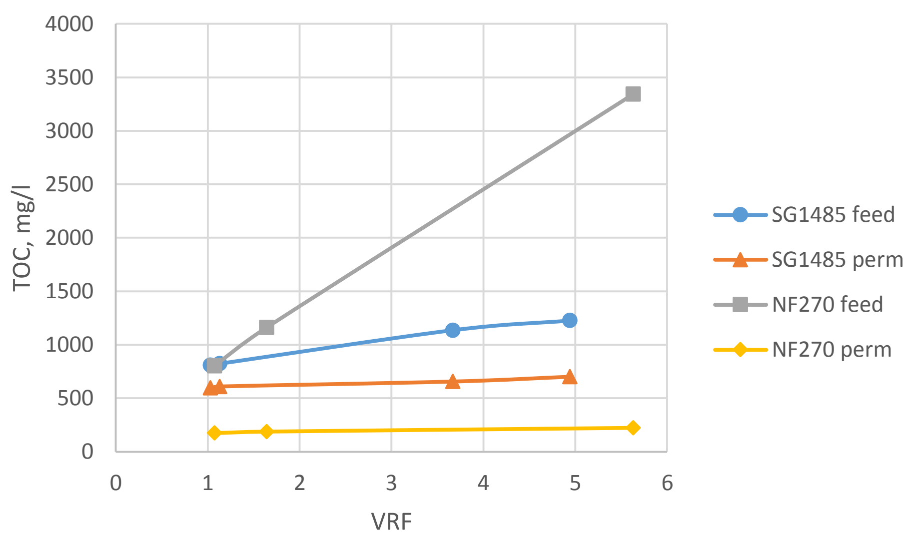


Figure 35: Change of TOC as a function of volume reduction factor of feed.

Both membranes retained UV absorbing compounds well. UVA_{254} values as a function of VRF are shown in Figure 36. Retention at the beginning of the filtration was 89% with NF270 and 77% with SG1485 membrane. As the permeate quality did not change significantly during the filtration and feed water continuously concentrated, retention even increased. At VRF of 5.6, retention of UVA_{254} was 97% with NF270. Corresponding retention with SG1485 at VRF 4.9 was 94%. Larger UV_{365} absorbing compounds penetrated the membranes hardly at all.

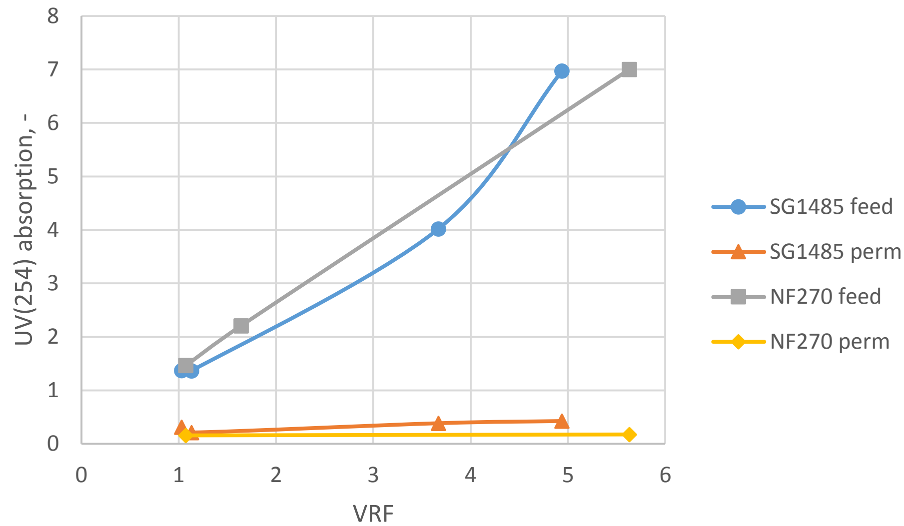


Figure 36: Change of UVA(254) as a function of volume reduction factor of feed.

Retention of dissolved solids was poor with SG1485 membrane, which indicates that they include mostly small compounds with molecular weight under 600 mg/l. Concentration of suspended solids in permeate was zero with both of the membranes. Therefore, measured total solids (TS) in permeate comprise only dissolved ones. Change of TS as a function of VRF is presented in Figure 37. Initial retention of dissolved solids was 75% with NF270 and only 14% with SG1485.

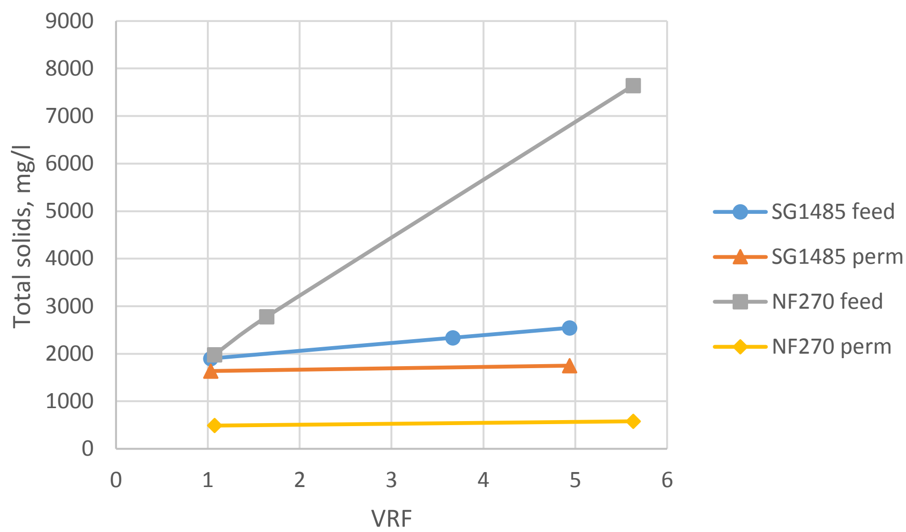


Figure 37: Change of total solids (TS) as a function of volume reduction factor of feed.

Initial retention of conductivity was 34% with the NF270 membrane, while it was only 17% with SG1485 membrane. SEM analysis revealed that NF270 separated mainly calcium, phosphorus, magnesium, sulphur and part of potassium. Figure 38 presents the color of SG1485 feed, permeate and final concentrate. Color was removed fairly well with both of the membranes.

Figure 38: Color removal in salad water samples. Left: original feed water, center: SG1485 permeate, right: SG1485 final concentrate

Quality of permeate decreased slightly during the filtrations. Summary of the measured parameters and retention with nanofiltration membranes is presented in Table XI and Table XII. For example, TOC value in SG1485 permeate increased from 596 to 701 mg/l, while TOC of

NF270 permeate increased from 174 to 223 mg/l. SG1485 presented generally more fouling than NF270 membrane, in terms of tap water permeability difference before and after the filtration of salad washing waters (Figure 34).

Table XI: Measured TOC, UVA(254), UVA(365) and conductivity values during salad washing water filtration with NF membranes. Samples of permeate were taken from the pipe.

	sample	TOC (mg/l)		UVA(254)		UVA(365)		Conductivity, µS/cm	
		initial	final	initial	final	initial	final	initial	final
NF SG1485	conc	809	1226	1.37	6.97	0.21	2.46	640	950
	perm	596	701	0.31	0.38	0.01	0.01	533	660
	ret. %	20	46	77	94	95	100	17	31
NF NF270	conc	802	3343	1.46	7	0.52	2.21	684	1315
	perm	174	223	0.16	0.18	0.04	0.03	452	495
	ret. %	78	93	89	97	92	99	34	62

Table XII: Measured pH, TS, TSS and fixed solids values during salad washing water filtration with NF membranes. Samples of permeate were taken from the pipe. N.A. = no data available

	sample	pH		Total solids (mg/l)		TSS (mg/l)		Fixed solids (mg/l)	
		initial	final	initial	final	initial	final	initial	final
NF SG1485	conc	7.5	6.4	1900	2545	90	389	400	537
	perm	6.8	6.5	1637	1750	0	0	N.A.	N.A.
	ret. %	N.A.	N.A.	14	31	100	100	N.A.	N.A.
NF NF270	conc	4.3	4.2	1980	7643	39	159	410	838
	perm	N.A.	N.A.	489	579	0	0	N.A.	N.A.
	ret. %	N.A.	N.A.	75	92	100	100	N.A.	N.A.

