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DIPLOMARBEIT

Applying Reverse Osmosis/Electrodialysis to Isolate Organic Carbon from Water Samples

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EIDESSTATTLICHE ERKLÄRUNG

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KURZFASSUNG

Ein wichtiger Parameter zur Bewertung der Wasserqualität, besonders im Hinblick auf die indirekte Wiederverwendung von Abwasser in der Trinkwasserversorgung, ist der Gehalt an gelöstem organischen Kohlenstoff (DOC). Da organische Kohlenstoffverbindungen im Wasser zahlreiche Reaktionen auslösen, besteht großes Interesse diese Verbindungen genauer zu charakterisieren. Analysemethoden wie Feststoff ^{13}C-Nuklear Magnetresonanzspektroskopie oder Fourier-transformierte Infrarot Spektroskopie benötigen den organischen Kohlenstoff als Feststoffprobe in konzentrierter und entsalzener Form. Die gängigste Form zur Isolierung von organischem Kohlenstoff ist momentan die Methode mit Ionenaustauscher-Harzen (XAD-8, XAD-4), welche jedoch mit einigen Nachteilen behaftet ist.

Das Ziel dieser Diplomarbeit war die Optimierung und Anwendung eines Umkehrosmose/Elektrodialyse (RO/ED) Versuchsaufbaues zur Konzentrierung und Entsalzung organischen Kohlenstoffes in Wasserproben. Organischer Kohlenstoff wurde aus Oberflächenwasser (NOM), bzw. aus geklärtem Abwasser (EfOM) isoliert und die Proben der einzelnen Teilströme wurden auf diverse Parameter hin analysiert (z.B. DOC, UVA_{254}). Durch Tests verschiedener ED-Membranen wurde jene Membrankombination ausgewählt, welche für das vorliegende Projekt am geeignetsten erschien. Ein weiteres Ziel dieser Arbeit war die Untersuchung des Abbauverhaltens von organischem Kohlenstoff in DOC-Isolaten unterschiedlicher Konzentrationen. Mit Hilfe von Batch-Reaktoren wurde der Anteil an biologisch abbaubarem organischen Kohlenstoff bestimmt.

Die ED-Membrantests ergaben die besten Resultate für eine monoselective Membrankombination von Asahi Glass. Mit den NOM- und EfOM- Proben wurden DOC-Rückhalteraten von 97% bzw. 96% im Entsalzungsprozess erreicht. DOC-Verluste im Umkehrosmose-Konzentrationsprozess durch Migration ins Permeat und Adsorption betrugen 18% bzw. 12%. Die DOC Wiederfindungsrate für das gesamte System betrug in beiden Versuchen ca. 87%. Die Abbautests in den Batch-Reaktoren zeigten, daß die Substrat Konzentration den limitierenden Faktor beim DOC Abbau darstellt. Ergebnisse der Size Exclusion Chromatographie zeigten vernachlässigbar kleine Verluste an DOC während des Entsalzungsprozesses und bestätigten so die Ergebnisse der DOC Massebilanzen.

Die hohen DOC-Rückhalteraten der ausgewählten ED-Membrankombination sowie deren geringe Fouling-Verluste machen die Umkehrosmose/Elektrodialyse-Methode in der Probenaufbereitung zu einer potentiellen Alternative zu den Verfahren mit Ionenaustauscher-Harzen.

ABSTRACT

Potable reuse of wastewater requires reliable parameters to assess water quality during and after treatment. One of these important parameters is dissolved organic carbon (DOC). Organic constituents are involved in various reactions in the aqueous environment and are therefore of high interest for further characterization. Characterization tools, such as carbon-13 nuclear magnetic resonance spectroscopy, or Fourier transformed infrared spectroscopy require the organic carbon in a concentrated, desalted, and lypholizated form. The most common method to isolate organic carbon is XAD-resin fractionation, but this method is associated with several disadvantages.

One research goal of this study was to optimize and apply a novel approach using reverse osmosis and electrodialysis (RO/ED) to concentrate and desalt organic carbon from water samples. A natural organic matter (NOM) sample and an effluent organic matter (EfOM) sample were investigated using the novel approach. The samples were analyzed for DOC-concentration, UVA_{254}, ion concentration (F, Cl, NO_3, SO_4, PO_4, Na, K, Mg, Ca), and molecular weight distribution using size exclusion chromatography (SEC). Prior to the RO/ED experiments, several ED-membrane combinations were tested to determine the most appropriate configuration for laboratory-scale operation. Another objective was to investigate the bioavailability of concentrated organic carbon in the generated RO/ED isolates. Therefore, degradation studies were performed to determine the fraction of biodegradable dissolved organic carbon (BDOC) in the DOC-isolates using batch reactors with microbiologically acclimated sand.

The ED-membrane tests favored a monoselective membrane combination of Asahi Glass to be applied in the laboratory-scale ED-stack. With this ED-membrane combination DOC-rejection of 97% and 96% was achieved during desalination of NOM and EfOM samples, respectively. RO concentration showed DOC-losses of 18% for the NOM sample and 12% for the EfOM sample due to migration into the permeate and adsorption processes. The overall DOC-recovery of the approach was approximately 87%. Biodegradation studies suggest that substrate concentration may be the limiting factor controlling degradation of DOC. The results of SEC showed almost no loss of organics during ED treatment and hence confirmed the DOC mass balances of the desalination process.

High DOC rejection combined with low fouling behavior of the selected membranes and fast concentration/desalination of high sample volumes favors the approach in comparison with XAD-resin fractionation.

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ABBREVIATIONS

AEC	Anion exchange compartment
AEM	Anion exchange membrane
AOC	Assimilable organic carbon
BDOC	Biodegradable dissolved organic carbon
BOM	Biodegradable organic matter
CEC	Cation exchange compartment
CEM	Cation exchange membrane
^{13}C-NMR	^{13}Carbon-Nuclear magnetic resonance spectroscopy
DBP	Disinfection by-products
DC	Direct current
DI	deionized
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
ED	Electrodialysis
EfOM	Effluent organic matter
FEP	Fluorinated ethylene propylene
FT-IR	Fourier transformed infrared spectroscopy
GPH	Gallons per hour
HAA	Haloacetic acids
IC	Ion chromatography
NOM	Natural organic matter
NRC	National Research Council
PEG	Polyethylen glycol
RO	Reverse osmosis
SAT	Soil-aquifer treatment
SEC	Size exclusion chromatography
SMP	Soluble microbial products

SOC	Synthetic organic compounds
$SUVA_{254}$	Specific ultraviolet light adsorbance
THM	Trihalomethanes
TOC	Total organic carbon
UVA_{254}	Ultraviolet light adsorbance at a wavelength of 254 nm
WWTP	Wastewater treatment plant
XAD-4, XAD-8	Ion exchange resins

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1 Introduction

1.1 Background of the Study

Reclamation of treated sewage effluents for artificial groundwater recharge will play a significant role in the near future to meet increasing demands for drinking water in the Southwest of the United States and other arid regions all over the world (U.S. National Research Council, 1994). Soil aquifer treatment (SAT) systems facilitate the recharge of treated water into the subsurface and its final purification. Water quality transformations during SAT, such as the removal of organic carbon, rely on natural processes. However, a variety of other processes and technologies is being applied when wastewater is reused to augment potable supplies.

Potable reuse is always associated with potential adverse effects to human health. Therefore, potable reuse requires a reliable set of tools to control water quality during and after water treatment. Total organic carbon (TOC) is a key parameter to assess water quality since it includes identified and unidentified organic compounds in one parameter. The California Department of Health Services selected TOC as a parameter to be monitored in reclaimed water (State of California, 2001). Organic carbon in drinking water is involved in a variety of disadvantageous reactions in the aqueous environment, such as its potential role to serve as a precursor for disinfection by-product formation.

In order to improve our understanding of reactivity and fate of organic carbon it is necessary to investigate its physical, chemical, and biochemical characteristics. Only a small number of organic compounds are identifiable at a molecular level and little is known about organic compounds present in operationally defined fractions of XAD-resin adsorption chromatography (National Research Council, 1998). Sophisticated analytical techniques, such as carbon-13 nuclear magnetic resonance spectroscopy, elemental analysis, or Fourier transformed infrared spectroscopy allow to characterize isolated organic carbon. The application of these advanced characterization techniques requires the organic carbon in a concentrated, desalted, and freeze dried form. XAD-resin adsorption chromatography was first proposed by Thurman and Malcolm (1981) and today still is the most commonly used organic carbon isolation procedure. However, a couple of disadvantages such as chemical alteration of organic matter due to large pH-gradients during the isolation process and sample contamination through resin bleeding justifies to seek for improved concentration and desalting procedures.

1.2 Research Objectives

This study, which was part of a research project entitled “Soil-aquifer Treatment for Sustainable Water Reuse” funded by the American Water Works Association Research Foundation and the U.S. Environmental Protection Agency, aimed to gain further insight into the complex physical, chemical, and biochemical processes during isolation of organic carbon. The main research goal of this study was to optimize and apply a novel approach using reverse osmosis and electrodialysis (RO/ED) to concentrate and desalt organic carbon from water samples, intended as an alternative method to XAD-resin adsorption chromatography. Therefore, the fate of natural organic matter (NOM) and effluent organic matter (EfOM) during membrane treatment processes was investigated and compared to each other. Of special interest were the achieved DOC rejection rates in the two different membrane systems. Furthermore, the removal of selected ions from the feed sample was examined as well as the molecular weight distributions in the different sample fractions. Prior to NOM and EfOM concentration and desalination, several ED membrane combinations were tested to determine the most appropriate stack configuration for laboratory-scale operation.

An additional objective was to investigate the bioavailability of concentrated organic carbon in the generated DOC isolates. Therefore, degradation studies were performed to determine the fraction of biodegradable organic carbon (BDOC) in the DOC isolates using batch reactors with microbiologically acclimated sand. It was hypothesized that the concentration of organic carbon in water samples might be influencing the degree of DOC removal. To elucidate the behavior of organic carbon in the reactors, different dilutions of each DOC-type were exposed to the microbial population.

2 Theoretical Background

2.1 Organic Substances in Water

Organic carbon in water, generally quantified as total organic carbon (TOC) or dissolved organic carbon (DOC) is an important measure to assess water quality. The importance to understand chemical reactions of organic carbon in water becomes evident when focus is set on the reactivity of dissolved organic matter (DOM) with various other substances in water. DOM refers to the entire organic molecule including also elements such as oxygen or hydrogen (Thurman, 1985). DOM has been shown to bind organic as well as inorganic contaminants like pesticides or metals. While bioavailability is reduced, binding on DOM of such contaminants enhances their aqueous solubilities and transport. A portion of DOM reacts also with disinfectants used in drinking water treatment and contributes to the formation of undesirable disinfection by-products (DBPs) (Kitis et al., 2001). Increasing interest in behavior and detection of organic matter in water is especially caused by the increasing industrial usage of synthetic organic compounds coupled with a wide variety of organic substances.

Another way to describe organic matter in water is its separation based on the pH-dependent affinities of organic molecules for certain types of commercially available chromatographic resins. Organic substances are divided into hydrophobic and hydrophilic compounds or subdivided into acidic, basic, and neutral compounds (National Research Council, 1998). Organic carbon in natural water or wastewater can also be classified on the basis of molecular weight distribution, elemental composition (e.g., percent C, N, O, H, P), functional group distribution (e.g., aromatic versus aliphatic carbon), and chemical or biochemical compounds distribution (e.g., carbohydrates, amino acids).

2.1.1 Major Sources of Organic Compounds

Organic compounds found in water derive from the following three major sources (Cohn et al. 1999):

1. Breakdown of naturally occurring organic materials
2. Reactions that occur during water treatment and transmission
3. Domestic and commercial activities

Figure 2.1 shows these three organic carbon sources within the cycle of water use and reuse. Surface or groundwater serves as a source for drinking water, which is usually treated before consumption. Discharging the treated wastewater into ground or surface water closes the cycle again.

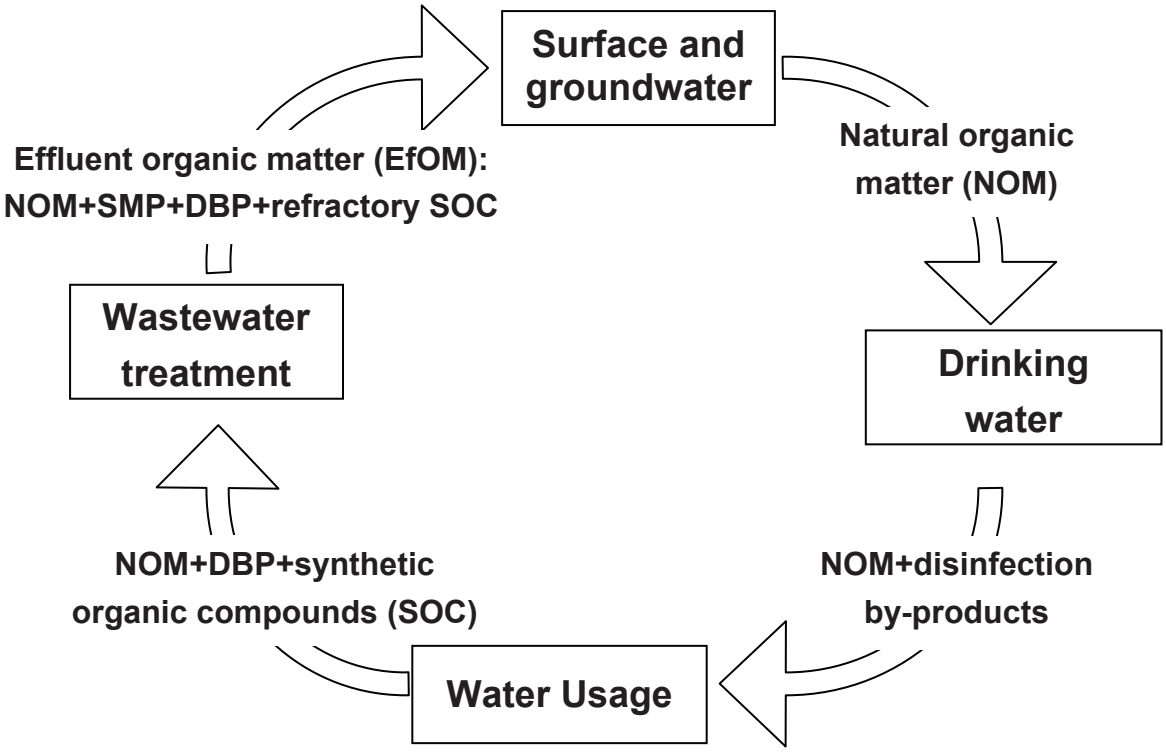

Figure 2.1: Cycle of water use and reuse (Rauch, 1999)

2.1.1.1 Naturally Occurring Organic Matter

There are two main sources of organic matter in natural waters such as surface or groundwater. Allochthonous sources refer to organic carbon derived from soils or plants while autochthonous sources imply organic carbon that originates in the aquatic environment like excretion products of algae or microorganisms. Natural organic matter (NOM) is composed of six major groups of organic compounds. The main portion of DOC in an average NOM sample is humic substances. They contribute about 50 percent DOC as fulvic acid (40 %) and humic acid (10 %) to the total DOC concentration. Hydrophylic acids are about 30 percent of the overall DOC. The remaining 20 percent are carbohydrates, carboxylic acids, amino acids and hydrocarbons (Thurman, 1985).