8.5.1.2. Treatment with ultrafiltration membranes

UF membranes were not sufficient to retain organic material, dissolved solids and ions. Overview of the measured parameters is shown in Table XIII and Table XIV. TOC values in permeate were close to the feed concentration, which indicates almost all of the organic material passed the UF membranes. TOC in concentrate also increased only 5-7 % at VRF of 4. Retention of total solids and conductivity was close to 0% as well. Suspended solids were retained, however, so weak retention was attributed only to dissolved ones. However, UV_{254} absorption value doubled and UV_{365} value tripled with both of the used UF membranes. Therefore, at least part of the larger organic molecules was retained by the membranes.

Table XIII: Measured TOC, UVA(254) and UVA(365) values, when washing water was treated with UF membranes. Final permeate values are average values of the whole filtration period. N.A. = no data available

	sample	TOC (mg/l)		UVA_{254}		UVA_{365}	
		initial	final	initial	final	initial	final
UF UC030	conc	705	742	1.16	2.43	0.39	1.2
	perm	N.A.	693	N.A.	0.48	N.A.	0.06
UF RC70	conc	705	755	1.16	2.58	0.39	1.26
	perm	N.A.	679	N.A.	0.6	N.A.	0.10

Table XIV: Measured conductivity, TS and TSS values, when washing water was treated with UF membranes. Final permeate values are average values of the whole filtration period.

	sample	Conductivity, µS/cm		Total solids (mg/l)		TSS (mg/l)	
		initial	final	initial	final	initial	final
UF UC030	conc	612	631	2207	1745	37	N.A.
	perm	N.A.	615	N.A.	2097	0	0
UF RC70	conc	612	650	2207	1774	37	N.A.
	perm	N.A.	597	N.A.	1498	0	0

8.5.2. PCD treatment of salad washing waters

Pulsed corona discharge oxidation clearly degraded organic compounds but did not achieve mineralization of them in sample waters. Effects of the PCD treatment on TOC, IC and UVA_{254} values and $UVA_{(250/365)}$-ratio in the process water are displayed in Figure 39. Figure 40 presents the similar parameters (IC excluded), when SG1485 permeate was treated. Figures also present the values initially obtained in the permeates of SG1485 and NF270 filtration. It can be seen that using only PCD, similar purification results than in filtration were not achieved.

TOC value in washing water remained rather constant within the limits of inaccuracy during the PCD treatment. Inorganic carbon concentration (both in concentrate and permeate) first increased up to 30 minutes of treatment and decreased rapidly after that. Dissolved organic matter is known to oxidize into inorganic matter, like CO_2, HCO_3^-, CO_3^{2-} and H_2CO_3, increasing inorganic carbon content [68]. However, since the initial TOC concentration is significantly higher than IC concentration, 736 mg/l compared to 11 mg/l, the changes in IC are not clearly seen in TOC values.

UVA values of all measured wavelengths (254, 280, 250 and 365 nm) decreased notably during PCD treatment, indicating degradation of organic material. For example, UV_{254} decreased by 54% in salad washing water and 52% in permeate during 120 min treatment. Changes in UVA_{254} and UVA_{280} values were only minor after 30 min. $UVA_{250/365}$ –ratio increased both in washing water and permeate up to 90 min, which indicates degradation of organic compounds to smaller molecular weight substances.

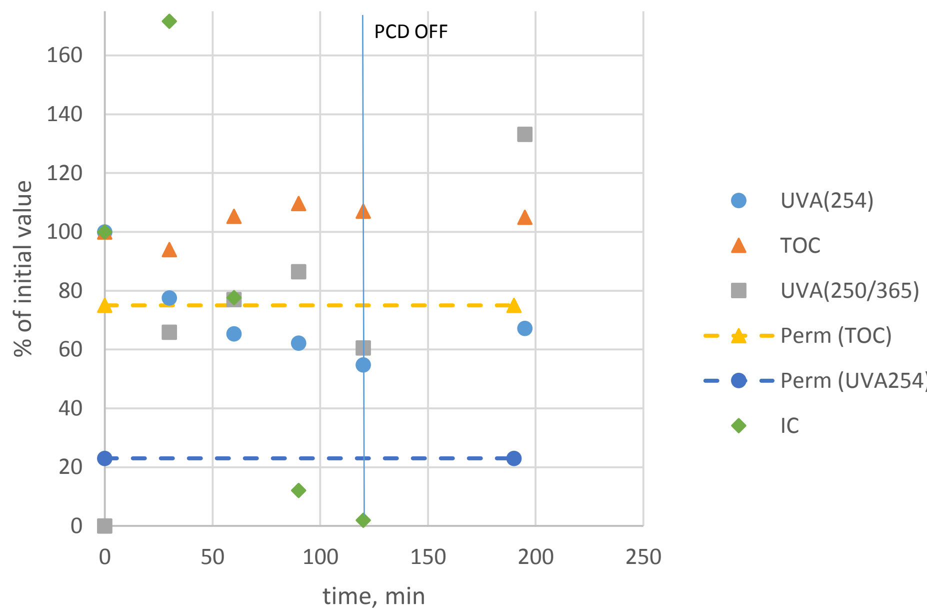


Figure 39: Effect of PCD on TOC, UVA(254nm) and IC values and UVA(250/365) ratio of salad washing water. Dotted lines present the values initially measured in SG1485 permeate. PCD on between 0-120 min. Maximum delivered energy: 4 kWh/m^3.

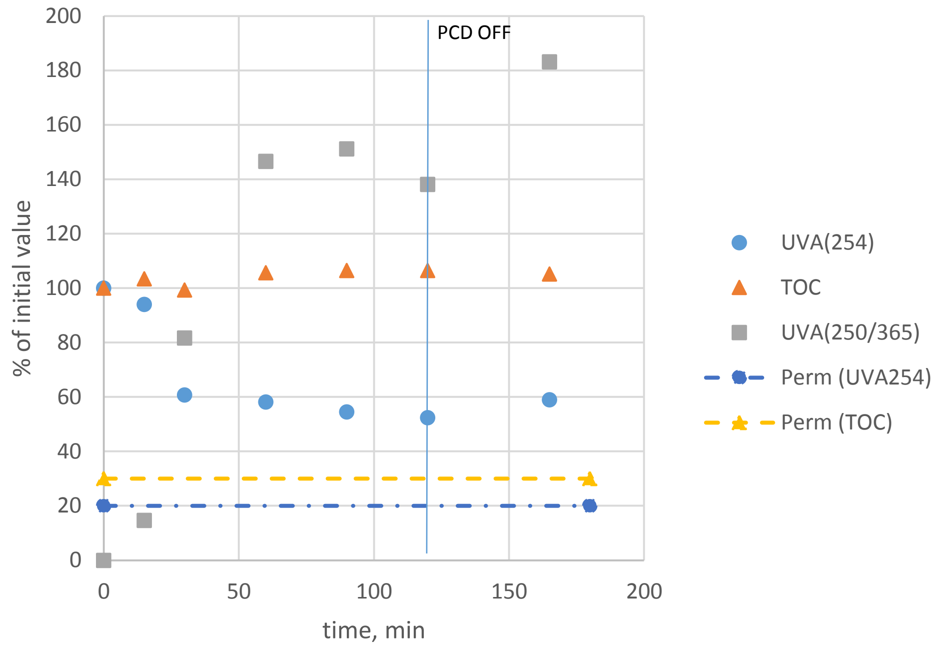


Figure 40: Effect of PCD on TOC, UVA(254nm) and UVA(250/365) ratio of membrane (SG1485) permeate. Dotted lines present the values initially measured in NF270 permeate. PCD on between 0-120 min. Maximum delivered energy: 4 kWh/m^3.

Effect of pulsed corona discharge treatment on all the measured parameters in salad washing water and SG1485 membrane permeate is shown in Table XV and Table XVI. PCD treatment decreased the amount of suspended solids in water, while dissolved solids content was seemingly increasing. Suspended solids were presumably degraded to particles which are able to dissolve. Conductivity increased slightly, likely due to nitrates, which were formed in the water during the oxidation. SUVA values decreased to half during the treatment, which indicates hydrophilicity of the compounds further increased.

Table XV: Effect of PCD oxidation on TOC, UVA(254, UVA(365) and SUVA, when salad washing water and SG1485 permeate were treated.

	time	sample	TOC (mg/l)		UVA_{254}		UVA_{365}		SUVA	
			initial	final	initial	final	initial	final	initial	final
PCD	2h	washing water	736	787	1.34	0.74	0.256	0.093	0.18	0.09
		SG1485 permeate	563	599	0.83	0.49	0.323	0.073	0.15	0.07

Table XVI: Effect of PCD oxidation on TOC, UVA(254) and UVA(365), when salad washing water and SG1485 permeate were treated. N.A. = No data available.

	time	sample	Conductivity, µS/cm		pH		Total solids (mg/l)		TSS (mg/l)	
			initial	final	initial	final	initial	final	initial	final
PCD	2h	washing water	636	682	5.3	4.3	1708	2055	91	13
		SG1485 permeate	552	607	5.7	4.9	1257	1135	N.A.	N.A.

8.5.3. Washing water treatment with combination of PCD and NF

Permeate flux was lower in combined PCD + NF treatment, compared to plain filtration experiment with salad washing water (chapter 8.5.1.1.). As shown in Figure 41, permeability was higher without PCD during the whole filtration period. PCD treatment has degraded organic material in water, presumably increasing the fouling by pore blocking and consequently decreasing the flux. The distance between PCD unit and membrane was probably overly long, that produced ozone and other oxidants could reduce fouling of the membrane.

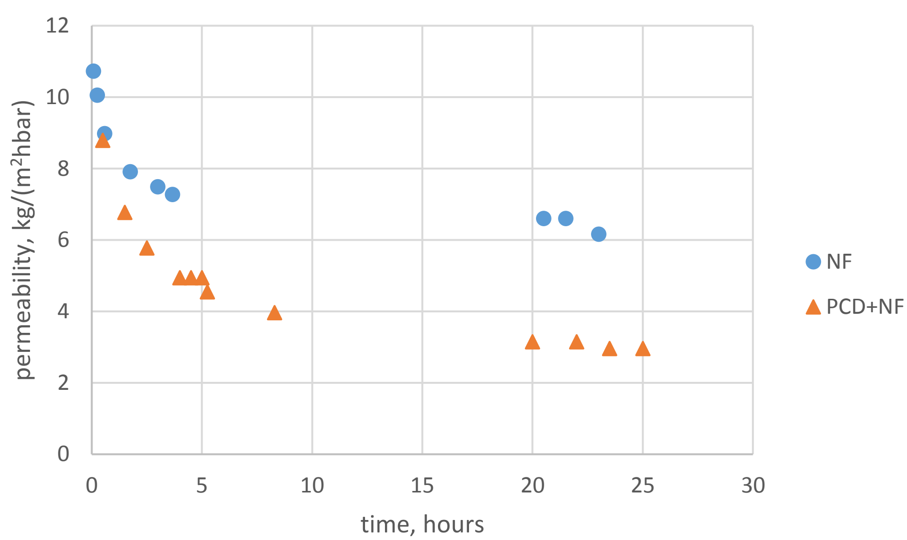


Figure 41: Permeability in combined PCD and nanofiltration (SG1485) experiment as a function of filtration time. Permeability is temperature corrected to 20°C. TMP 3.7 bar and flowrate 6 l/min.

Measured parameters in combined PCD + NF experiment at the beginning and end of the PCD treatment are shown in Table XVII and Table XVIII. PCD did not deteriorate the quality of permeate during the combined experiment. In fact, it seemed to purify permeate slightly, as TOC, TS and UV_{254} absorption values were lower in the permeate after the oxidation. For example, TOC in permeate decreased from 578 to 489 mg/l after the PCD treatment of one hour. Decrease of TOC was interesting, since it slightly increased in separate PCD experiment when permeate of SG1485 membrane was treated (see Table XV). This could indicate either that pre-treatment with PCD treatment caused mineralization of small organic material which already went through the membrane, or that it changed TOC to form, which was retained by the membrane. No suspended solids were measured in the permeate.

Table XVII: Change in TOC, UVA(254) and UVA(365) as a result of combined PCD + NF (SG1485) treatment.

	time	sample	TOC (mg/l)		UVA_{254}		UVA_{365}	
			initial	final	initial	final	initial	final
PCD+NF	1h	feed	695	771	1.56	1.38	0.61	0.51
		perm	578	489	0.27	0.25	0.03	0.05

Table XVIII: Change in conductivity, pH, total solids (TS), total suspended solids (TSS) and fixed solids (FS) as a result of combined PCD + NF (SG1485) treatment N.A. = no data available.

	time	sample	Conductivity (μS/cm)		pH	Total solids (mg/l)		TSS (mg/l)	FS (mg/l)
			initial	final	initial	initial	final	initial	initial
PCD+NF	1h	feed	639	634	4.48	1667	1758	70	344
		perm	555	561	5.19	1488	1339	0	N.A.

8.6. Selection of the membrane and sequence for cleaning the washing waters

Combining PCD treatment with nanofiltration was not profitable, since PCD oxidation decreased the permeability of the used SG1485 membrane. UF membranes and SG1485 were not tight enough to remove water constituents. NF270 membrane gave the best results: permeability was the highest with least fouling and permeate quality better than with other of the tested membranes. NF270 membrane was then finally used in a spiral wound module with high surface area, in order evaluate the usability of nanofiltration in large scale purification. It was also evaluated, if PCD oxidation is effective in treatment of membrane permeates or as a pretreatment for filtration.

8.6.1. Washing water treatment with spiral wound NF270 membrane

The NF270 membrane in spiral wound module experienced fouling during filtration of lettuce washing water (batch 2). Permeability values in the beginning and end of filtrations are presented in Figure 42. Corresponding changes in tap water permeability before and after treatment are presented in Figure 43. Permeability decreased from 6.8 to 1.9 kg/(m^{2}hbar) during the 11.5 h filtration period. Initial tap water permeability decreased from 12.3 to 3.4 kg/(m^{2}hbar). When the permeate was filtrated again, permeability stayed rather constant, when the increase in temperature is taken into account. Function of the membrane was restored with basic chemical cleaning.

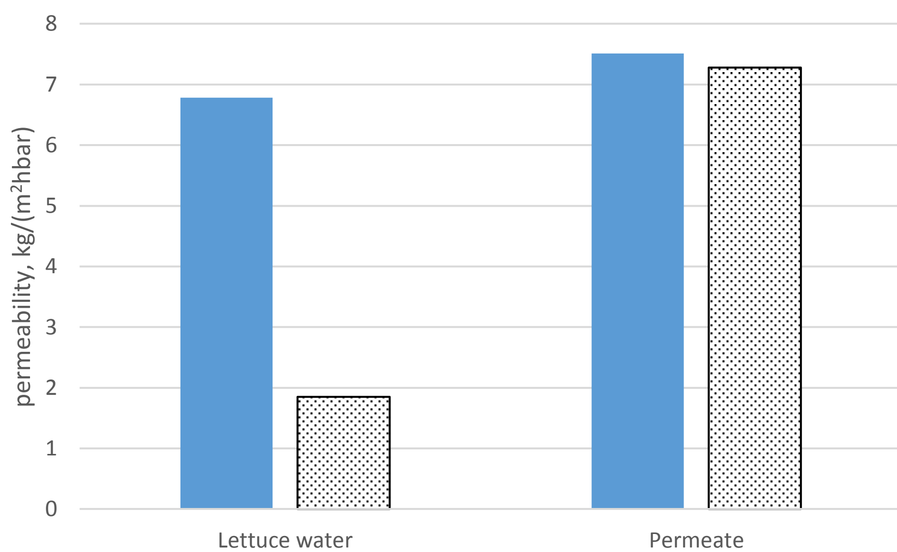


Figure 42: Permeability of NF270 membrane in the beginning and end of filtration. Lettuce washing water was filtrated and the produced permeate was filtrated again.