Humic acid is per definition that portion of humic substances that precipitate in acid at pH one whereas fulvic acid remains in solution. Fulvic acid exhibit molecular weight

ranges from 500 to 2000 Dalton. Molecular weight ranges of humic acid are generally considered to be approximately 2000 to 5000 Dalton (Thurman, 1985; Ranville & Macalady, 1997).

Groundwater shows according to Thurman (1985) a median DOC concentration of 0.7 mg/L whereas surface waters in rivers and lakes have higher DOC concentrations, ranging from 2 mg/L to 10 mg/L. It should be noted that NOM is generally well degraded and refractory in character. Due to residence times in the aquifer up to thousands of years, groundwater contains a higher portion of low molecular weight compounds than surface water.

The most abundant class of organic compounds in natural waters is organic acids. They account for approximately 90 percent of all dissolved organic carbon (Thurman, 1985). The carboxylic acid group contributes solubility and acidity to an organic molecule and it is responsible for the anionic character of the organic matter. The reaction below shows that the anionic character comes from the dissociation of carboxylic acid functional groups. R stands for an aliphatic backbone of the compound.

$$R\text{-}COOH <-> R\text{-}COO^- + H^+$$

The negative charge of most of the organic compounds at neutral pH as well as a high portion of low molecular weight compounds can cause losses in the concentration and desalting procedure resulting in lower recoveries (e.g. electrodialysis, reverse osmosis), which will be discussed in Section 2.2.1.

2.1.1.2 Organic Compounds Derived from Wastewater Treatment Processes

A variety of soluble organic compounds including residual degradable and non or slowly biodegradable organic compounds are found in effluents of wastewater treatment systems. The majority of DOC in wastewater can be classified as soluble microbial products (SMP) and is formed during secondary treatment (Quanrud, 2000). SMP define the pool of organic compounds that are released into solution from substrate metabolism and biomass decay (Barker and Stuckey, 1999). Past research has focused especially on parameters such as molecular weight distribution, biodegradability and toxicity to get information about the characteristics of SMP. The molecular weight distribution of SMP is affected by the substrate type as well as by the operating conditions of the system and a greater amount of high molecular weight compounds is found in many biological effluents than in the influent. According to Boero et al. (1990), SMP are less biodegradable than original organic

substrates and they may be polymeric in character. SMP have also been found to be more toxic than the original organic compounds present in the wastewater of aerobic treatment systems (Barker and Stuckey, 1999).

Disinfection processes such as chlorination of drinking water and wastewater form also a variety of organic contaminants. When free chlorine comes in contact with organic matter disinfection by-products (DBPs) are formed (National Research Council, 1998). Main classes of DBPs are trihalomethanes (THMs) (e.g. chloroform) and haloacetic acids (HAAs) (e.g. di- and trichloroacetic acids) (Cohn et al., 1999). DBP are classified as trace organics since their concentrations in water are usually in the range of parts per billion (Quanrud, 2000). Despite the relatively low substance concentrations in drinking water, DBPs are suspected carcinogens and mutagens. THMs for example, such as chloroform was shown to be a carcinogen in animal studies. Also, epidemiological studies showed an association between chlorinated surface water and cancer, and suggested a human health risk (Barrett et al., 2000). However, much work remains to be done to determine the potential risk of DBPs in drinking water to human health.

2.1.1.3 Organic Compounds Derived from Domestic and Commercial Activities

Due to domestic and commercial activities synthetic organic compounds (SOC) are added to wastewater, agricultural runoff, urban runoff, and leachate from contaminated soils. SOC include a variety of organic substances such as pesticides, medical drugs, surfactants, organic nitrogen compounds, organic sulfur compounds, and complexing agents (Rauch, 1999). These substances are usually extremly persistent in character and many of them can still be tracked in wastewater influenced aqueous environments (National Research Council, 1998). Concentrations of SOC are usually to be found in the ng/L range (trace organics) but they still can cause serious health problems on living organisms exposed to them. In the last century many new SOC not previously existing in nature were produced. The total mass of organic compounds produced is increasing rapidly. About 250,000 new chemical compounds are synthesized each year, and 300-500 new compounds go into production. This results in an annual production of organic compounds in the world of 100-200 million tons (Dojlido and Best, 1993).

However, the different groups of DOC remaining in the wastewater after treatment such as NOM, SMPs, and anthropogenic trace organics are contributing to the DOC of wastewater effluents and hence are defined as effluent organic matter (EfOM) (Drewes et al., 2002).

2.2 DOC Isolation Methods

Isolation of organic matter from water samples becomes necessary prior to advanced carbon characterization techniques such as 13-carbon nuclear magnetic resonance spectroscopy (^{13}C-NMR spectroscopy) or Fourier transformed infrared spectroscopy (FT-IR spectroscopy). These carbon characterization tools require the organic carbon in an isolated and solid state form. An undesired side effect of many organic carbon concentration techniques is an enhanced salt content of the sample which requires a subsequent desalination step to get clear and meaningful ^{13}C-NMR- and FT-IR spectra (Kitis et al., 2001).

2.2.1 Membrane Techniques

The combination of two well known membrane separation techniques – reverse osmosis and electrodialysis – is a novel approach to isolate organic carbon from water samples. Reverse osmosis is employed to concentrate organic carbon from water samples while desalination of the sample is accomplished by subsequent electrodialysis treatment.

2.2.1.1 DOC Concentration Using Reverse Osmosis

Pressure driven membrane processes such as reverse osmosis and nanofiltration allow to separate dissolved organics and salts from water by applying a pressure greater than the osmotic pressure which is caused by the dissolved salts in the water (Metcalf and Eddy, 1991). The basic elements of a reverse osmosis unit are the membrane element, a containing vessel and a high pressure pump. Feed water is introduced into the membrane element by the high pressure pump. Operating pressures vary from atmospheric to 7000 kN/m^2 (Brandt et al., 1993). A regulating valve in the brine stream, as shown in Figure 2.2, provides back pressure and controls the permeate flux.

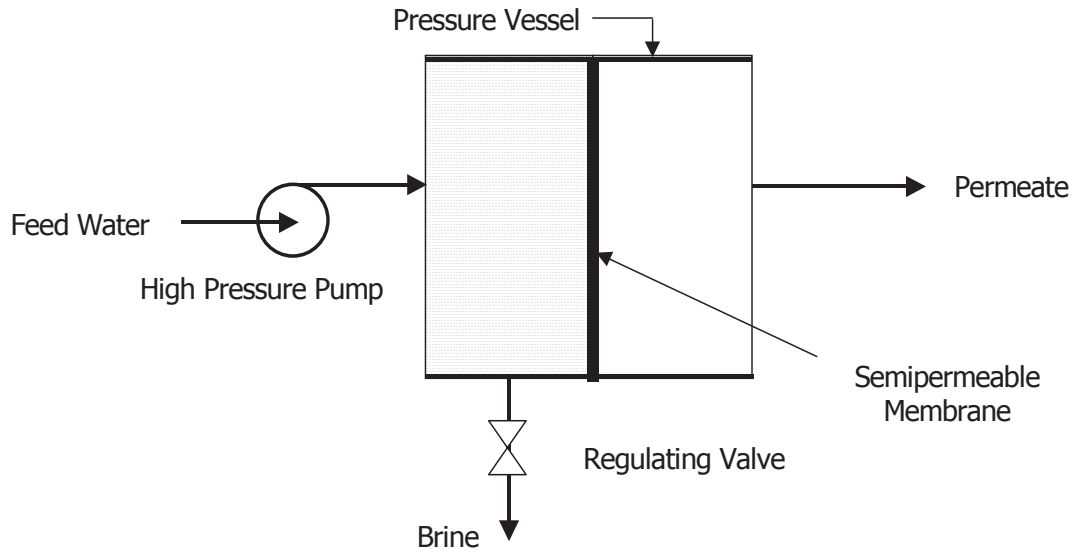

Figure 2.2: Principle of reverse osmosis (Brandt et al., 1993)

The salt transport (Q_s) through the membrane, described by Equation 2.1, is dependant on the salt concentration differential across the membrane (ΔC), the membrane permeability coefficient (K_s), the membrane surface area (A), and the membrane thickness (**0**) but it is independant on the applied pressure.

$$Q_s = K_s (\Delta C)A/\mathbf{0} \qquad \text{(Equation 2.1)}$$

The main driving force to accomplish separation of solute from solvent is the pressure gradient across the membrane but the presence of dissolved and colloidal matter in the solvent influences the pressure gradient Δp and hence the permeate flux due to accumulation of materials on the membrane. This phenomenon is called membrane fouling and will be discussed in the following paragraph. Reverse osmosis and nanofiltration membranes are generally defined by their molecular cut-off threshold, i. e. the maximum molecular mass which is capable of passing through the membranes expressed in the unit Dalton (Alborzfar et al., 1998). Commonly used membrane types are thin film composite membranes (e.g. polyamide membranes) and cellulosic membranes (e.g. cellulose acetate membranes). Polyamide membranes have several advantages compared to cellulose acetate membranes such as lower operating costs and pressure, higher removal efficiency, and a higher operating life (Drewes et al., 2002).

The accumulation of materials on and within a membrane is blocking pores and produces an additional layer of resistance to permeate flux. Washing the membrane, either hydraulically or chemically may remove some of the accumulated materials

and partially restore the permeate flux. Irreversible reduction in permeate flux is referred to as membrane fouling. Two different fouling mechanism may occur during operation of reverse osmosis and nanofiltration membranes. Adsorptive fouling is mainly caused by adsorption of organic matter onto membrane surfaces. The characteristics of organic materials that determine their relative propensity to foul membranes include their affinity for the membrane, molecular weight, functionality, and conformation (Wiesner and Aptel, 1996). On the other hand most commercial composite reverse osmosis membranes carry some degree of negative surface charge at neutral pH levels due to the presence of carboxylic groups in the aromatic polyamide skin layer, which make them more susceptible to fouling by charged organic molecules. Only certain types of cellulose acetate membranes have almost a neutral surface charge which predestines these types of membranes to be the choice for high fouling applications (Gerard et al., 1998). In addition to the surface charge, the hydrophilicity of the membrane is also known to have an effect on the fouling tolerance of a membrane. Jucker and Clark (1994) demonstrated the preferential adsorption of hydrophobic compounds onto hydrophobic membranes. Mänttäri et al. (2000) concluded that charged organics such as humic acids showed increased fouling behavior at acidic pH while at neutral pH humic acid increased the membrane hydrophilicity and fouling was dominated by hydrophobic forces.

Precipitative fouling, also called scaling, is either caused by the removal of bulk concentration of the salts from the salt solution as water permeating through the membrane or it is a result of concentration polarization. Scaling is mainly caused by ions such as magnesium and calcium. To minimize precipitation of these ions on the membrane, the water should be softened prior to membrane treatment by passing it through an ion exchange resin. Another pretreatment step is necessary before feed water enters the membrane unit. Microfiltration removes particulate matter and prevents the membrane from fouling. Fouling mechanisms not only lower the membrane permeability but they also influence the DOC-mass balances of organic carbon concentration processes. The overall DOC loss due to fouling and permeation through the membrane can range between 4 and 20 percent (Ozaki and Li, 2001; Kitis et al., 2001; Rybacki et al., 1998). Huber (1998) found that mainly hydrophobic organic carbon and polysaccharides adsorb onto the membrane which is consistent with results of Manttäri et al. (2000) who reported also increasing fouling behavior of humic acids at low pH.

The fraction of DOC permeating through RO and NF membranes consists up to 50 percent of low molecular weight acids and neutrals representing a molecular weight range of ~500 Dalton and less (Drewes et al., 2002; Wiesner and Buckley, 1996).

DOC-isolation using reverse osmosis was first proposed by Perdue et al. (1990). The advantages of the reverse osmosis isolation technique are according to Kitis et al. (2001):

- Absence of harsh chemical conditions such as extremes in pH or contact with chemical solvents
- Very large recoveries of DOC with minimal fractionation
- Concentration of samples to high values
- Processing of large volumes of water in a short period of time

Unfortunately, the reverse osmosis-method faces also some disadvantages:

- Concentration of inorganic ions along with DOC which may need to be removed prior to subsequent DOC characterization
- Losses of some DOC components due to sorption onto the membrane, leakage via permeate or precipitation within the concentrate
- High cost of the membrane system compared to other isolation techniques

The high salt content of reverse osmosis DOC-isolates requires a subsequent desalination step to be able to apply sophisticated analytical techniques such as ^{13}C-NMR spectroscopy or FT-IR spectroscopy. In a novel approach electrodialysis, one of the major desalination technologies in use today, has been successfully employed to desalt DOC-concentrates (Rybacky et al., 1998).

2.2.1.2 Electrodialysis Desalination Process

Electrodialysis is a well proven membrane separation technique which allows separation of charged from neutral molecules under the influence of a direct current electric potential (Metcalf and Eddy, 1991). The process was proposed for the first time in 1890 by Maigrot and Sabates to deminaralize sugar syrup (Shaposhnik and Kesore, 1997). Nowadays electrodialysis is applied in various processes such as whey-, organic acid-, and sugar demineralization, amino acid and blood treatments, mineral acid concentration, preparation of isotonic solutions, wine stabilization and a number of desalting processes. Modern electrodialysis cells consist of an array of alternating anion-selective and cation-selective membranes. Gaskets separate adjacent membranes from each other and form together with spacer meshes small compartments through which fluids can be passed. Holes in the membranes and gaskets form together with the compartments two different flow paths. One flow path

connects all depletion compartments and is called the feed stream while the second flow path connects all enrichment compartments where all the salts end up. This flow path is also called the concentrate stream. Modern ion exchange membranes show low electrical resistance, good mechanical strength, good chemical stability and high ion selectivity. Anion exchange membranes, only permeable for anions, typically consist of polystyrene and have positively charged quaternary ammonium groups chemically bonded to the phenyl groups in the polystyrene. On the other hand, cation exchange membranes, only permeable for cations, typically consist of polystyrene and having negatively charged sulphonate groups chemically bonded to most of the phenyl groups in the polystyrene (McRae, 1983).

A group of membrane pairs is called a stack. A single stack can be equipped with several hundred pairs of cation- and anion exchange membranes. When a direct current potential is applied to the sample, cations tend to move through cation exchange membranes toward the negatively charged cathode but they are not able to pentrate the anion exchange membranes. Similarly anions tend to move only through anion exchange membranes toward the positively charged anode. However, the result is a demineralized feed stream and a concentrate stream containing the transferred ions (McRae, 1983). Due to the alternating array of cation- and anion exchange membranes the ions transferred from the feed compartments get trapped in the concentrate compartment. The two internal manifold flow paths are usually connected with external sample containers to be able to process high volumes of sample. Figure 2.3 shows the principle of the electrodialysis process.