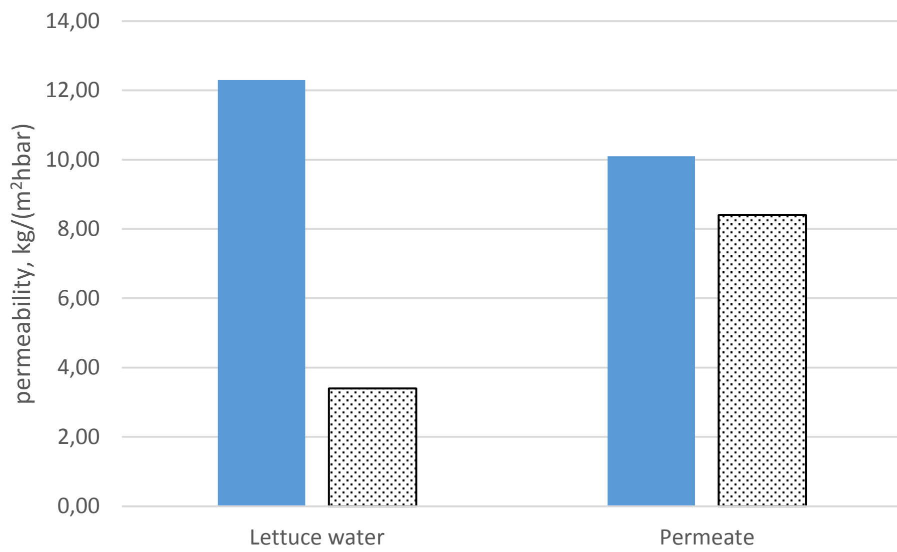


Figure 43: Permeability of NF270 membrane with tap water before and after filtration. Lettuce washing water was filtrated and the produced permeate was filtrated again.

Retention of organic material was high with NF270 in spiral wound module during washing water filtration from batch two. In this configuration, retention of TOC and alkalinity decreased when filtration proceeded, contrary to the results obtained with the NF270 membrane in flat-sheet module. Changes in TOC and UVA_{254} as a function of volume reduction factor (VRF) are shown in Figure 44, while the corresponding changes in conductivity and total solids is shown in Figure 45. Initial retention of TOC was 92%, which decreased to 82% at VRF of 10. Retention of conductivity also decreased from 51% to 39%. However, retention of UVA_{254} slightly increased from 81% to 87% at VRF of 10. This can be attributed to retention of not degraded substances still containing aromatic and unsaturated bonds. The ability of membrane to retain small molecules seems to have decreased during the filtration.

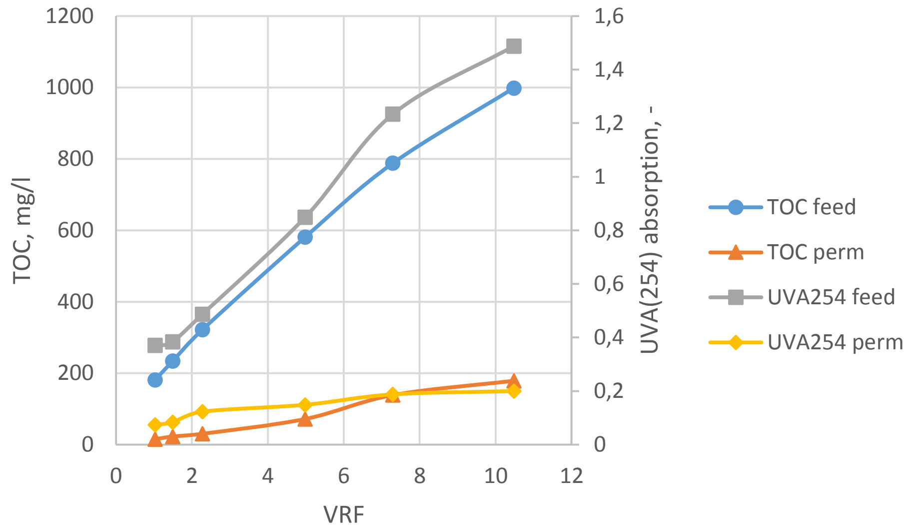


Figure 44: TOC and UVA_{254} as a function of volume reduction factor of feed. Second batch of lettuce washing water was filtrated with NF270 in spiral wound module.

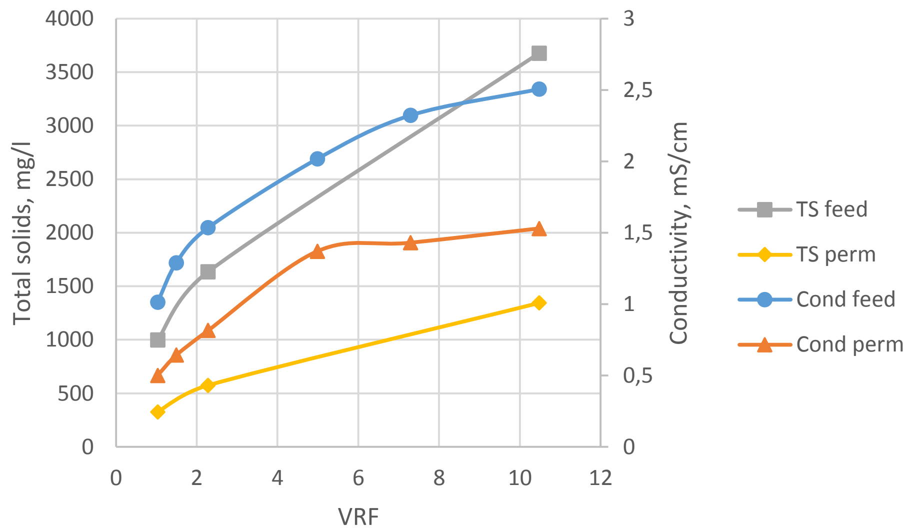


Figure 45: Conductivity and total solids (TS) as a function of volume reduction factor of feed. Second batch of lettuce washing water was filtrated with NF270 in spiral wound module.

Re-filtration of NF270 permeate purified the washing water further. Changes in permeate filtration TOC and UVA_{254} as a function of VRF are shown in Figure 46. Corresponding changes in conductivity and total solids are presented in Figure 47. Retention of TOC was especially high, 68% at the beginning of filtration, increasing to 78% at a VRF of 10. Retention of conductivity was 53%, decreasing to 39% at VRF of 10. Continuing filtration further to VRF >20 caused significant deterioration of permeate, and those results are not thus presented.

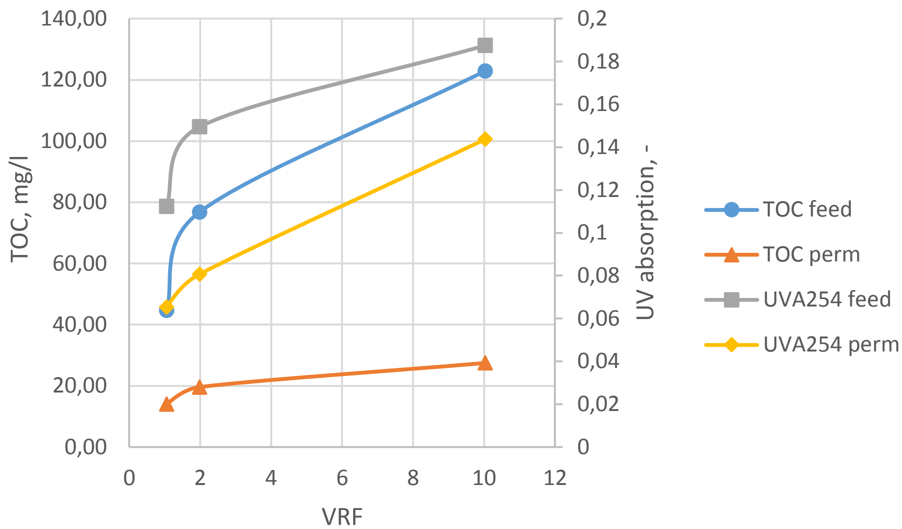


Figure 46: TOC and UVA$_{254}$ as a function of volume reduction factor of feed. Permeate from NF270 spiral wound configuration was re-filtrated.

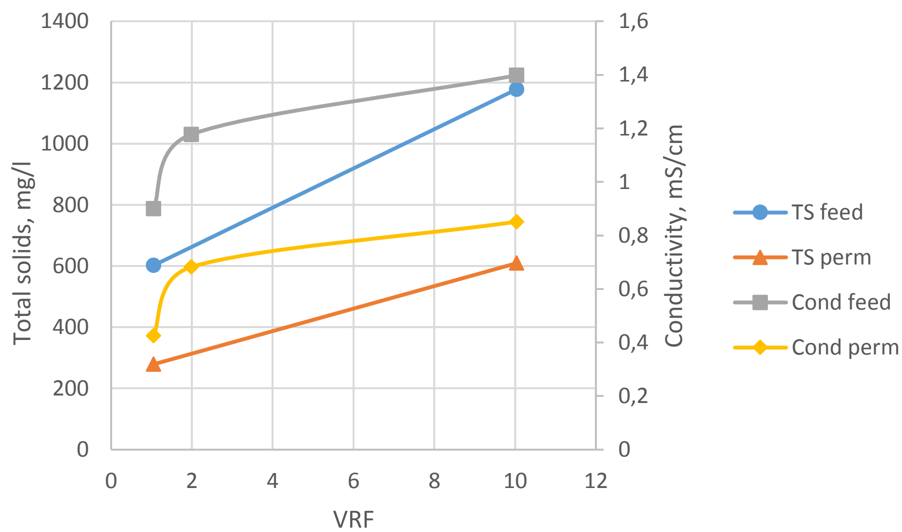


Figure 47: Conductivity and total solids (TS) as a function of volume reduction factor of feed. Permeate from NF270 spiral wound configuration was re-filtrated.

Measured parameters in the beginning and end of filtrations are presented in Table XIX and Table XX. The tables also include corresponding retention values.

Table XIX: Analysis results for TOC, UVA(254) and UVA(365). Results shown at the beginning and end of filtration with NF270 membrane in spiral wound module.

Feed	time	sample	TOC (mg/l)		UVA_{254}		UVA_{365}	
			initial	final	initial	final	initial	final
washing water	11.5h	conc	181	998	0.37	1.49	0.03	0.11
		perm	15	179	0.07	0.2	0.01	0.02
		ret. (%)	92	82	81	87	67	82
NF270 permeate	6.3h	conc	44	123	0.11	0.19	0.010	0.014
		perm	14	27	0.06	0.14	0.008	0.008
		ret. (%)	68	78	42	24	14	47

Table XX: Analysis results for conductivity, pH, total solids and fixed solids. Results shown at the beginning and end of filtration with NF270 membrane in spiral wound module.

feed	time	sample	Conductivity (µS/cm)		pH		Total solids (mg/l)		Fixed solids (mg/l)
			initial	final	initial	final	initial	final	initial
washing water	11.5h	conc	1010	2500	9.1	7.7	1000	3680	604
		perm	500	1530	8.9	8.1	330	1340	288
		ret. (%)	51	39	-	-	67	64	52
NF270 permeate	6.3h	conc	900	1400	8.1	8.5	600	1180	N.A.
		perm	430	850	8.3	8.6	280	610	N.A.
		ret. (%)	53	39	-	-	54	48	N.A.

8.6.2. PCD treatment of the washing water (second batch)

PCD treatment purified second batch lettuce washing water less effectively than NF270 membrane in spiral configuration. Figure 48 presents change in TOC and UVA_{254} values in function of treatment time, and corresponding values obtained in filtration. Similar TOC, UVA, TS or conductivity removal could not be obtained with PCD even in treatment of four hours. However, it has to be noted that the values obtained in filtration (which were used in comparison) were initial values, before deterioration of permeate quality happened.

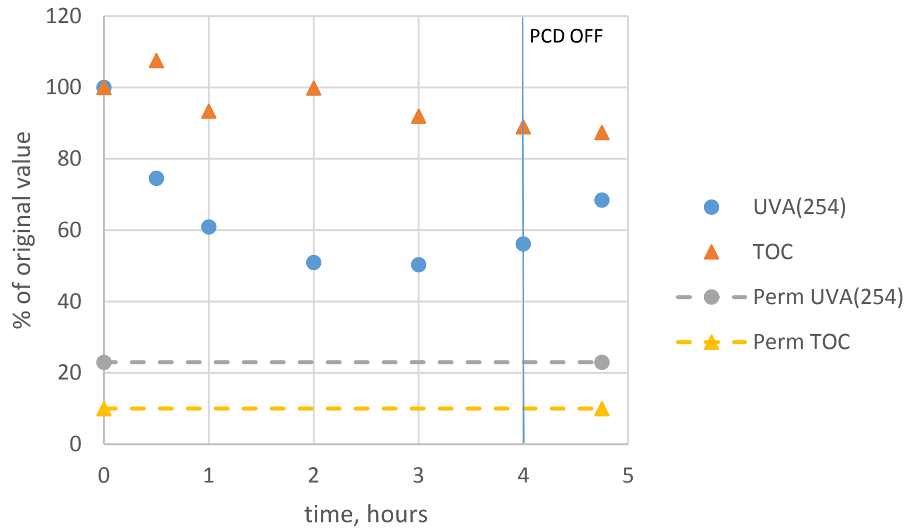


Figure 48: UVA(254) and TOC development in function of PCD treatment time. PCD on between 0-4 hours. Maximum energy dose: 8 kWh/m3. Dotted lines represent values initially obtained in the permeate of NF270 spiral wound membrane, when lettuce washing water was filtrated.

Post-treatment of the NF270 membrane permeate with PCD resulted in rather profitable results compared to re-filtration. Figure 49 shows changes in TOC and UVA_{254} values as a function of treatment time, and corresponding values initially obtained in filtration. Organic material clearly degraded further due to the treatment. Similar UVA_{254} reduction than in filtration could be achieved in less than one hour PCD oxidation. TOC decreased by 29% during treatment of four hours. However, conductivity increased by 40% and total solids by 15% during the same time.

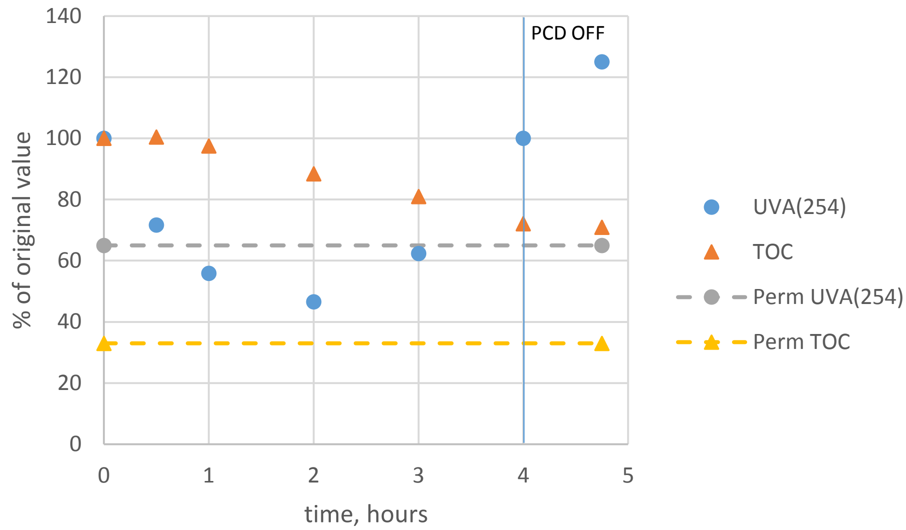


Figure 49: Development in UVA(254) and TOC values as a function of PCD treatment time. Feed water was permeate of NF270 membrane (spiral wound) filtration. PCD on between 0-4 hours. Maximum energy dose: 8 kWh/m3. Dotted lines represent values initially obtained in the permeate of NF270 spiral wound membrane, when permeate was re-filtrated.

Measured values before and after the PCD treatments are shown in Table XXI and Table XXII. Increasing PCD oxidation time from two to four hours did not improve the treatment significantly. During treatment of membrane permeate, UVA values of all measured wavelengths actually increased after in longer than two hours treatment, while there was only 10% further decrease in TOC. pH decreased notably in the experiments with second water batch, presumably due to formation of organic acids and decrease in chlorine concentration. pH change was significant especially in permeate, from 8.2 to 3.1.