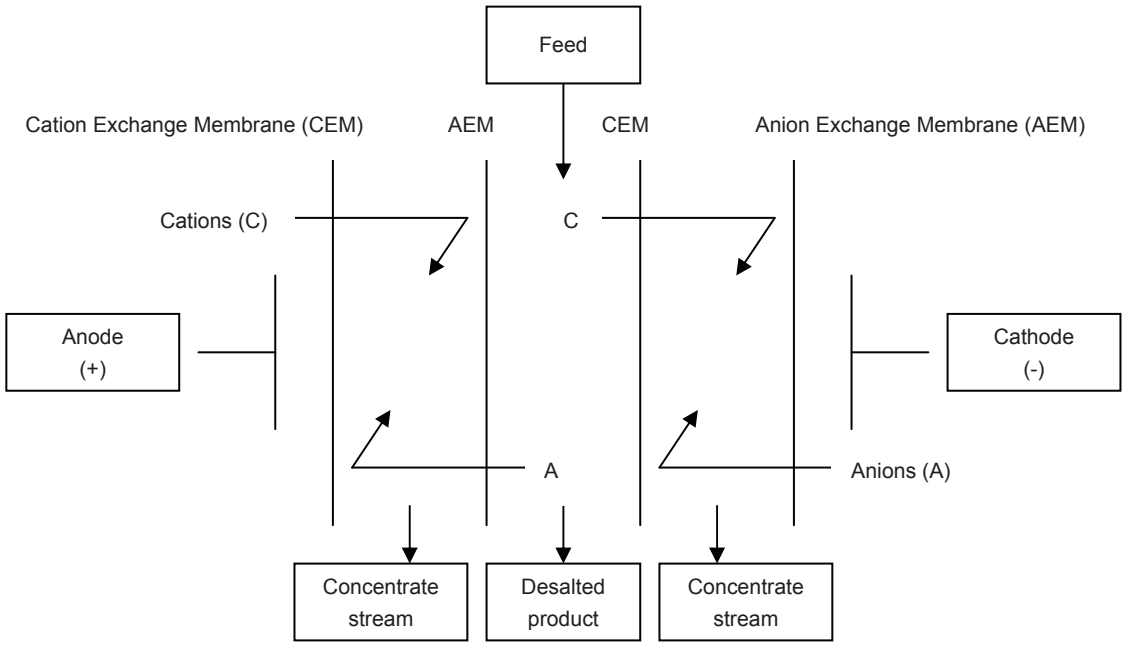

Figure 2.3: Principle of electrodialysis (Bailly et al., 2001; modified)

In addition to the feed- and concentrate loop a third flow path, called the electrode rinse stream, is necessary to equalize pH-changes and to remove generated gas from the closed electrode compartments at the outer sides of the electrodialysis cell. The pH-changes are caused by electrochemical reactions which result in the formation of hydroxyl ions in the cathode rinse compartment and hydrogen ions in the anode rinse compartment respectively (Schoeman and Thompson, 1996).

The electrodes should be made of inert metals because they are exposed to harsh electrochemical conditions during operation of the electrodialysis cell. Usually anodes are made of platinum-plated metal and stainless steel is used for cathodes.

2.2.1.2.1 Separation Mechanisms of Electrodialysis

The main driving forces of the electrodialysis separation process is an electric potential difference and a concentration gradient between the feed and the concentrate stream (Schoeman, 1996). Further parameters influencing the ion transport rate ($F_{tot,i}$) are presented in Equation 2.2.

$$F_{tot,i} = RT\frac{d(\ln c_i)}{dx} + F\frac{z_i d\varphi}{dx} \qquad \text{(Equation 2.2)}$$

where: c_i = ion concentration

z_i = ion valency

R = gas constant

T = absolute temperature

x = membrane thickness

F = Faraday's constant

φ = electric potential within membrane

Under the influence of an electrical potential difference, ions are forced to migrate from the feed compartments through the membranes into the concentrate compartments. Additionally ions tend to diffuse into the concentrate stream driven by the concentration gradient between the feed and the concentrate stream. The ion flux caused by diffusion is not as strong as the flux caused by the electrical field. This is important since at a certain point of the process the ion concentration in both loops become equal and backdiffusion is to begin (Schoeman, 1996). When the feed stream gets more and more depleted the resistance of the cell becomes greater and the process is approaching an endpoint.

With regard to limitations accompanying the electrodialysis process a number of influencing factors have to be considered. An important physical quantity in the electrodialysis process is the limiting current density which is reached when current density is increased until the current to transfer ions exceeds the number of ions available to be transferred (Yu and Admassu, 2000). At this point the thin layer of concentrated ions, which is formed immediately adjacent to the membrane surface becomes so depleted in ions that the electrical resistance rises sharply. The result of the increased resistance is an increased voltage, which can cause dissociation of the water molecules. However, at this point which is called the polarization point, pH changes of the process streams occur and the process in general becomes more and more inefficient (Schoeman and Thompson, 1996). Inefficient operation of an electrodialysis cell is reflected in higher operating costs. The costs related to energy consumption is a strong function of the operating parameters such as current density, potential drop across the stack, and operating time (Parulekar, 1998).

The energy requirement of the electrodialysis process can also be reduced by operating the ED-cell in an elevated temperature mode. An increase in temperature of the saline water increases the degree of ionization and the mobility of the ions, resulting in a decrease of solution and membrane resistance. Elevated temperature operation is also accociated with decreased viscosity of the electrolyte. Thus the energy requirement (e.g. lower voltage, lower pumping costs) decreases with increasing temperature (Hodgkiess, 1987).

Beside type and concentration of the electrolyte and operating mode of the ED-cell especially the chosen type of ion exchange membranes has a big impact on the separation efficiency during the electrodialysis process. As already mentioned, ion exchange membranes consist of a base polymer with charged groups chemically bonded to the phenyl groups in the polymer. Negatively charged sulphonate groups are typical for cation exchange membranes and positively charged quarternary ammonium groups are usually used in anion exchange membranes. The negative charges of the sulphonate groups and the positive charges of the ammonium groups respectively, are electrically balanced by so called counter ions of the opposite charge (McRae, 1983).

Since ion exchange membranes are prone to fouling by organic matter a lot of effort has been put into development of membranes with low fouling characteristics. Especially anion exchange membranes are more sensitive to fouling because most of the organic substances present in natural water and effluents are negatively charged (Schoeman and Thompson, 1996). The physical parameters of the solute that influence fouling on and in the membrane are charge, hydrophobicity, molecular

size, and solubility (Lindstrand et al., 2000[a)]). Organic fouling increases the membrane resistance and hence the energy consumption of the process. Sometimes it causes also a loss in selectivity of the membrane (Lindstrand et al., 2000[b)]).

Methods to reduce organic fouling on ion exchange membranes are adjustment of the degree of cross-linking or usage of aliphatic polymers instead of aromatic polymers. The pore size of commercially manufactured electrodialysis membranes usually varies from 10 to 100 Ångström depending on the application (Bazinet et al., 1998). Certain types of anion exchange membranes are coated with a thin layer of cation exchange groups which cause electrostatic repulsion of organic constituents (Schoeman and Thompson, 1996).

Organic fouling can also cause problems when electrodialysis is used to desalt organic carbon isolates for further characterization. Grünheid (2001) found in single organic compound experiments that charged organic carbon fractions contributed the highest portion to the overall DOC-loss due to fouling. Furthermore certain fractions of organic carbon of low molecular weight tend to penetrate through the membranes and are not available for characterization (Rybacky et al., 1998; Grünheid, 2001). Therefore a proper membrane choice is very important to achieve high DOC recovery rates. Grünheid (2001) was able to lower the DOC-loss during desalination of RO-concentrate from 57 down to 25 percent only by changing the membrane configuration.

2.2.2 Other Separation Techniques

A common method to isolate organic carbon from water samples is XAD resin adsorption chromatography. Resin adsorption based isolation of aquatic DOC has been used by many researchers since the 1970's but the method proposed by Aiken et al. (1992), employing a combination of XAD-8 and XAD-4 resins to isolate different fractions of DOM is today the most commonly used approach (Quanrud, 2000).

Adsorption chromatography utilizes the affinity of organic carbon present in the water sample to the macroporous resins. At pH 2 the acidic groups of humic substances such as fulvic and humic acids become protonated rendering the molecules nonionic and allowing the polar carbon skeletons to adsorb onto the XAD-8 resin. Subsequently the remaining fraction of lower molecular weight acids is sorbed onto the XAD-4 resin which has a much larger specific surface area than the XAD-8 resin (Quanrud, 2000). Elution with base (e.g. sodiumhydroxide solution) or an organic solvent (e.g. acetonitrile solution) allows to recover the adsorbed organic fractions from the resin matrix. With XAD resin adsorption chromatography, up to five different fractions of organic carbon in water samples can be separated: Hydrophobic acids

and neutrals, transphilic acids and neutrals, and hydrophilic compounds (Drewes et al., 2002; Aiken et al., 1992). According to Quanrud (2000) a number of disadvantages are associated with the application of XAD resin adsorption chromatography:

- Chemical alteration or contamination of the sample
- Physical losses of organic carbon
- Nonrepresentativeness of extracts
- Blurring of fractions

Attainable overall organic carbon recovery rates of the XAD-8/XAD-4 resin fractionation method are to be found in the range of 45 to 80 percent depending on quality and concentration of the DOC (Drewes et al., 2002; Rauch, 1999; Leenheer et al., 1999; Rybacky, 1998).

Beside reverse osmosis/electrodialysis and XAD resin adsorption chromatography two other DOC-isolation methods need to be mentioned. Vacuum rotary evaporation and freeze drying have the disadvantage that dissolved salts are concentrated along with organics thus, a subsequent desalination step becomes necessary (Quanrud, 2000). Furthermore, the application of vacuum evaporation is limited because only small sample volumes can be processed and hence, the method becomes very time consuming (Gjessing, 1999). The presence of sophisticated XAD fractionation techniques is the reason that older methods such as vacuum rotary evaporation and freeze drying receive nowadays less attention (Quanrud, 2000).

2.3 Removal and Measurement of Organic Carbon

The presence of residual biodegradable organic carbon in treated water is associated with a broad spectrum of potential health risks since it can serve as a substrate that promotes the regrowth of microorganisms. Residual biodegradable organic carbon is especially of concern for water in soil aquifer treatment (SAT) systems used for indirect potable reuse (Drewes and Jekel, 1998). Residual organic matter might mobilize organic contaminants and metals and can cause a variety of other undesirable effects during SAT (see also Section 2.1). Limiting the amount of biodegradable organic matter minimizes microbial regrowth, which may also reduce the initial disinfectant dose and consequent generation of disinfection by-products (Khan et al., 1999). The fate of organic carbon in SAT systems is basically determined by processes such as volatilization, chemical and biochemical

transformation and adsorption. Removal rates are strongly influenced by the type of the organic carbon and the sub-surface environment (Bouwer et al., 1984).

Today there are two major established methods to quantify the biodegradable fraction of organic matter in water (Escobar and Randall, 2001). In the assimilable organic carbon (AOC) bioassay the growth of test organisms is correlated with the concentration of biodegradable organic matter (BOM). This method should be used when bacterial re-growth is the matter of concern. The measured parameter is typically bacterial biomass and the organic matter producing this growth is AOC. The second method is called the biodegradable dissolved organic carbon (BDOC) assay in which the consumption of DOC through the ability of a mixed microflora to catabolize organic carbon to carbon dioxide and/or biomass is measured. This method is used if the concern is for example the reduction in chlorine demand of disinfection by-products formation potential through a biological process (Huck, 1990). The BDOC concentration represents the fraction of DOC that is both mineralized and assimilated by heterotrophic flora, determined as the difference between the initial DOC concentration and the minimum DOC concentration observed during the incubation period (Escobar and Randall, 2001; Frias et al., 1992).

2.3.1 Biodegradation

The removal of BDOC is accomplished principally by bacteria which are also contributing to a variety of other important mechanisms during biological water treatment processes such as coagulation and stabilization of organic matter. Microorganisms are converting dissolved carbonaceous organic matter into various gases, metabolites and cell tissue. To be able to keep the microbial metabolism going the microorganisms must be provided with a source of energy, carbon for the synthesis of new cellular material, and nutrients (inorganic elements). Light or a chemical oxidation reaction can serve as an energy source. Nutrients, rather than carbon or energy, may at times be the limiting factor for cell synthesis and growth. Beside inorganic nutrients such as N, S, P, K, Mg, Ca, Fe, Na, and Cl, organic nutrients such as amino acids, purines and pyrimidines, and vitamins may also be needed by the microorganisms. Additionally nutrients in minor amounts are required for biosynthesis including Zn, Mn, Mo, Se, Co, Cu, Ni, V, and W (Metcalf and Eddy, 1991).

Chemoheterotrophic organisms that generate energy by enzyme-mediated electron transport from an electron donor to an external electron acceptor have a respiratory metabolism. In contrast, fermentative metabolism does not involve the participation of

an external electron acceptor. A typical electron acceptor in aerobic bacterial reactions is molecular oxygen (O_2). In an anaerobic environment nitrate (NO_3^-), sulfate (SO_4^{2-}), or carbon dioxide (CO_2) can serve as an electron acceptor (Metcalf and Eddy, 1991).

A variety of important parameters have to be considered when the liquid environment of microorganisms needs to be controlled. Such parameters of concern are pH, temperature, nutrient or trace-element concentration, oxygen addition or exclusion, and proper mixing. Furthermore, microorganisms must be allowed to remain in the system long enough to reproduce. Equation 2.3 defines the rate of growth of bacterial cells.

$$r_g = \mu X \qquad \text{(Equation 2.3)}$$

where: r_g = rate of bacterial growth, mass/unit volume · time

μ = specific growth rate, time^{-1}

X = concentration of microorganism, mass/unit volume

Growth in a batch culture system would approach zero after depletion of all substrate and nutrient sources. In a continuous culture system, growth is limited. The effect of a limiting substrate or nutrient can be described by Equation 2.4 proposed by Monod (Metcalf and Eddy, 1991).

$$\mu = \mu_m \frac{S}{K_s + S} \qquad \text{(Equation 2.4)}$$

where: μ = specific growth rate, time^{-1}

μ_m = maximum specific growth rate, time^{-1}

S = concentration of growth-limiting substrate in solution, mass/unit volume

K_s = half-velocity constant, substrate concentration at one-half the maximum growth rate, mass/unit volume

Figure 2.4 shows the effect of substrate concentration on the specific growth rate.

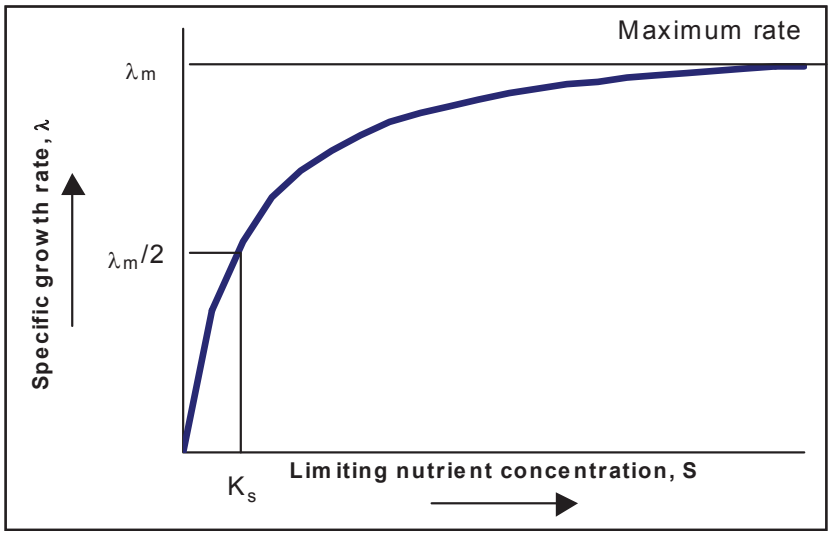

Figure 2.4: Relationship between limiting substrate concentration and specific growth rate (Metcalf and Eddy, 1991)

2.3.2 Adsorption

Beside microbial degradation of organic carbon the rate of adsorption of DOC onto the soil surface is of concern during BDOC studies in the lab or in the field. Sorption of dissolved solute onto a solid matrix, whether as adsorption to mineral surfaces or partitioning with nonaqueous organic phases, requires the transfer of solute from bulk solution to sites of immobilization. Resistance to such mass transfer may stem from transport across a fluid boundary layer external to the particle (external mass transfer), from diffusion to internal sites of the immobile phase (intrasorbent diffusion), or from rate limitations of the sorption process itself (chemical kinetics) (Ball and Roberts, 1991). Adsorption takes place when the change in Gibb's free energy (ΔG) between adsorbent and adsorbate is negative, (Quanrud, 2000).

$$\Delta G = \Delta H - T\Delta S \qquad \text{(Equation 2.5)}$$

where: ΔH = change in enthalpy

ΔS = change in entropy

T = Temperature

Adsorption may be driven by a change in enthalpy, a change in entropy or a combination of the two. According to Jardine et al. (1989) hydrophobic bonding, a physical adsorption process driven by a change in entropy, is the main mechanism of DOC adsorption onto soil. Hydrophobic nonpolar compounds out of a polar aqueous phase are attracted by hydrophobic solid organic matter. The hydrophobic

compounds in aqueous solution are enclosed within a shell structure of water molecules. During attachment of the hydrophobic compound onto a hydrophobic organic surface the shell collapses and entropy increases (Hassett and Banwart, 1989).