Table XXI: PCD treatment results for TOC, UVA(254) and UVA(365). Feed water samples were salad washing water (second batch) and NF270 permeate.

	time	sample	TOC (mg/l)		UVA(254)		UVA(365)	
			initial	final	initial	final	initial	final
PCD	4h	washing water	172	153	0.32	0.18	0.022	0.015
		permeate	42	30	0.1	0.1	0.009	0.009

Table XXII: PCD treatment results for conductivity, pH, total solids and fixed solids. Feed water samples were salad washing water (second batch) and NF270 permeate. N.A. = no data available.

	time	sample	Conductivity (µS/cm)		pH		Total solids (mg/l)		Fixed solids (mg/l)	
			initial	final	initial	final	initial	final	Initial	Final
PCD	4h	washing water	1020	1140	8.8	4.3	930	980	560	580
		perm	800	1130	8.2	3.1	570	650	N.A.	N.A.

8.7. Energy efficiency of PCD in lettuce water treatment

Comparing the purification effect of PCD to filtration is complicated, since the processes are clearly distinct. Similar results in PCD treatment and filtration could be achieved in reduction of UV absorption values. TOC, dissolved solids and conductivity seemed to merely be constant or increase during PCD treatment of lettuce washing waters. It was calculated that, to achieve the same 75% UVA_{254} reduction than in filtration with SG1485 membrane, it would take 190 min PCD treatment in the used conditions. This corresponds to 6.3 kWh/m^3 energy need. When permeate from NF270 spiral membrane filtration was treated, same UVA_{254} reduction was achieved in 45 min than what was obtained in re-filtration. Energy demand for that is 1.5 kWh/m^3.

Chang et al. [69] estimated, that the energy consumption of nanofiltration with tight membranes and high operating pressures is close to that of reverse osmosis. They reported that average consumption of seawater reverse osmosis plants is 3.5 kWh/m^3. Park et al. [70] measured specific energy consumption of 1.0 kWh/m^3 with NF270 nanofiltration system at 40% recovery, when low salinity seawater (TDS 28000 mg/l) was treated. In turn, Turan et al. [71] measured specific energy consumption of 4 kWh/m^3 at 10 bar TMP in the beginning of nanofiltration treatment of an effluent from dairy industry (COD 30-46 mg/l, conductivity 15-22 µS/cm).

Based on these results, energy consumption of PCD can be comparable to nanofiltration. Treatment of membrane permeates seems energy efficient in reduction of organic material. PCD treatment of membrane concentrates might be another suitable application area. In order to better evaluate the usefulness of PCD oxidation in lettuce washing water treatment, additional analysis methods showing the nature of organic material are required. Effectiveness of PCD treatment in disinfection of bacteria also has to be studied.

9. Conclusions

Water used for washing fresh-cut product can be almost 90% of the total water usage in the production process. Lettuce washing waters may contain plant residues, soil, dirt, pesticides and microorganisms like bacteria. Disinfection and removal of organic substances is the main goal of treatment. TOC, COD and UV absorption at wavelengths 254 nm and 280 nm are the most common analysis methods for measuring oxidation potential against organic compounds.

Advanced oxidation processes are based on reactive radicals with high oxidation potential and unselective oxidation. Hydroxyl radical is the most important of these radicals. Ozone, hydrogen peroxide, ultraviolet light, ferric ions and electricity are commonly used for oxidation, while combinations of these usually achieve better treatment results. Highest oxidation potential is typically achieved at high temperature and relatively high pH, because these conditions increase the formation of reactive radicals. For example, ozone itself reacts selectively with unsaturated bonds and aromatic groups in organic matter. This reaction is favorable at low temperatures and pH values.

Oxidation primarily causes degradation of organic material by destruction of unsaturated and aromatic bonds, which is seen in significant reduction of UV_{254} and UV_{280} absorbance of sample. However, mineralization in terms of TOC/DOC/COD reduction is usually low. Pre-oxidation usually mitigates fouling of membranes in combined process. Most importantly, hydrophobic natural organic matter is removed or changed to hydrophilic form. Natural organic matter has been reported to cause the majority of fouling of membranes during treatment of surface waters.

Pulsed corona discharge (PCD) produces several radicals and ozone, but also different ions, hydrogen peroxide, shockwaves, ultraviolet light, high temperature gradients and electrohydraulic cavitation can be formed. PCD has been reported highly effective to degrade organic matter compared to other advanced oxidation technologies. Optimal reactor design is crucial to achieve high energy efficiency. Important factors in design are gap distance between electrodes, phases where discharges happen and how water is induced into the reactor. Changing voltage and frequency of discharges can lead to different reaction mechanisms and affect the efficiency of treatment. Oxygen gas injection and catalysts are commonly used to enhance PCD treatment. Low temperature increases absorption of oxygen into water and extends the lifetime of radicals, but decomposition rate of ozone and formation rate of radicals is decreased.

In this study, highest ozone concentrations in water were achieved when oxygen gas was injected to discharge shell during the PCD treatment. Decreasing the temperature of water also increased ozone concentration, as assumed. Decomposition rate of ozone was faster than expected, presumably due to different oxidants formed simultaneously. Conductivity increased in all experiments with PCD. This was connected to formation of nitrates in oxygen-nitrogen atmosphere. Conductivity increased most significantly in pure water with low conductivity and when oxygen was not injected, which are supporting this theory. pH decreased notably in the presence of organic substances in water, which is connected to production of organic acids. Decrease of inorganic carbon in water samples was also measured.

PCD treatment caused quick degradation of humic acids, but their mineralization was slower. This reaction was seen in significant decrease in UVA_{254}, but low decrease in TOC values. Amount of small molecular weight substances increased in solutions and organic compounds were transferred more hydrophilic based on SUVA values. Despite highest ozone concentration observed in cold water, humic acids degraded most efficiently in warm water. This means other oxidants produced by PCD were also important in the degradation. Oxygen injection improved the degradation significantly. Clear degradative effect lasted for an hour after PCD was turned off, which indicates presence of long living oxidative species. Even PCD treatment of 150 minutes was not sufficient to degrade and mineralize all of the humic acids (concentration 120 mg/l) in 30 l of water: there was still 18% UVA_{254} and 59% TOC left after the treatment. Permeate quality started to deteriorate in the experiments after 20-40 min PCD treatment, which could be seen in gradual increase of TOC and UVA values. No liquid phase ozone was detected in the experiments with humic acids or washing water, so all ozone was assumed to be consumed immediately.

Lettuce washing waters contain high amount of organic substances, dissolved solids and ionic compounds. Water was measured to have TOC content 800 mg/l, conductivity 640 µS/cm, pH 4.2-7.5, total solids 1800 mg/l and suspended solids 35 mg/l. 78% of the washing water consisted of organic material. Most of the dissolved substances penetrated membrane with a molecular weight cut-off of 600 g/mol. Batch 2 of the water was pre-chlorinated in vegetable processing plant and contained only one-fourth of TOC compared to the batch 1. All five of the used membranes fouled by lettuce washing waters, measured by changes in tap water permeability before and after the filtration. Alkaline cleaning was necessary to restore the function of membranes.

NF270 membrane in flat-sheet configuration was the most effective in purifying the washing waters. Initial retention was 78% for TOC, 90% for UV_{254} absorption, 94% for UV_{365} absorption, 76% for dissolved solids and 34% for conductivity. The membrane had higher and more stable flux than SG1485 ceramic nanofiltration membrane. NF270 in spiral wound module revealed more permeate quality deterioration than its flat-sheet counterpart did. However, it presented higher permeate flux and good initial permeate quality. UF membranes penetrated most of the organic material, dissolved solids and ionic species. The permeability of UF membranes also decreased significantly. Therefore, UF membranes were not appropriate to purify salad washing waters.

PCD treatment degraded the organic compounds in salad washing waters. Significant decrease in UV-absorption values at wavelengths 254, 280, 250 and 365 nm was measured. In one hour UVA_{254} had already decreased by 40-50%, and there was no significant change in longer treatment. Amount of small molecular weight substances increased similarly, expressed by $UVA_{250/365}$ -ratio. PCD oxidation caused slow mineralization of organic material, as there was no change in TOC during treatment of two hours. Results of PCD oxidation were similar, when PCD was used for post-treatment of membrane permeates.

When PCD was combined with nanofiltration treatment, it caused decreased permeability compared to plain nanofiltration. Compounds in water were likely not degraded sufficiently and were fouling the membrane. The distance between PCD unit and membrane was presumably too long, that produced ozone and other oxidants could reduce the fouling. It proved better to post-treat membrane permeates with PCD, as organic compounds in permeate degraded as effectively as in feed water. It is left to evaluate if longer and more energy-intensive PCD treatment would increase the permeability in long run, since the experiments performed now lasted for relatively short time. Though in longer treatment, more degradation happens and permeate quality could deteriorate.

PCD treatment alone was not sufficient to purify lettuce washing water, but it can provide applications in pre-treatment of water or post-treatment of membrane concentrates and permeates. While re-filtrating permeate of NF270 filtration produced initially better quality water than its PCD treatment, there was also deterioration of permeate quality and frequent requirements for chemical cleaning. Energy consumption of PCD was comparable to filtration in terms of UV absorbance reduction. In order to better evaluate the effects of PCD treatment for washing water purification, additional analysis methods are needed. Optimizing PCD treatment could also reduce energy requirements. Continuous oxygen injection, sequential discharge, improved reactor design, as well as optimal temperature and pH of water are only some possible ways to enhance the treatment.

References

[1] L. Manzocco, A. Ignat and M. Anese, "Efficient management of the water resource in the fresh-cut industry: Current status and perspectives," *Trends in Food Science & Technology,* vol. 46, no. 2, pp. 286-294, 2015.

[2] M. Gil, M. Selma and F. Lopez-Galvez, "Fresh-cut product sanitation and wash water disinfection: problems and solutions," *International Journal of Food Microbiology,* vol. 134, no. 1-2, pp. 37-45, 2009.

[3] F. Lopez-Galvez and M. Selma, "Electrochemical disinfection: An efficient treatment to inactivate Escherichia coli O157:H7 in process wash water containing organic matter," *Food Microbiology,* vol. 30, no. 1, pp. 146-156, 2012.

[4] S. Mukhopadhyay and R. Ramaswamy, "Application of emerging technologies to control Salmonella in foods: A review," *Food Research International,* vol. 45, no. 2, pp. 666-677, 2012.

[5] D. Schmidt, M. Kerley and J. Porter, "Structural and nonstructural carbohydrate, fat, and protein composition of commercially available, whole produce," *Zoo Biology,* vol. 24, no. 4, pp. 359-373, 2005.

[6] S. Geluwe, L. Braeken and B. Bruggen, "Ozone oxidation for the alleviation of membrane fouling by natural organic matter: A review," *Water Research,* vol. 45, no. 12, pp. 3551-3570, 2011.

[7] X. Shi, G. Tal and N. Hankins, "Fouling and cleaning of ultrafiltration membranes: A review," *Journal of Water Process Engineering,* vol. 1, pp. 121-138, 2014.

[8] T. Wang, G. Qu and J. Ren, "Evaluation of the potentials of humic acid removal in water by gas phase surface discharge plasma," *Water Research,* vol. 89, pp. 28-38, 2015.

[9] R. Williams, S. Sumner and D. Golden, "Inactivation of Escherichia coli O157:H7 and Salmonella in Apple Cider and Orange Juice Treated with Combinations of Ozone, Dimethyl Dicarbonate, and Hydrogen Peroxide," *Journal of Food Science,* vol. 70, no. 4, pp. 197-201, 2005.

[10] The Standing Committee of Analysts, "The Microbiology of Drinking Water - Part 4 - Methods for the isolation and enumeration of coliform bacteria and Escherichia coli," in *Methods for examination of water and associated materials*, Bristol, UK Environment Agency, 2009.

[11] M. Tomar, Quality Assessment of Water and Wastewater, CRC Press, 1999.

[12] SFS-EN 1484, Water analysis. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC), Finnish Environment Institute, 1997.

[13] SFS 3008, Determination of total residue and total fixed residue in water, sludge and sediment, Finnish Environment Institute, 1990.

[14] SFS-EN 872, Water quality. Determination of suspended solids. Method by filtration through glass fibre filters., Finnish Environment Institute, 1996.

[15] B. Milman, "Chapter 2: Techniques and methods for identification," in *Chemical identification and its quality assurance*, Berlin, Springer-Verlag, 2011, pp. 23-38.

[16] R. Albrektiene, M. Rimeika and A. Zagorskis, "Determination of Organic Matter by UV Absorption in the Ground Water," *Journal of Environmental Engineering and Landscape Management,* vol. 20, no. 2, pp. 163-167, 2012.

[17] A. Zouboulis, K. Kzymanska and D. Zamboulis, "Hybrid membrane processes for the treatment of surface water and mitigation of membrane fouling," *Separation and Purification Technology*, vol. 137, pp. 43-52, 2014.

[18] A. Ribeiro, O. Nunes and M. Pereira, "An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU," *Environment International,* vol. 75, pp. 33-51, 2014.

[19] B. Jiang, J. Zheng and S. Qiu, "Review on electrical discharge plasma technology for wastewater remediation," *Chemical Engineering Journal,* vol. 236, pp. 348-368, 2014.

[20] S. Geluwe, C. Vinckier and E. Bobu, "Eightfold increased membrane flux of NF 270 by O3 oxidation of natural humic acids without deteriorated permeate quality," *Journal of Chemical Technology & Biotechnology,* vol. 85, no. 11, pp. 1480-1488, 2010.

[21] M. Rajab, C. Heim and T. Letzel, "Electrochemical disinfection using boron-doped diamond electrode – The synergetic effects of in situ ozone and free chlorine generation," *Chemosphere,* vol. 121, pp. 47-53, 2015.

[22] S. Ganiyu, E. Hullebusch and M. Cretin, "Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: A critical review," *Separation and Purification Technology,* vol. 156, pp. 891-914, 2015.

[23] S. Buyn, J. Taurozzi and V. Tarabara, "Ozonation as a pretreatment for nanofiltration: effect of oxidation pathway on the permeate flux," *Separation and Purification Technology*, vol. 149, pp. 174-182, 2015.

[24] J. Kim, S. Davies and M. Baumann, "Effect of ozone dosage and hydrodynamic conditions on the permeate flux in a hybrid ozonation–ceramic ultrafiltration system treating natural waters," *Journal of Membrane Science,* vol. 311, no. 1-2, pp. 165-172, 2008.

[25] D. Dobrin, M. Magureanu and C. Bradu, "Degradation of diclofenac in water using pulsed corona discharge," *Chemical Engineering Journal*, vol. 234, pp. 389-396, 2013.

[26] U. von Gunten, "Ozonation of drinking water: Part I. Oxidation kinetics and product formation," *Water Research,* vol. 37, pp. 1443-1467, 2003.

[27] J. Sotelo, F. Beltran and F. Benitez, "Ozone decomposition in water: Kinetic study," *Industrial & Engineering Chemistry Research* , vol. 26, pp. 39-43, 1987.

[28] A. Asghar, A. Raman and W. Daud, "Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: a review," *Journal of Cleaner Production,* vol. 87, pp. 826-838, 2015.

[29] K. Turhan, I. Durukan and A. Ozturkcan, "Decolorization of textile basic dye in aqueous solution by ozone," *Dyes and pigments,* vol. 92, no. 3, pp. 897-901, 2012.

[30] S. Geluwe, C. Vinckier and L. Braeken, "Ozone oxidation of nanofiltration concentrates alleviates membrane fouling in drinking water industry," *Journal of Membrane Science,* vol. 378, no. 1-2, pp. 128-137, 2011.

[31] S. Lehman and L. Liu, "Application of ceramic membranes with pre-ozonation for treatment of secondary wastewater effluent," *Water Research,* vol. 43, no. 7, pp. 2020-2028, 2009.

[32] Y. Song, B. Dong and S. Xia, "Huangpu River water treatment by microfiltration with ozone pretreatment," *Desalination,* vol. 250, no. 1, pp. 71-75, 2010.

[33] H. Ölmez and U. Kretzschmar, "Potential alternative disinfection methods for organic fresh-cut industry for minimizing water consumption and environmental impact," *Food Science and Technology,* vol. 42, no. 3, pp. 686-693, 2009.