The quantity of organic carbon that can be taken up by soil or another adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature (Metcalf and Eddy, 1991).

3 Experimental Approach

A system, consisting of a microfiltration/softening unit, a one-stage laboratory-scale reverse osmosis unit and a laboratory-scale electrodialysis unit was used to isolate and desalt dissolved organic matter from selected water samples. The three mobile units, schematically depicted in Figure 3.1, were operated in succession.

Prior to the RO/ED laboratory-scale experiments a bench-scale ED membrane test unit was employed to test ED membrane combinations of Asahi Glass (ACS/CMS) and Tokuyama (AM-2/CM-3) in terms of DOC rejection and ion migration. RO concentrate from the Scottsdale Water Campus in Arizona served as a DOC source for these experiments. After obtaining positive results from the bench scale membrane tests the pilot scale ED cell was equipped with a set of Asahi Glass ACS/CMS membranes. Two experiments were conducted with the laboratory-scale RO/ED-system. A 200 L surface water sample was taken from Clear Creek in Golden, Colorado to generate a desalted concentrate of natural organic matter (NOM). In a second experiment effluent organic matter (EfOM) was concentrated from a 130 L sample of secondary effluent water from the Boulder Wastewater Treatment Plant in Boulder, Colorado. At the Boulder Wastewater Treatment Plant mainly domestic effluent water is treated. The process employs bar screens, a grit chamber, primary settling tanks, trickling filters, a solids contact basin, secondary clarifiers and chlorination-dechlorination before the water is discharged into Boulder Creek.

To be able to determine the amount of biodegradable dissolved organic carbon (BDOC) in the Clear Creek- RO/ED concentrate and in the Boulder secondary effluent RO/ED concentrates, a series of batch reactors with microbiologically acclimated sand was utilized.

Finally, single organic compound experiments were performed to study the influence of molecular weight on the fate of organic carbon during the ED process. Therefore, three different polyethylene glycol (PEG) standards with molecular weights of 200, 600 and 6000 Dalton were used.

Table 3.1 gives an overview of all conducted experiments.

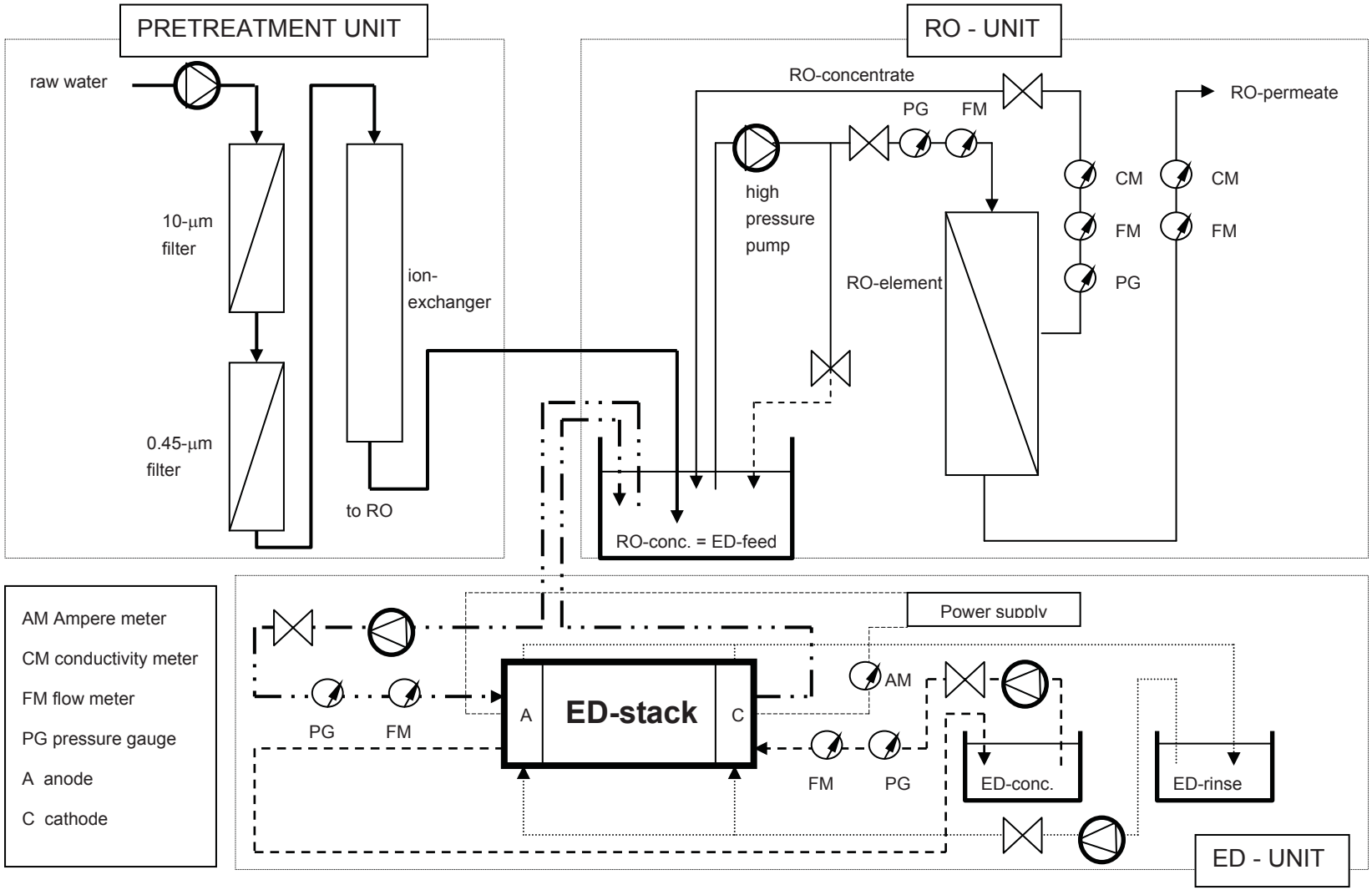

Figure 3.1: Process schematic of the reverse osmosis/electrodialysis laboratory-scale system

Table 3.1: Summary of conducted experiments

Exp. No.	Objective	Membrane combination	Feed solution	Sample volume [L]	DOC [mg/L]	DOC re-jected [%]
Bench-scale ED membrane test unit						
1	Comparison of two different ED membrane combinations regarding DOC rejection and ion migration rates	AM-3/CM-2	Scottsdale RO concentrate	0.5	37.6	74
2		ACS/CMS			37.6	92
Laboratory-scale ED unit						
3	Study of the influence of the molecular weight on the fate of organic compounds in the ED process	AMX/CMX	Polyethylene glycol standard 200	10	19.4	88
4			Polyethylene glycol standard 600		19.1	88
5			Polyethylene glycol standard 6000		19.1	90
6		ACS/CMS	Polyethylene glycol standard 200		18.9	91
7			Polyethylene glycol standard 600		19.1	92
8			Polyethylene glycol standard 6000		19.1	94
Laboratory-scale RO/ED unit						
9	Concentration and desalination of natural organic matter, SEC and IC analysis	ACS/CMS	Clear Creek water	200	14.6	97
10	Concentration and desalination of effluent organic matter, SEC and IC analysis		Boulder WWTP final effluent water	130	39.9	96
Biodegradation tests						**DOC removed [%]**
11	Determination of biodegradable dissolved organic carbon in the RO/ED concentrate	-	Clear Creek RO/ED concentrate	5	1-14.6	~40
12		-	Boulder WWTP secondary effluent RO/ED concentrate		4-39.9	~45

3.1 Materials and Methods

3.1.1 Bench-scale Membrane Test Unit

A bench scale ED membrane test unit was employed to test a pair of Asahi Glass ACS/CMS membranes regarding DOC rejection and ion migration. These highly crosslinked monovalent ion permselective membranes were suspected to minimize the DOC loss during the ED process. The achieved DOC rejection of the ACS/CMS membrane combination was compared to the results gained from a test of Tokuyama AM-3/CM-2 membranes with low diffusion characteristics. Table 3.2 gives a summary of the membrane properties.

Table 3.2: Properties of tested ED membranes (Tokuyama, 2001)

Grade	AM-3	CM-2	ACS	CMS
Manufacturer	Tokuyama	Tokuyama	Asahi Glass	Asahi Glass
Type	Strongly basic anion permeable	Strongly acidic cation permeable	Strongly basic anion permeable	Strongly acidic cation permeable
Characteristics	Low diffusion	Low diffusion	Mono anion permselective	Mono cation permselective
Electric Resistance [Ω-cm^2 in 0.5N NaCl]	2.8-5.0	2.0-3.5	3.0-6.0	1.5-3.5
Burst strength [kgf/cm^2]	2.0-4.0	1.5-3.0	2.0-4.0	1.3-3.0
Thickness [mm]	0.11-0.16	0.12-0.16	0.12-0.20	0.14-0.17
Application	Purification of organics Concentration of inorganics	Purification of organics Concentration of inorganics	Purification o pharmaceuticals Desalination of amino acids	Deacidification of metal solution

The ED membrane test unit was designed to be able to test the permeability for organics of the anion and the cation exchange membrane in one experiment and separately. Five rectangular acrylic glass chambers with side and top openings were clamped together, separated through ion exchange membranes in between, as shown in Figure 3.2. The active membrane area was 66 cm^2. Rubber gaskets prevented the unit from leaking. The middle or feed compartment, which was covered with the anion exchange membrane towards the anode side and with the cation exchange membrane towards the cathode side, contained a sample volume of 500 mL (Scottsdale RO-concentrate). During the desalination process the sample was stirred with a magnetic stirrer to avoid boundary layer effects. The adjacent anion and

cation concentrate compartments were operated with 425 mL each of 0.2 N NaCl solution. Feed and concentrate chambers were operated in batch mode. The two very outer rinse compartments contained the anode or cathode, respectively. A pump drive (Masterflex, model L/S 7554-90) equipped with peristaltic pumps (Masterflex, model 7518-00) provided the two 375 mL rinse compartments with 0.1 M Na_2SO_4-solution. The rinse solution was pumped at a flow rate of 120 mL/min from a 3 L storage container to both rinse compartments and back using Masterflex precision tubing (Tygon® silicon). Thus, the circulating rinse solution removed produced gas from the chambers and equalized pH differences. A Hewlett Packard DC power supply (model 6434B) provided the energy to build up an electric field within the chambers. The applied voltage was 42 Volt and a Radioshack® multimeter was employed to measure the streaming current. Samples were taken from the feed chamber and the two concentrate compartments at the beginning and end of each experiment. They were analyzed for UVA_{254}, DOC and ion concentration (F, Cl, NO_3, SO_4, PO_4, Na, K, Mg, Ca). The desalination process was controlled with a Cole Parmer conductivity meter (model 01481-61), measurements were taken every 15 minutes.

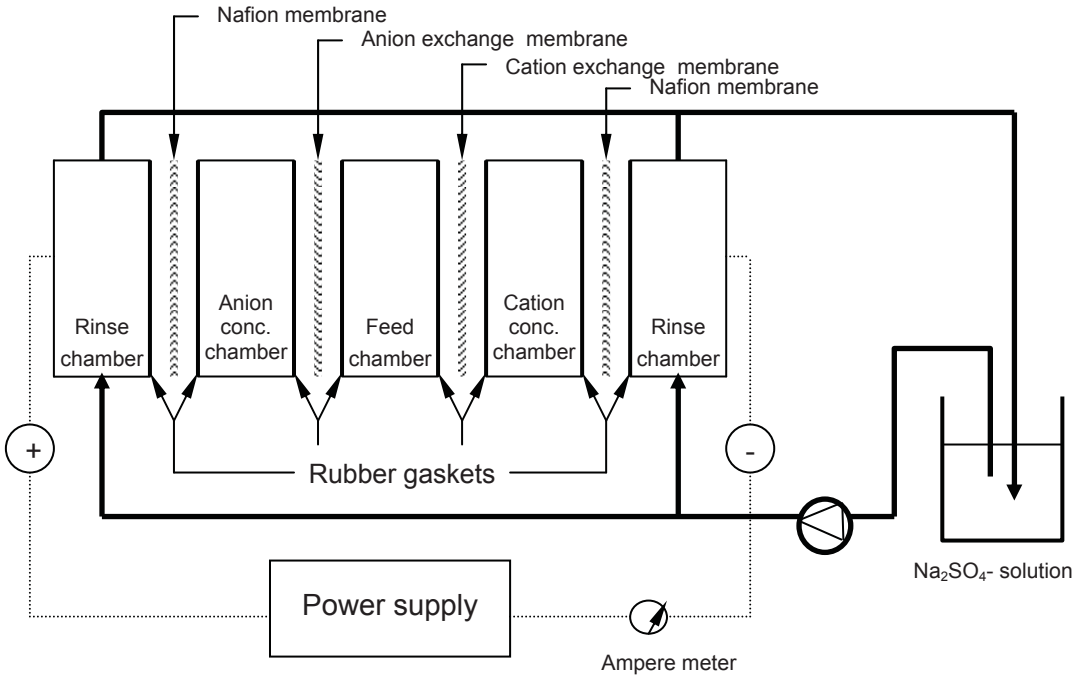

Figure 3.2: Process schematic of the bench-scale ED membrane test unit

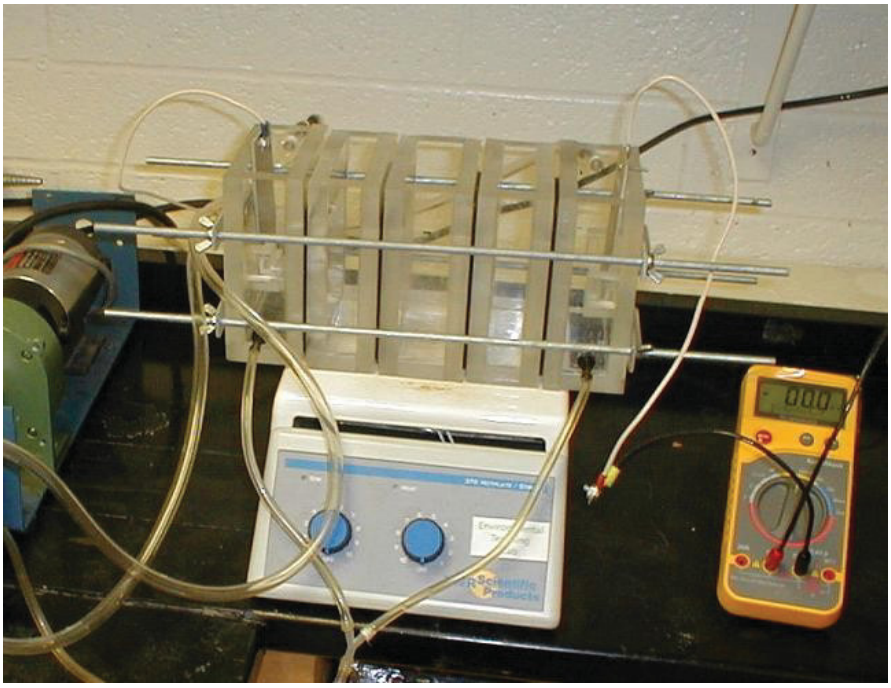

Figure 3.3: Bench-scale ED membrane test unit, close-up

3.1.2 Laboratory-scale Reverse Osmosis Unit

Concentration of DOC was achieved by applying reverse osmosis to water samples (see Figure 3.1). Therefore, a lab scale RO unit was designed and constructed using a Koch low pressure polyamide membrane element (TFC®-2540 HR). Membrane specifications are provided in Table 3.3. The spiral wound membrane was housed in an A&M Composites high pressure vessel. A Baldor industrial motor (model 35D12-73) in connection with a Procon pump head provided the system with the required water flow and pressure. Fluorinated ethylene propylene (FEP) tubing with an inner diameter of 0.635 cm was used to avoid any contamination of the sample due to interactions with tubing material. The unit was equipped with brass fittings and needle valves (Swagelok). Pressure

Table 3.3: RO membrane data*

Membrane area	2.5 m^2
Max. operating pressure	600 psi
Max. operating temp.	45 °C
Allowable pH-range	4-11
Max. feed turbidity	1 NTU
Length	1016 mm
Diameter	61 mm
Weight	1.4 kg

*(Koch, 2000)

gauges (Cole Parmer) were installed at the feed line and at the concentrate line to be able to monitor the pressure loss. Feed, concentrate, and permeate line were each equipped with flow meters (Cole Parmer). Two Cole Parmer conductivity controllers (model 19300-00 and 19300-10) measured online the conductivity of concentrate and permeate. Due to limited pressure resistance of the conductivity probes, shut off valves right before and after the probes allowed to bypass them in case of operating pressures above 200 psi (~1379 kPa).

3.1.2.1 Concentration Process

The system was operated with a constant feed pressure of 180 psi or a feed flow rate of 91 GPH. At a differential pressure of about 30 psi between feed and concentrate stream, the concentrate flow was approximately 67 GPH and the permeate flow was measured at 24 GPH. Throughout the experiment the permeate flow decreased slightly to about 22 GPH, due to fouling. While the permeate stream was separated from the feed, as shown in Figure 3.1, the concentrate was lead back into the feed container until concentration factors of 12 and 5 were achieved for Clear Creek and Boulder secondary effluent samples, respectively. Additional measurements included conductivity, pH, temperature and concentrate volume. All parameters were examined every 20 minutes.

3.1.2.2 Cleaning Procedure

DOC adsorbed to the membrane was removed by flushing the system before and after each experiment twice with 10 L of 0.01 N sodium hydroxide solution. Finally the unit was rinsed with 200 L DI-water. Mass balances were done for each experiment to determine DOC recovery and rejection rates. DOC recovered during final cleaning was not combined with the isolates.

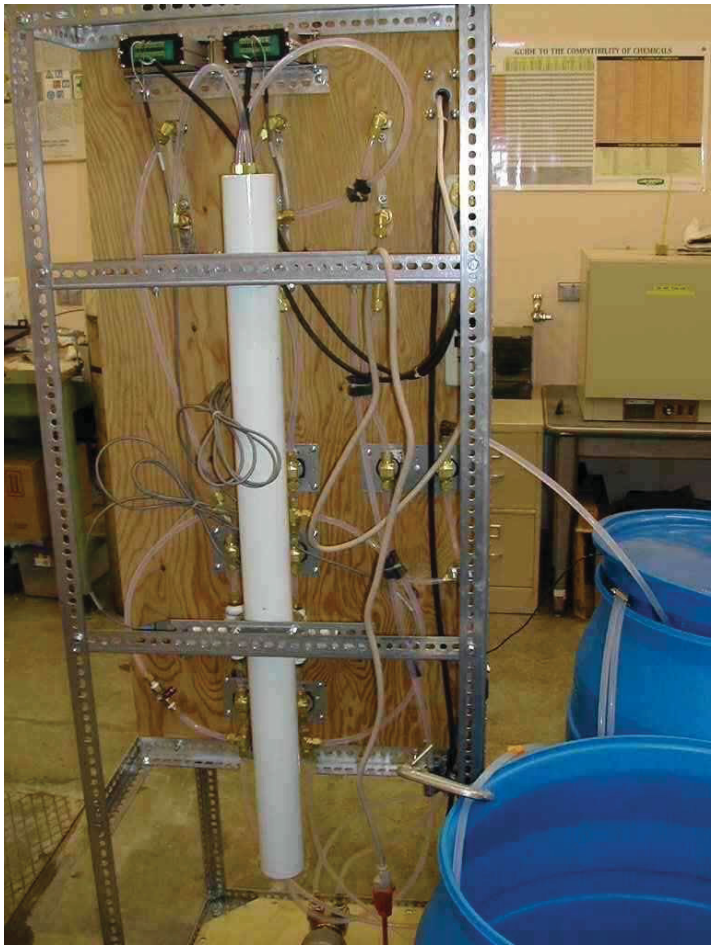

Figure 3.4: Laboratory-scale reverse osmosis unit

3.1.3 Laboratory-scale Electrodialysis Unit

The desalination tool used in this approach was a mobile electrodialysis unit constructed by Grünheid (2001). The unit was equipped with an Electrosynthesis ED cell (model ED-1) which consisted of a membrane stack and anode and cathode housing, which had connections for rinse-, concentrate- and feed-loop. These three loops were connected to four compartments within the cell, formed by gaskets and spacer meshes which separated the membranes from each other. Anode and cathode chamber were connected to a single loop as shown in Figure 3.1. Each loop was supplied with flow by a March centrifugal pump (model LC3-CP-MD). These pumps had magnetically driven pump heads covered with polypropylene to avoid any sample contamination. FEP tubing as described in Chapter 3.1.2 was used for all connections. Each loop was equipped with a needle valve to adjust flow rate and pressure. Beyond that, pressure gauges and flow meters allowed monitoring the water pressure and flow of the feed and concentrate loop. Pressure relief valves protected these two loops from system pressures above 15 psi. Anode and cathode

were made of titanium covered with platinum or stainless steel respectively to avoid electrical corrosion. The effective electrode area was 0.01 m^2 each. 20 anion exchange membranes and 20 cation exchange membranes with an individual membrane area of 0.01 m^2 were used which resulted in a maximum membrane area of 0.2 m^2 for each membrane type. Two different membrane combinations were used during the study. Membrane properties can be found in Table 3.4.

Polyethylene glycol (PEG) (formula: $HO\text{-}(CH_2CH_2\text{-}O)_nH$) is a hydroxyl-terminated polymer of ethylene oxide with an average molecular weight of 200-20,000 Dalton. They are widely used in cosmetics, pharmaceuticals, rubber chemicals, and many other applications. A very important feature of PEGs is their solubility in water. The water solubility of these polymers is due to hydrogen bonding between PEG and water. They also exhibit low toxicity, good stability, good lubricity, and can be mixed with water or other solvents to give a wide range of viscosities. Polymer structure and properties depend strongly on the inter- and intramolecular interactions between molecules. As the chain length of the polymer increases, the intermolecular interactions also increase. However, elongation of the polymer chain reduces concentration of the OH groups, and, in this way, the number of hydrogen bonds. Moreover, the dipole nature of the C-O bond causes conformational changes in the polymer chain, depending on the length of the chain. These effects may additionally influence the intermolecular interactions between polymer molecules. Thus, the physical properties will vary with changing molecular weight of PEGs (Drozdowski et al., 2002).

The experiments with Clear Creek and Boulder secondary effluent water were carried out only with the ACS/CMS combination. The membrane material consists of polydivinylbenzene and polystyrene polymers with minimal reinforcement. Cation exchange membranes, as CMX-SB or CMS respectively, were negatively charged due to fixed sulfonic acid groups, hence this membrane type is called strong acidic cation permeable. The anion exchange membranes, AMX-SB or ACS respectively, are strong basic anion permeable because of their positive charge caused by quaternary ammonium groups chemically bonded to most of the phenyl groups in the polystyrene. Nafion 117 perfluorinated copolymer cation exchange membranes (Dupont) were assigned to protect the electrode rinse compartments by preventing chloride from entering. Nafion membrane properties can also be found in Table 3.4.

Table 3.4: Membrane properties (Tokuyama, 2001)

Membrane	AMX-SB	CMX-SB	Nafion 117
Type	Strongly basic anion permeable	Strongly acidic cation permeable	Perfluorosulfonic acid cation exchange
Characteristics	High chemical and mechanical strength, low fouling	High chemical and mechanical strength, low fouling	Very high chemical resistance
Thickness [μm]	140-180	160-200	183
Water content [g H_2O/g dry membrane]	0.25-0.30	0.25-0.30	0.35
Electrical resistance [Ω-cm^2 in 0.5 M NaCl]	2.0-3.5	2.0-3.5	1.5 (measured in 0.6 M KCl)
Ion exchange capacity [meq/g dry membrane]	1.4-1.7	1.5-1.8	No details
Reinforcement	Yes	Yes	No
Application	Whey demineralization, organic purification	Whey demineralization, organic purification	HCL electrolysis, fuel cells

Direct current was supplied by a Hewlett Packard (model, 6434B) DC-power supply. In all conducted experiments a voltage of 42 Volt was applied to the sample. High current electrical cords connected the device with the electrodes. A RadioShack® multimeter was used for online current measurements. The chosen instrument range was 0-20 A.

3.1.3.1 Desalination Process

Before connecting the three sample containers for feed-, concentrate- and rinse-loop to the ED cell, each loop was set to an operating pressure of 5 psi by adjusting the needle valves while pushing DI-water through the system. This pressure or flow equalization was necessary to avoid water crossflows through the membranes caused by differential pressures in the loops. After achieving stable hydraulic conditions feed- concentrate- and rinse-containers were connected to the corresponding loops. The sample to desalt was applied to the feed loop. A 0.03 or 0.05 M NaCl solution was used in the concentrate loop to accelerate the desalination

process since the salt concentration caused a significant higher initial current than using just DI-water. Feed- and concentrate loop always were operated with equal volumes. The rinse loop was run with 10 L of 0.035 M Na_2SO_4 solution. Before starting the pumps and applying a constant voltage of 42 V to the cell, initial samples (15 mL each) were taken from the feed-, concentrate- and rinse tank. In the course of the experiment further samples were taken at intervals of 20 minutes to be able to draw profiles of DOC changes. Conductivity and pH of all three streams were measured at each sampling time.

3.1.3.2 Cleaning Procedure

Before and after each experiment the system was cleaned two times with 3 L of 0.1 N HCl and subsequently with 200 L of DI-water. To be able to determine the amount of DOC adsorbed in the feed chamber and in the concentrate chamber, the two compartments were rinsed separately. Carbon-mass balances included DOC measured in the feed-, concentrate- and rinse-solution as well as recovered DOC from the HCl-rinse.

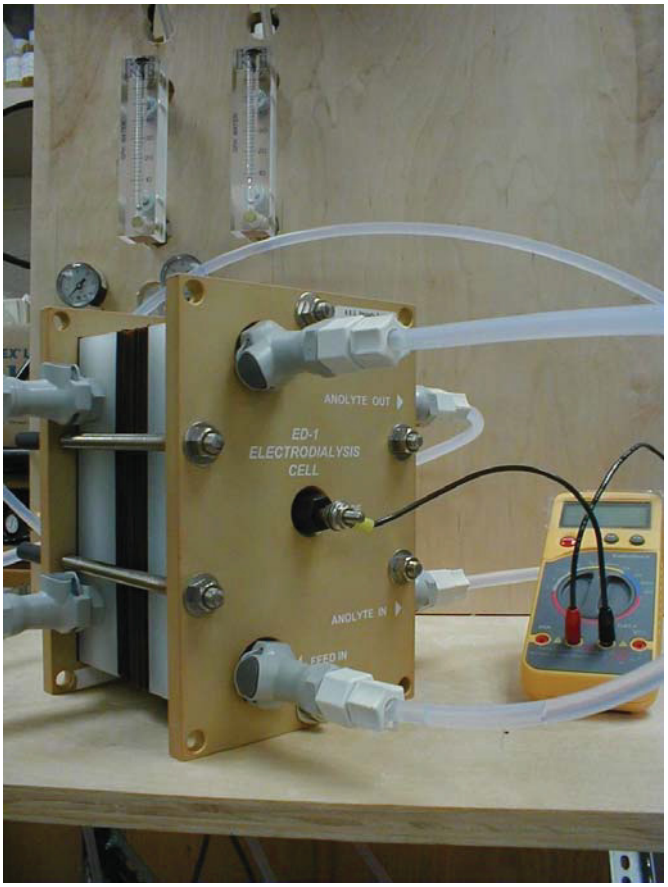

Figure 3.5: Laboratory-scale electrodialysis cell

3.1.4 BDOC Batch Reactors

Batch reactors with microbiologically acclimated sand were employed to determine the amount of biodegradable dissolved organic carbon (BDOC) of the RO/ED concentrates. The goal was to investigate the bioavailability of concentrated organic carbon after membrane treatment since the proposed hypothesis was that the concentration of organics in water samples is potentially influencing the degree of DOC removal. Glass jars with a total volume of 1000 mL were utilized, containing 200 g of acid (0.1 M HCl) and base (0.1 M NaOH) washed sand and a sample volume of 600 mL. The following samples of Clear Creek water and Boulder secondary effluent were investigated:

- Raw water samples, undiluted
- Desalted RO concentrates, undiluted
- Desalted RO concentrates, dilution factor 2
- Desalted RO concentrates, dilution factor 10
- Desalted RO concentrates + 0.002M NaN_3, undiluted

NaN_3 (sodium azide), which is highly toxic to aerobic bacteria, was added to the sample to eliminate microbial activity in order to determine DOC removal caused only by adsorption processes. Diluted samples were buffered using a 0.1M phosphate buffer solution (pH 7.2) to minimize pH-changes that can occur caused by metabolic activity. Before starting the biodegradation tests acclimation of microbial populations was achieved by dosing the reactors with secondary effluent over multiple 5-day cycles. Each sample was run in duplicate. The reactors were shaken manually every day to guarantee aerobic conditions in the system and they were kept in the dark in order to avoid algae growth. Dissolved oxygen measurements were performed in regular intervals, to make sure aerobic conditions are prevailing in the reactors. Samples of 30 mL were taken during a period of approximately two weeks, filtered and analyzed for DOC, UVA, and pH.

Figure 3.6: BDOC batch reactors

3.1.5 Analytical Methods

3.1.5.1 Sample Pretreatment

All water samples were filtered and softened immediately after collection using the pretreatment unit schematically depicted in Figure 3.1 and shown in Figure 3.7. The unit consisted of a 10 μm resin bonded cellulose filter (US-Filter, model RB-10) and a 0.45 μm double bag design submicron filter (Fin-L-Filters) in series followed by an ion exchange cartridge (HR-1) in potassium form to remove the hardness from the water. Flow was provided from a peristaltic pump (Masterflex) in connection with Masterflex tubing (model C-Flex 6424-18). The filtered samples were stored in 200 L plastic drums.