[34] S. Lee, M. Costello and D. Kang, "Efficacy of chlorine dioxide gas as a sanitizer of lettuce leaves," *Journal of Food Protection,* vol. 67, no. 1, pp. 1371-1376, 2004.

[35] J. Jin, M. El-Din and J. Bolton, "Assessment of the UV/chlorine process as an advanced oxidation process," *Water Research,* vol. 45, no. 4, pp. 1890-1896, 2011.

[36] Y. Chen, R. Peng and T. Shen, "A promising ozone-based advanced oxidation process for effective generation of hydroxyl radicals in acidic solution," *Separation and purification technology,* vol. 151, pp. 269-275, 2015.

[37] Z. Jeirani, A. Sadeghi and J. Soltan, "Effectiveness of advanced oxidation processes for the removal of manganese and organic compounds in membrane concentrate," *Separation and Purification Technology,* vol. 149, pp. 110-115, 2015.

[38] N. Koutahzadeh, M. Esfahani and P. Arce, "Removal of Acid Black 1 from water by the pulsed corona discharge advanced oxidation method," *Journal of Water Process Engineering,* vol. 10, pp. 1-8, 2016.

[39] M. Cheng, G. Zeng and D. Huang, "Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review," *Chemical Engineering Journal,* vol. 284, pp. 582-598, 2015.

[40] P. Bahmani, E. Ghahramani and A. Maleki, "Application of fenton oxidation process for degradation of reactive black 5 in aqueous system," in *13th International Conference of Environmental Science and Technology,* Athens, 2013.

[41] C. Murray and S. Parsons, "Removal of NOM from drinking water: Fenton’s and photo-Fenton's processes," *Chemosphere,* vol. 54, no. 7, pp. 1017-1023, 2004.

[42] M. Anese, M. Maifreni and F. Bot, "Power ultrasound decontamination of wastewater from fresh-cut lettuce washing for potential water recycling," *Innovative Food Science & Emerging Technologies,* vol. 32, pp. 121-126, 2015.

[43] S. Mukhopadhyay and R. Ramaswamy, "Application of emerging technologies to control Salmonella in foods: A review," 2011.

[44] I. Seymour, D. Burfoot and R. Smith, "Ultrasound decontamination of minimally processed fruits and vegetables," *International Journal of Food Science and Technology,* vol. 37, pp. 547-557, 2002.

[45] H. Destaillats, A. Colussi and J. Joseph, "Synergestic effects of sonolysis combined with ozonolysis for the oxidation of azobenzene and methyl orange," *The Journal of Physical Chemistry A,* vol. 104, pp. 8930-8935, 2000.

[46] V. Gomez-Lopez, J. Gobet and M. Selma, "Operating conditions for the electrolytic disinfection of process wash water from the fresh-cut industry contaminated with E. coli o157:H7," *Food Control,* vol. 29, no. 1, pp. 42-48, 2013.

[47] P. Lukes, M. Clupek and V. Babicky, "Ultraviolet radiation from the pulsed corona discharge in water," *Plasma Sources Science and Technology,* vol. 17, no. 2, pp. 1-11, 2008.

[48] H. Kim, K. Wright and J. Piccioni, "Inactivation of bacteria by the application of spark plasma in produced water," *Separation and Purification Technology,* vol. 156, pp. 544-552, 2015.

[49] B. Locke, M. Sato and P. Sunka, "Electrohydraulic Discharge and Nonthermal Plasma for Water Treatment," *Industrial & Engineering Chemistry Research,* vol. 45, pp. 882-905, 2006.

[50] Y. Yang, A. Gutsol and A. Fridman, "Removal of CaCO3 scales on a filter membrane using plasma discharge in water," *International Journal of Heat and Mass Transfer,* vol. 52, no. 21-22, pp. 4901-4906, 2009.

[51] K.-Y. Shih and B. Locke, "Chemical and Physical Characteristics of Pulsed Electrical Discharge Within Gas Bubbles in Aqueous Solutions," *Plasma Chemistry and Plasma Processing,* vol. 30, no. 1, pp. 1-20, 2010.

[52] M. Sato, "Environmental and biotechnological applications of high-voltage pulsed discharges in water," *Plasma Sources Science and Technology,* vol. 17, no. 2, pp. 1-7, 2008.

[53] R. Singh, V. Babu and L. Philip, "Disinfection of water using pulsed power technique: Effect of system parameters and kinetic study," *Chemical Engineering Journal,* vol. 284, pp. 1184-1195, 2015.

[54] I. Panorel, S. Preis and I. Kornev, "Pulsed corona discharge for degradation of aqueous humic substances," *Water Science & Technology Water Supply,* vol. 11, no. 2, pp. 238-245, 2011.

[55] A. Coelho, C. Sans and A. Aguera, "Effects of ozone pre-treatment on diclofenac: Intermediates, biodegradability and toxicity assessment," *Science of the total environment,* vol. 407, no. 11, pp. 3572-3578, 2009.

[56] P. Calza, V. Sakkas and C. Medana, "Photocatalytic degradation study of diclofenac over aqueous TiO2 suspensions," *Applied Catalysis B: Environmental,* vol. 67, no. 3-4, pp. 197-205, 2006.

[57] J. Hartmann, P. Bartels and U. Mau, "Degradation of the drug diclofenac in water by sonolysis in presence of catalysts," *Chemosphere,* vol. 70, no. 3, pp. 453-461, 2008.

[58] N. Koutahzadeh, M. Esfahani and P. Arce, "Removal of Acid Black 1 from water by the pulsed corona dischargeadvanced oxidation method," *Journal of Water Process Engineering,* vol. 10, pp. 1-8, 2016.

[59] N. Li, A. Fane and T. Matsuura, Advanced membrane technology and applications, John Wiley & Sons Inc., 2008.

[60] L. Wang, Y.-T. Hung and N. Shammas, "Chapter 7: Membrane Filtration," in *Advanced Physicochemical Treatment Processes*, Totowa, The Humana Press Inc, 2006, pp. 203-259.

[61] H.-S. Kim, K. Wright and D. Cho, "Self-cleaning filtration with spark discharge in produced water," *International Journal of Heat and Mass Transfer*, vol. 88, pp. 527-537, 2015.

[62] Inopor GmbH, "Ceramic NF membranes datasheet," 2016.

[63] J. Kestin, M. Sokolov and W. Wakeham, "Viscosity of liquid water in the range -8C to 150C," *Journal of Physical Chemistry,* vol. 7, no. 3, pp. 941-948, 1978.

[64] O. Nakari, A. Pihlajamäki and M. Mänttäri, "Permeability of dilute ionic liquid solutions through a nanofiltration membrane - Effect of ionic liquid concentration, filtration pressure and temperature," *Separation and purification technology,* vol. 163, pp. 267-274, 2016.

[65] I. Kornev, G. Osokin and A. Galanov, "Formation of Nitrite- and Nitrate-Ions in Aqueous Solutions Treated with Pulsed Electric Discharges," *Ozone Science and Engineering,* vol. 35, no. 1, pp. 22-30, 2013.

[66] Lenntech BV, "Ozone decomposition," [Online]. Available: http://www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm. [Accessed 7 March 2016].

[67] M. Magureanu, D. Piroi and M. N.B., "Degradation of antibiotics in water by non-thermal plasma," *Water Research,* vol. 45, no. 11, pp. 3407-3416, 2011.

[68] W. Graneli, M. Lindell and L. Tranvik, "Photo-oxidative production of dissolved inorganic carbon in lakes of different humic content," *Limnology and Oceanography,* vol. 41, pp. 698-706, 1996.

[69] Y. Chang, D. Reardon and P. Kwan, "Evaluation of dynamic energy consumption of advanced water and wastewater treatment technologies," Awwa Research Foundation, California, 2008.

[70] M. Park, J. Park and E. Lee, "Application of nanofiltration pretreatment to remove divalent ions for economical seawater reverse osmosis desalination," *Desalination and water treatment,* vol. 57, pp. 20661-20670, 2015.

[71] M. Turan, I. Koyuncu and D. Topacik, "Comparative evaluation of nanofiltration and reverse osmosis treatment of an effluent from dairy industry," *Journal of environmental science and health,* vol. 35, no. 5, pp. 741-754, 2000.