Figure 3.7: Pretreatment unit, close-up

3.1.5.2 UV Absorbance

Ultra-violet absorbance (UVA) measurements were carried out with a computer controlled Perkin Elmer single beam spectrophotometer (model Lambda 11) at a wavelength of 254 nm (path length of the quartz cell 0.01 m). Each sample was measured four times and similar values were averaged. Zero absorbance, using DI-water was checked and if necessary corrected after each sample. SUVA was calculated from the ratio of UVA and DOC. In order to warm up and stabilize the lamps the instrument was always switched on 30 minutes prior to the first measurement.

3.1.5.3 DOC Measurements

DOC measurements were performed with a Sievers total organic carbon (TOC) analyzer (model 800) in combination with a Sievers autosampler system (model 800 AS). The instrument had a detection limit of 0.05 ppb TOC and was computer controlled using Data Pro software (version 01.03 PAS). The analyzer was equipped with reservoirs for 6 M phosphoric acid (H_3PO_4) and 15% ammonium persulfate ($(NH_4)_2S_2O_8$). The pH of the samples was reduced to pH <2 by adding phosphoric acid. Acidification caused a conversion of inorganic carbon (IC) to CO_2 which was detected in the IC-CO_2 sensor. In a second stream organic carbon is oxidized to CO_2

by persulfate in the presence of ultraviolet light. A TOC-CO_2 sensor measured the concentration of total carbon (TC) so that the concentration of TOC was to be computed as the difference of total carbon minus total inorganic carbon (TOC=TC-TIC). The filtered samples with a volume of 15 mL each were pumped into the analyzer at a flow rate of about 0.35 mL/min. Each sample was analyzed 2 times and the values were averaged. Potassium hydrogen phthalate standards in concentrations of 1, 5 and 10 ppm were measured with every set of samples to check the calibration of the TOC-analyzer. Samples with DOC concentrations expected higher than 10 ppm were diluted.

3.1.5.4 Ion Chromatography

A Dionex ion chromatograph (model DX 600) consisting of an autosampler (Dionex AS 50), an absorbance detector (Dionex AD 25), a conductivity detector (Dionex CD 25), and a gradient pump (Dionex GP 50) was employed to determine the concentration of selected anions and cations in the samples. The chromatograph was equipped with a Dionex cation exchange column (model Ion Pac CS12A). As an eluent served methanesulfonic acid (20 mM) which was passed through the column at a flow rate of 1 mL/min. The sample injection volume was 25 µL. In the anion exchange column (Dionex, model Ion Pac AS14A) 8 mM Na_2CO_3 served as an eluent. The flow rate in the column was also 1 mL/min but the injection volume was only 10 µL. Depending on the expected ion concentration the samples were analyzed in different dilutions. Calibration standards were prepared to be able to measure the following ions: Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^-, F^-, NO_3^-, SO_4^{2-}, PO_4^{3-}. Obtained data was processed online using Peak Net software (version 6).

3.1.5.5 Size Exclusion Chromatography

Size exclusion chromatography (SEC) analyses were performed at the Department of Environmental Engineering at the University of Colorado in Boulder. The molecular weight distribution was measured using a high performance liquid chromatograph (HPLC, LC 600 Shimadzu) with online UVA (SPD-6A Shimadzu) and TOC (modified Sievers Turbo Total Organic Carbon Analyzer) detection. Helium gas was purged into the eluent in a mobile phase reservoir to eliminate inorganic carbon and oxygen that can cause interferences or react with mobile or stationary phases. A TSK-50S column was employed to separate compounds on the basis of hydrodynamic molecular size. Depending on the effective size of the sample molecules, substances with molecules larger than the pore size of the column packing material were excluded and eluted therefore first whereas smaller molecules penetrated throughout the porous infrastructure and were attenuated. Hence, low molecular weight

substances caused a higher retention time than high molecular weight substances which had less interactions with the column. TOC and UVA signals were detected every 4 seconds using a non- dispersive infrared (NDIR) or a UV-detector respectively. A modified Labview software processed the data.

3.1.5.6 Conductivity

During the RO concentration process conductivity was measured online using 2 conductivity controllers described in Section 3.1.2. All other conductivity measurements were conducted employing a Cole Parmer conductivity meter (model 01481-61) for conductivity measurements over six decades from 0 to 200 millimhos. The instrument was calibrated prior to measurements choosing a standard solution closest to the value of the sample solution.

3.1.5.7 pH-Measurements

A calibrated Accumet pH-meter (model AP 63) was used for all pH-measurements. Calibration standards with pH 4, 7 and 10 were applied to calibrate the instrument prior to measurements.

4 Results and Discussion

A study performed by Grünheid (2001) indicated that reverse osmosis in combination with electrodialysis might be a promising alternative to XAD resin adsorption chromatography to isolate organic carbon from water. The RO/ED approach showed important advantages compared to the resin method, such as no chemical alterations of the sample and easy and fast desalination. This work aimed to continue previous RO/ED DOC isolation studies to be able to optimize the process in terms of higher DOC recoveries.

4.1 ED Membrane Selection

Results of previous studies showed that the fraction of not recovered DOC (adsorbed or penetrated through the membrane) consisted to a large amount of charged low molecular weight organics. Membrane studies of Grünheid (2001) revealed that the loss of DOC could be significantly reduced by employing membranes that meet special requirements. Such membranes should show low fouling behavior and are supposed to be tight enough to prevent small organic molecules from passing through. Based on these criteria a highly crosslinked monoselective membrane combination of Asahi Glass (ACS/CMS) was tested and compared to the membrane pair (AM-2/CM-3 of Tokuyama) that performed best in Grünheid's (2001) experiments. RO-concentrate from Scottsdale Water Campus in Arizona served as feed water for both experiments performed with the bench scale ED membrane test unit described in Section 3.1.1. Table 4.1 shows the results of conductivity and current measurements in the course of the experiment and the calculated $SUVA_{254}$ values (see also Appendix 7.1). Due to the higher membrane resistance of the ACS/CMS combination, caused by the higher degree of crosslinking, the desalination process took significantly more time to achieve the same final feed conductivity of approximately one mS/cm in comparison with the AM-2/CM-3 experiment.

Table 4.1: Results of the ED membrane test experiments

Membrane combination	**ACS/CMS**	**AM-2/CM-3**
Duration of the experiment [min]	180	110
Initial current [A]	0.82	1.18
Final current [A]	0.25	0.21
Initial feed conductivity [mS/cm]	6.85	6.81

Table 4.1 continued: Results of the ED membrane test experiments

Membrane combination	ACS/CMS	AM-2/CM-3
Final feed conductivity [mS/cm]	1.03	0.89
Desalination rate [%]	83.6	86.9
Initial feed $SUVA_{254}$ [L/m mg]	1.72	1.72
Final feed $SUVA_{254}$ [L/m mg]	1.63	1.51
Final CEM concentrate $SUVA_{254}$ [L/m mg]	0.87	0.61
Final AEM concentrate $SUVA_{254}$ [L/m mg]	1.43	1.84

The ACS/CMS membrane combination achieved higher rates in terms of DOC rejection, than the AM-2/CM-3 membrane pair. Figure 4.1 represents the DOC mass balances of both experiments. About 92% of the feed DOC was rejected by the ACS/CMS combination, compared to only 74% by the AM-2/CM-3 membranes. The main loss of DOC was caused, as expected, by permeation through the anion exchange membranes. DOC transported through the cation exchange membranes was found to be only 2.9% (AM-2/CM-3) and 1.1% (ACS/CMS). Dilution errors are probably the cause for the total DOC mass of more than 100% in the ACS/CMS balance. Figure 4.1 indicates also that the ACS/CMS membrane pair is less prone to organic fouling. The ACS/CMS mass-balance shows no losses of DOC due to adsorption compared to 9% adsorbed DOC in the AM-2/CM-3 experiment.

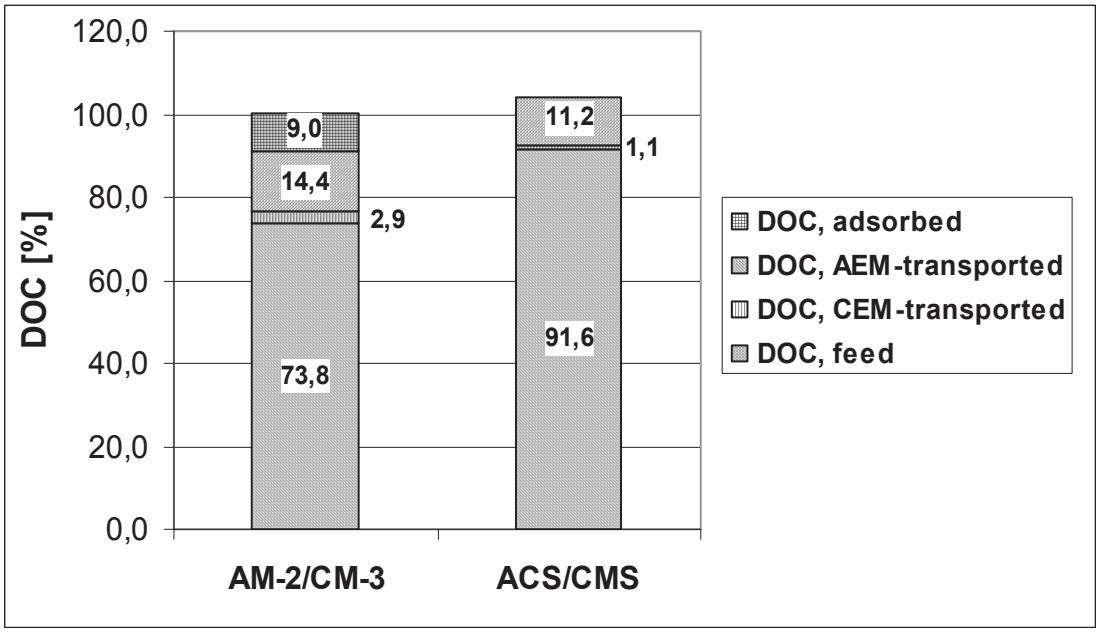

Figure 4.1: DOC mass balances of the bench-scale ED membrane tests

The calculation of the $SUVA_{254}$ showed in the case of the AM-2/CM-3 experiment a slight concentration of aromatic DOC in the anion concentrate compartment, while the $SUVA_{254}$ of the anion concentrate using the ACS/CMS membranes was lower compared to the $SUVA_{254}$ of the initial feed (Table 4.1). This indicates that the ACS membrane is less permeable for aromatic organic compounds compared to the AM-2 membrane.

These findings, especially the high DOC rejection rates combined with low fouling behavior, clearly favored the ACS/CMS membrane combination to be applied in an ED cell for desalination of DOC concentrates. Therefore the ED cell, described in Section 3.1.3, was equipped with 20 pairs of ACS/CMS membranes and tested with different types of organic matter under laboratory-scale conditions.

4.2 Single Organic Compound Experiments

Two different ED membrane combinations were employed for a series of experiments with single organic compound solutions: A set of ACS/CMS membranes of Asahi Glass, as discussed in Section 4.1 and an AMX/CMX combination of Tokuyama, which was already used in experiments previously performed by Grünheid (2001). Polyethylen glycol (PEG) served as a DOC-source. PEG with molecular weights of 200, 600, and 6000 Dalton was added to the 0.05 M NaCl feed solution. All PEG experiments were performed with the laboratory-scale ED-unit described in Section 3.1.3. The goal of the single organic compound experiments was to determine whether the molecular cut-off of the membranes is higher than 200 Dalton, since the molecular weights of a variety of problematic organic compounds dissolved in water, such as pesticides and pharmaceuticals, are to be found in the range of 200 to 500 Dalton.

4.2.1 ACS/CMS Membrane Study

The DOC mass balances (Figure 4.2) of the ACS/CMS membrane studies show minimum differences in the DOC distributions after 60 minutes of ED treatment. Feed DOC rejection rates ranged from 91% in the PEG 200 experiment to 93.7% in the PEG 6000 run. Almost all DOC could be recovered after rinsing feed and concentrate loop with 0.1 N HCl. The high DOC-rejection rates of more than 90%, even in the PEG 200 experiment, indicate that the molecular cut-off of the membranes is lower than 200 Dalton. The high DOC-rejection rates as well as the low fouling behavior are also consistent with results of the bench scale membrane test discussed in Section 4.1 although these results are not directly comparable, since there were

significant differences in the operating conditions of the two units as described in Chapter three.

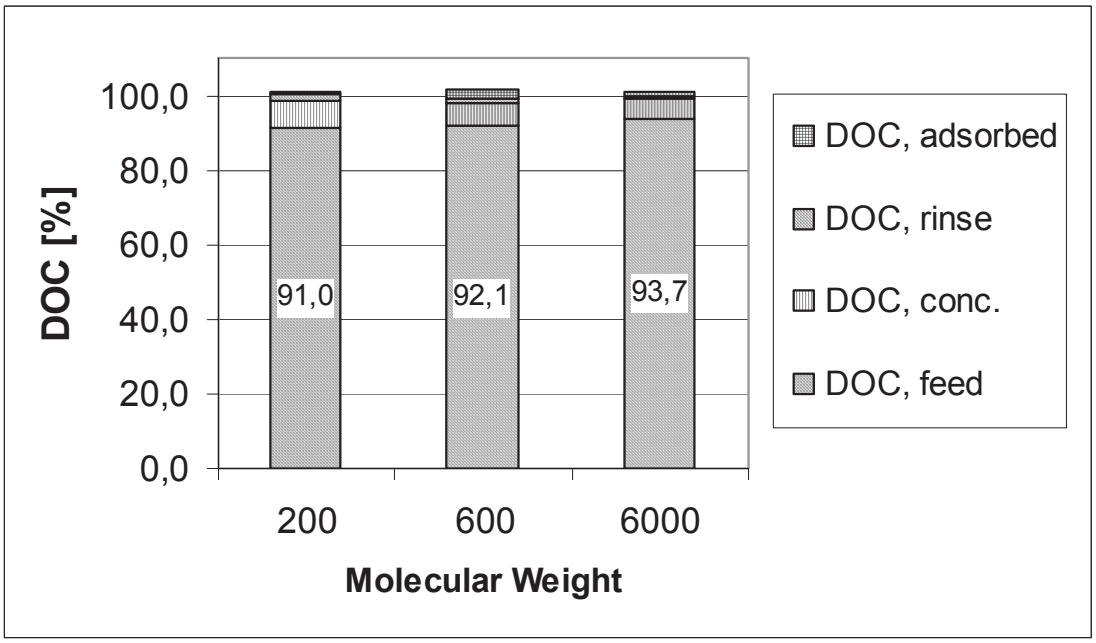

Figure 4.2: DOC mass balances of the ACS/CMS membrane studies

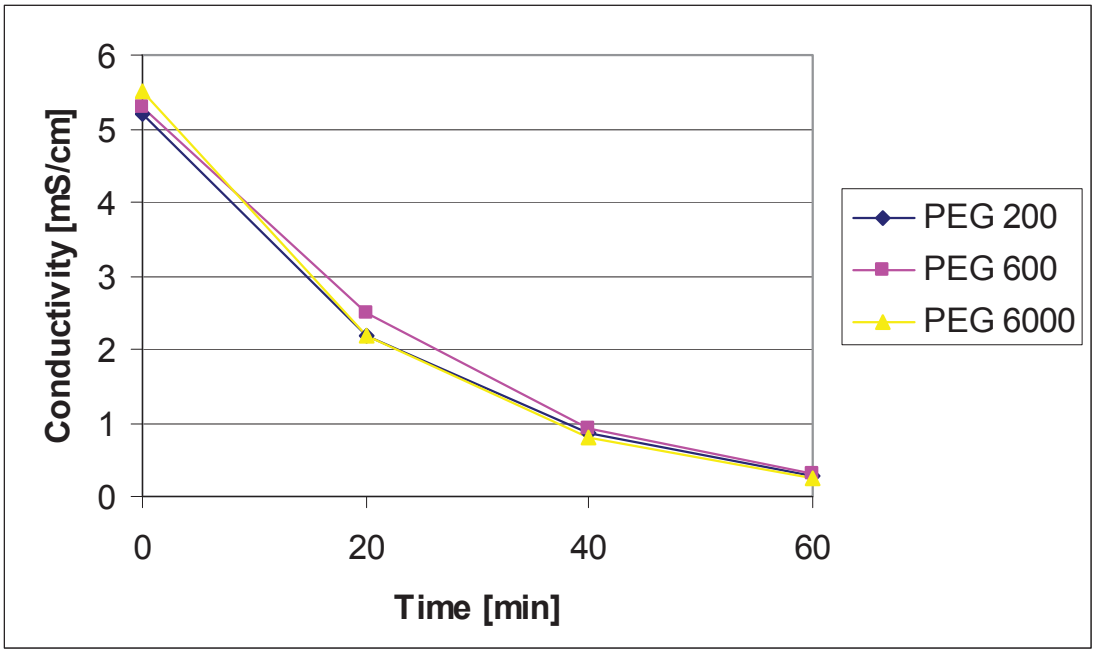

Figure 4.3: Change of feed conductivity during the ACS/CMS membrane studies

Conductivity measurements in the course of the experiment allowed to calculate the achieved desalination rates of the three runs. The desalination rates were found to be 94.4, 93.9, and 95.3%, respectively. In Figure 4.3, the change of feed conductivity is presented. Desalination was most efficient during the first 20 minutes of the experiment. The graphs show a decrease of the conductivity after 20 minutes ED treatment by more than 50% of its initial value. A similar conductivity development was observed at all conducted ED experiments.

4.2.2 AMX/CMX Membrane Study

The PEG experiments using the AMX/CMX membranes showed surprising results in terms of DOC rejection. Figure 4.4 compares the DOC distributions after ED treatment of the three runs and reveals that the DOC loss is almost as low as in the ACS/CMS experiment although the AMX/CMX membranes show a lower degree of crosslinking than the ACS/CMS combination do.

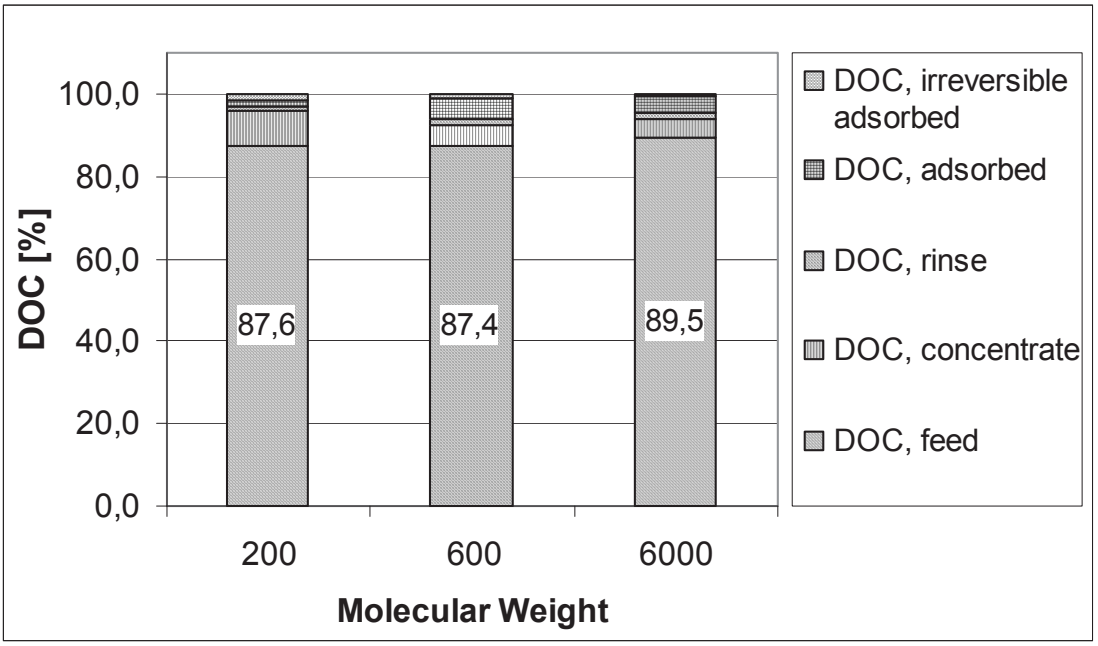

Figure 4.4: DOC mass balances of the AMX/CMX membrane studies

In the PEG 200, 600, and 6000 experiment only 12.4, 12.6, and 10.5% of the initial feed DOC, respectively were lost due to migration into the concentrate loop or adsorption processes. Although the PEG experiments showed very similar rejection of different DOC types, Figure 4.2 and Figure 4.4 indicate that PEG 6000 was slightly better retained than PEG 600 and PEG 200 which may be caused by steric effects associated with the different molecular weights. Comparing these results with the results of Grünheid's (2001) single organic compound experiments, where he used

the same set of membranes, it can be concluded that the molecular cut-off of the AMX/CMX membranes is to be found somewhere between 166 and 200 Dalton.

Similar to the ACS/CMS-membrane study, the desalination rates were 92.0%, 92.8%, and 92.5%, respectively.

4.3 Isolation of NOM and EfOM

RO/ED experiments, using feed water samples from Clear Creek in Golden, Colorado and Boulder secondary effluent from Boulder WWTP in Boulder, Colorado, were conducted to be able to compare the fate of NOM and EfOM, respectively, during membrane treatment processes. The combination of reverse osmosis and electrodialysis is a novel method to isolate organic carbon from water for subsequent characterization. The main goal of the experiments was to determine the achievable DOC recovery rates of the RO/ED approach employing a well proven RO-membrane element (Drewes et al., 2002; Grünheid, 2001) in combination with the tested ACS/CMS ED membranes of Asahi Glass.

4.3.1 RO Concentration Process

Prior to the RO-concentration process both samples were filtered and softened using the pretreatment unit described in Section 3.1.5. The initial volumes were 190 L of Clear Creek water and 111 L of secondary effluent water from the Boulder wastewater treatment plant. Due to the significantly higher DOC concentration of the Boulder water compared to the Clear Creek water, a smaller sample volume was sufficient to achieve high DOC concentrations in the RO retentate. The concentrate stream of the RO system was recycled into the feed reservoir until a final volume of 15 L of Clear Creek RO concentrate and 22 L of Boulder RO-concentrate remained in the tank.

DOC mass balances of the RO concentration process show DOC rejection of 82% for the Clear Creek water compared to 88% for the Boulder secondary effluent sample (Figures 4.5 and 4.6). The different DOC rejections are probably caused by the different character of the DOC in the two samples. NOM consist usually of more low molecular weight organics than EfOM due to the long retention time in the natural environment (see also Section 2.1.1.1). Small organic molecules are prone to penetrate through the membrane or to contribute a DOC loss due to fouling.

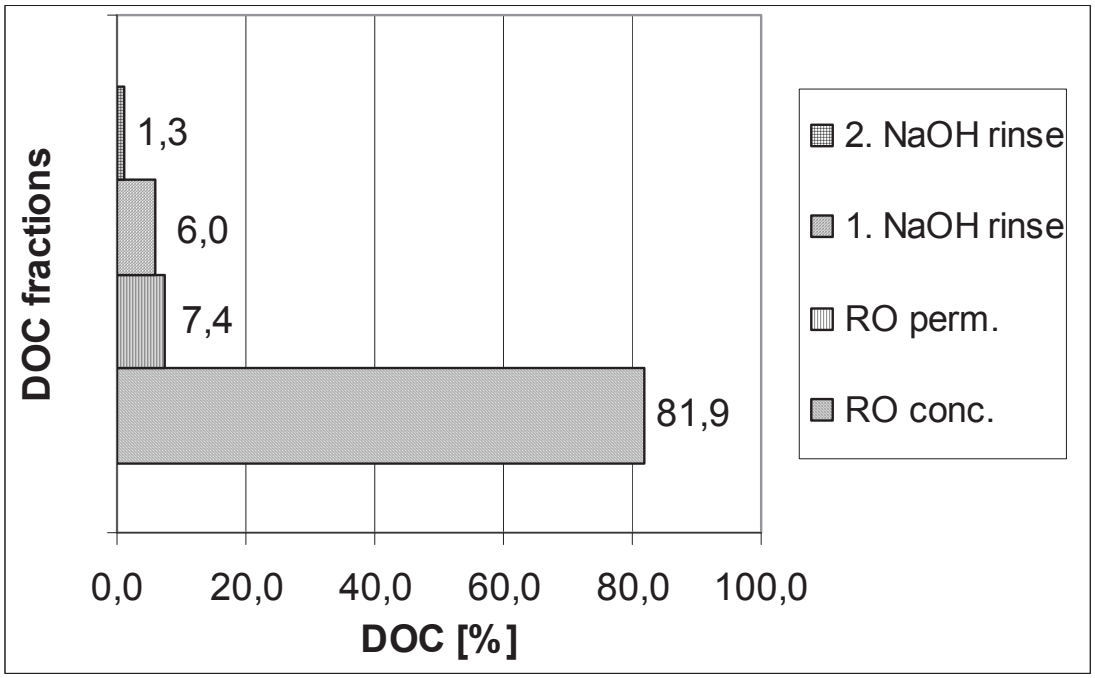

Figure 4.5: DOC mass balance of the Clear Creek water RO concentration process

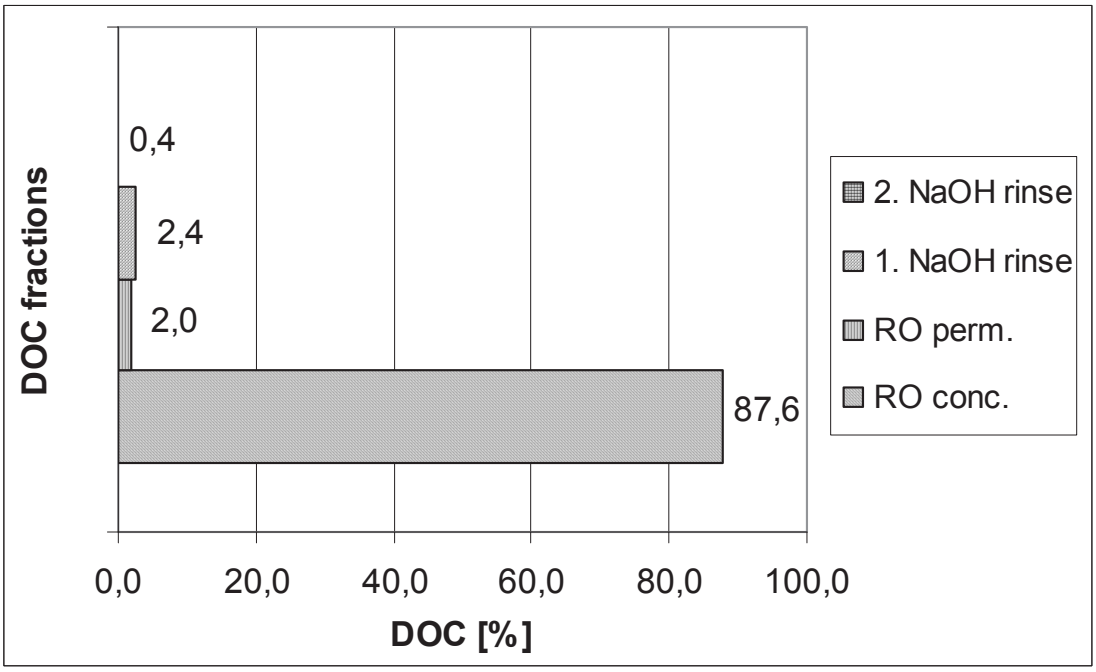

Figure 4.6: DOC mass balance of the Boulder secondary effluent RO concentration process

During the Clear Creek experiment 7.4% of the initial DOC was lost into the RO permeate while DOC migration through the RO membrane was found to be only

2.0% in the Boulder experiment. Based on similar studies of Rybacki et al., (1998) and Drewes et al., (2002) it is assumed that mostly low molecular weight organics penetrated through the RO-membrane. After each concentration process the RO system was rinsed with 0.01N NaOH twice but it was not able to recover the entire amount of DOC, neither in the Clear Creek experiment nor in the Boulder experiment. Therefore it is postulated that the missing DOC of 4% and 8% in the Clear Creek- and Boulder-RO balance, respectively, is adsorbed onto the membrane and/or represent dilution errors, as a result of the relatively high DOC concentrations.

Table 4.2 summarizes the most important results of the RO concentration step (see also Appendix 7.3). The $SUVA_{254}$ results of both experiments show that UV-active organic compounds are better retained by the RO membrane than non aromatic compounds. These results are consistent with $SUVA_{254}$ studies of several other researchers. Kitis et al. (2001), Kastelan-Kunst et al. (1997), and Grünheid (2001) have found that membranes applied in water treatment processes, such as RO and ED membranes, are mostly penetrated by non aromatic, low molecular weight organics.

Table 4.2: DOC, UVA, and $SUVA_{254}$ results of the RO concentration process

Sample	**DOC** [mg/L]	**UVA** [1/m]	**SUVA** [L/mg m]
CC*-softened	1.4	2.45	1.75
CC-RO concentrate	14.6	30.19	2.07
CC-RO permeate	0.1	0.19	1.68
CC-NaOH rinse 1	1.6	9.18	5.70
CC-NaOH rinse 2	0.3	1.89	5.66
B-softened**	9.0	13.95	1.54
B-RO concentrate	39.9	71.86	1.80
B-RO permeate	0.2	0.22	0.99
B-NaOH rinse 1	1.7	2.49	1.46
B-NaOH rinse 2	0.3	0.76	2.36

* Clear Creek sample, ** Boulder secondary effluent sample

The increased $SUVA_{254}$ values of the rinse solutions in the Clear Creek experiment indicate that UV-active material was preferentially adsorbed onto the membrane. It is assumed that adsorption of organic carbon is caused by hydrophobic interactions with the membrane since the presence of hydrophobic fractions of DOC is usually associated with enhanced UV-activity.

4.3.2 ED Desalination Process

ED as a post treatment to RO concentration was chosen to decrease the amount of dissolved salts in RO concentrates. 10 L of the Clear Creek RO concentrate and 14 L of the Boulder RO concentrate were processed through the ED unit, described in section 3.1.3. The ED stack was equipped with ACS/CMS membranes of Asahi Glass as mentioned in Section 4.1. The Clear Creek sample was treated in the ED cell for 150 minutes until a final feed conductivity of approximately one mS/cm was achieved. In order to decrease the duration of the desalination process the NaCl concentration in the concentrate loop was increased from 0.01N in the Clear Creek experiment to 0.02N in the Boulder experiment. This caused a lower initial resistance of the concentrate compartments and hence faster desalination particularly during the first minutes of ED treatment. However, the final feed conductivity of approximately one mS/cm in the Boulder sample was achieved in just 120 minutes.

Figures 4.7 and 4.8 represent the DOC mass balances after ED treatment of Clear Creek and Boulder secondary effluent RO concentrate, respectively. With respect to bulk organics rejection similar rates were achieved in both experiments. Approximately 97% of the initial feed DOC of the Clear Creek RO concentrate were retained in the feed loop after 150 minutes of ED treatment. The experiment with Boulder secondary effluent RO concentrate showed also highly efficient DOC rejection of more than 95%. The DOC mass balances reveal that DOC migration from the feed into the concentrate loop is slightly lower in the Clear Creek experiment compared to the Boulder experiment (4.9% versus 6.1%). This is surprising since the Clear Creek sample was expected to contain more low molecular weight compounds than the Boulder sample. DOC migration into the rinse loop was found to be below one percent in both experiments. According to Figures 4.7 and 4.8 no irreversible fouling occurred during ED treatment.

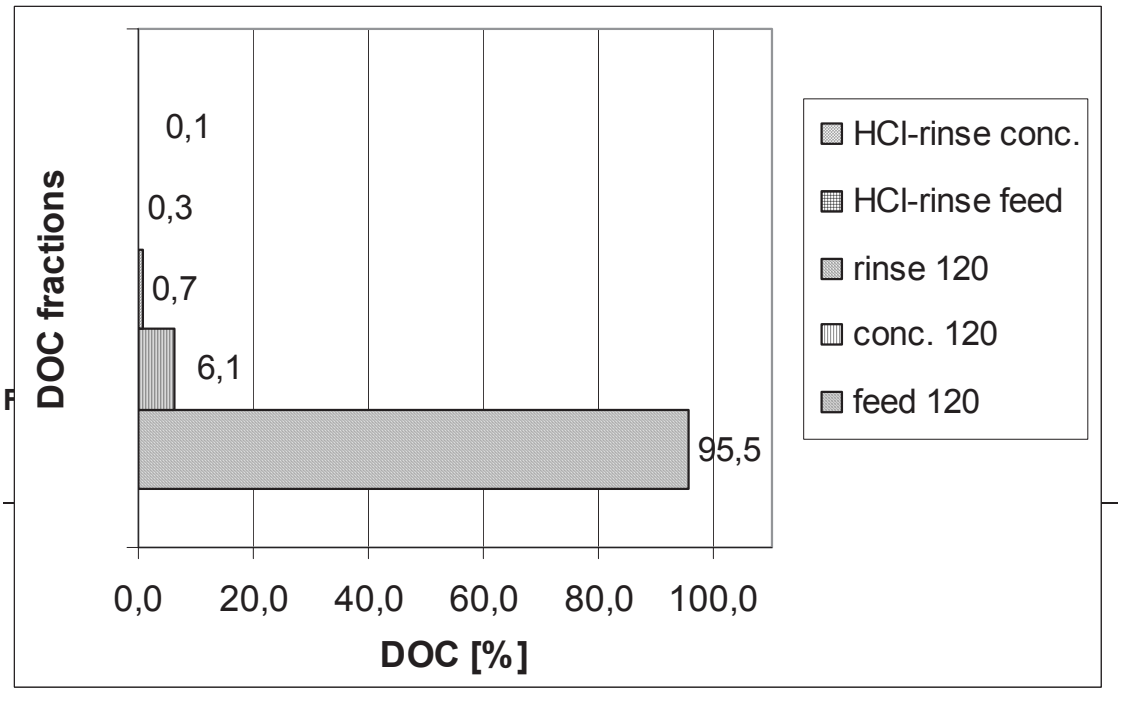

Figure 4.8: DOC mass balance of the Boulder ED desalination process

Feed and concentrate loop were rinsed separately with 0.1N HCl after each experiment and it was found that a higher portion of DOC, lost due to fouling, was adsorbed in the feed loop. Calculated $SUVA_{254}$ values showed that the recovered DOC in the rinse water was more UV-active than the DOC of the initial samples. This indicates that the membranes were also penetrated by low molecular weight aromatics. Table 4.3 presents DOC-, UVA-, and $SUVA_{254}$-results of the desalination experiments. For further data see Appendix 7.4.

Table 4.3: DOC, UVA, and $SUVA_{254}$ results of the ED desalination process

Sample	**DOC** [mg/L]	**UVA** [1/m]	**SUVA** [L/mg m]
CC*-ED feed 0	14.6	30.19	2.07
CC-ED feed 150	14.1	28.21	2.00
CC-ED concentrate 150	0.7	2.52	3.54
CC-ED rinse 150	0.1	0.48	3.69
CC-HCl rinse feed	0.2	0.95	5.72
CC-HCl rinse conc.	0.2	0.84	5.68
B-ED feed 0**	39.9	70.98	1.78
B-ED feed 120	38.1	69.49	1.82
B-ED concentrate 120	2.4	5.29	2.18
B-ED rinse 120	0.4	0.84	2.03
B-HCl rinse feed	0.5	2.95	5.64
B-HCl rinse conc.	0.2	1.12	5.63

* Clear Creek sample, ** Boulder secondary effluent sample

4.3.3 Desalting Efficiency

The different sample fractions were analyzed for ion concentrations in order to determine the ion removal efficiency. Selected ions were: F, Cl, NO_3, SO_4, PO_4, Na, K, Mg, and Ca. Figures 4.9 and 4.10 present the ion removal rates after ED treatment of Clear Creek and Boulder water sample, respectively. Since both samples were softened prior to RO/ED treatment, Mg and Ca concentrations were found to be near detection limit and therefore were not considered in the diagrams.

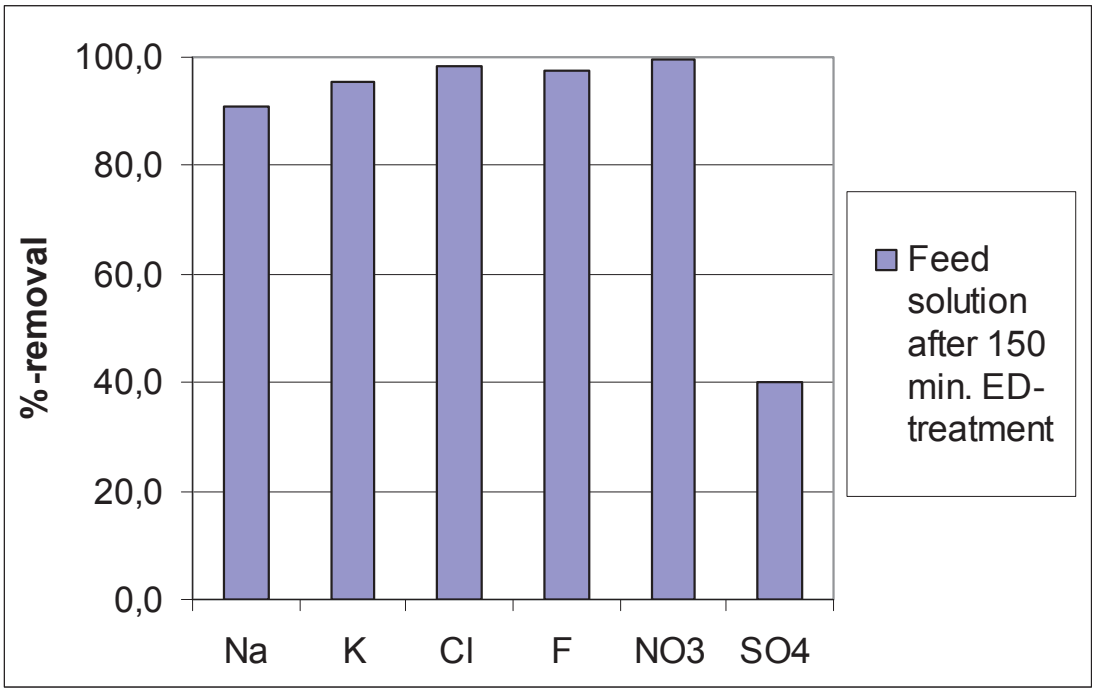

Figure 4.9: Anion and cation removal in the Clear Creek sample

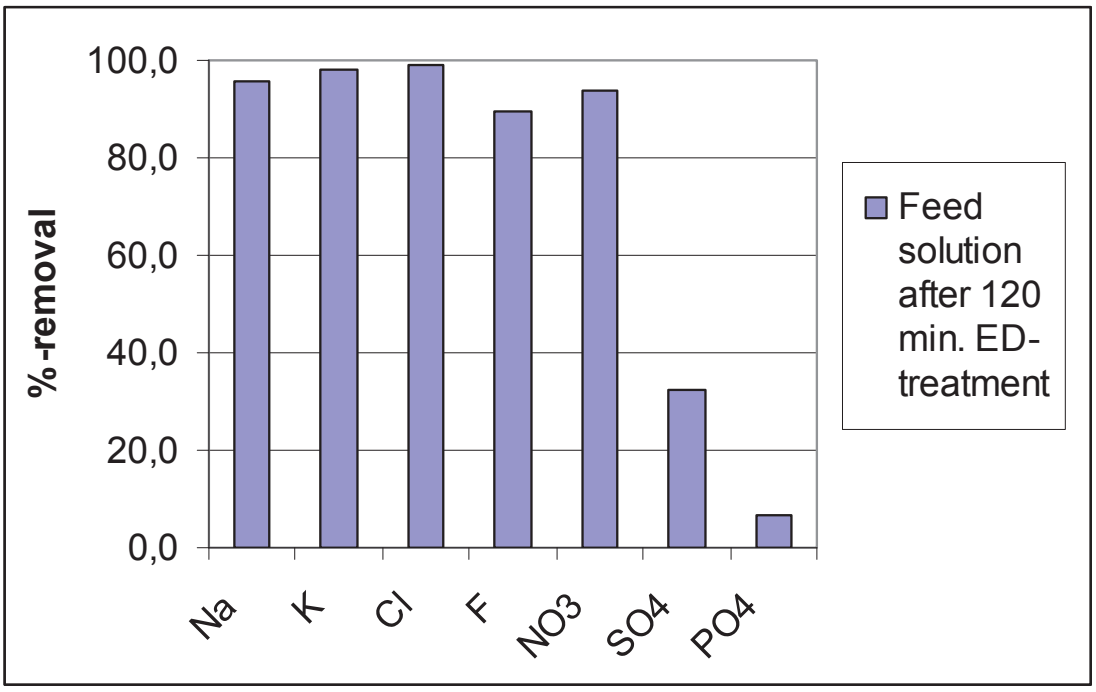

Figure 4.10: Anion and cation removal in the Boulder sample

Monovalent ions were removed from the feed more efficiently than multivalent ions. The highly crosslinked monoselective ion exchange membranes were too tight for sulfate or phosphate ions to pass through easily. Sulfate removal was found to be 40% and 35%, respectively. Phosphate was not detected in the Clear Creek sample and depletion in the Boulder sample was very poor. The initial phosphate concentration was decreased by only 10%. On the other hand the removal rates of all monovalent ions were found to be in the range from 90% to 99%. The low removal efficiency in terms of multivalent ions is probably responsible for the relatively low desalination rates compared to previous studies. Desalination rates were calculated to be only 80% for the Clear Creek sample and 70% for the Boulder sample. This relatively low degree of desalination and the high electrical resistance of the membranes which result in an increased duration of the desalination process and hence in higher energy consumption are the main disadvantages of the ACS/CMS membrane combination.

4.3.4 Size Exclusion Chromatography

Size exclusion chromatography with online DOC and UVA detection was employed to get information about the impact of membrane treatment on the molecular weight distribution of the RO/ED samples. Figure 4.11 presents the SEC chromatogram of Boulder secondary effluent samples prior to (RO-conc.) and after (ED product 120) ED treatment. Additionally, the ED rinse solution (0.1 N HCl) was analyzed. The SEC results show almost no loss of organic carbon due to adsorption or migration through the membranes. The different peak areas in the chromatogram indicate and quantify the different fractions of DOC. The fraction of polysaccharides is represented by the peak at elution time 1,600-2,300 seconds. High molecular weight organics, such as humics, and the different constituents of low molecular weight organics (500 Dalton and less) are represented by the peak at elution time 2,800-3,400 seconds and elution time >3,400 seconds, respectively. After 3,400 seconds generally low molecular weight acids followed by amphiphilics elute (Huber, 1996; Drewes et al., 2002). The lines of “RO-conc.” and “ED product 120” in Figure 4.11 are almost identical which indicates no or only minor loss of organic carbon. Only a negligible amount of low molecular weight organics (elution time >3,400 seconds) was detected in the HCl rinse solution. Huber (1998) found that the polysaccharidic compounds of DOC are responsible for organic fouling in pressure driven membrane processes. As shown in Figure 4.11, no loss of polysaccharides occurred during ED treatment. This indicates that fouling mechanisms in pressure driven membrane processes are not applicable to processes using ion exchange membranes. However, the SEC results

indicate very high DOC rejection of the selected ED membranes and they are consistent with the DOC mass balance presented in Section 4.3.2 (Figure 4.8).

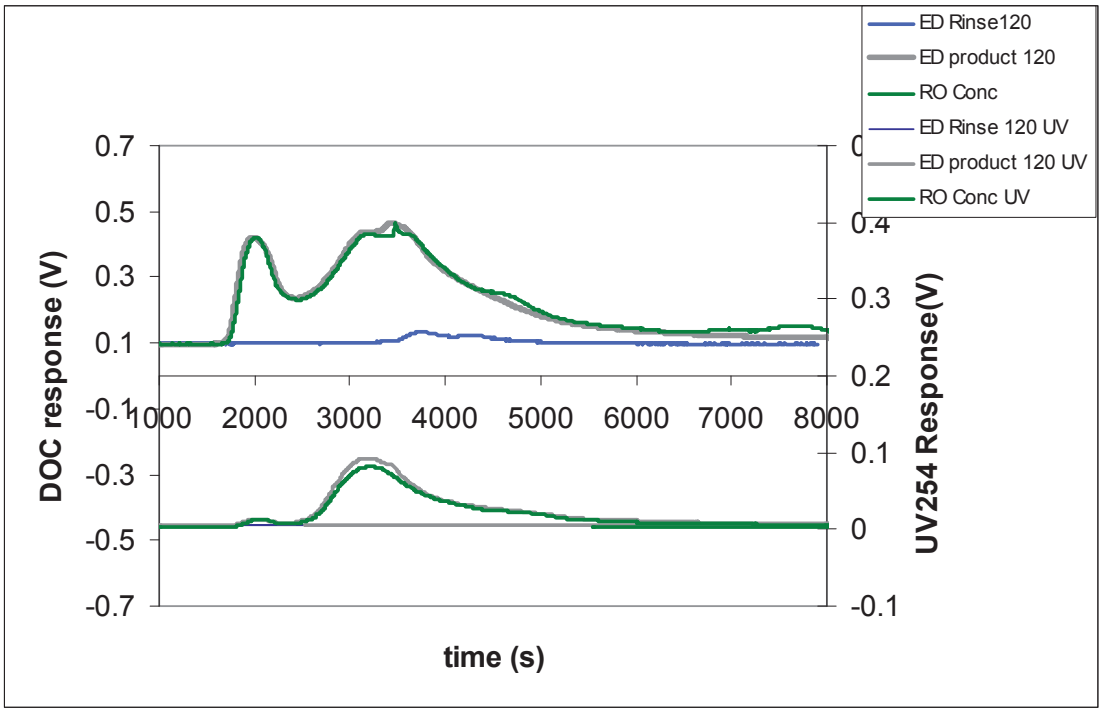

Figure 4.11: SEC chromatogram of the ED membrane study using Boulder secondary effluent

Due to analytical problems no comparable SEC chromatogram of the Clear Creek sample can be provided, but based on the DOC mass balances (Figures 4.7 and 4.8) and the one SEC chromatogram of the Boulder secondary effluent sample it can be concluded that only a minor amount of the initial DOC, probably low molecular weight organics, was lost due to migration and adsorption processes during ED treatment of the Clear Creek sample.

Additional SEC analyses were performed using desalted DOC isolate of Clear Creek water prior to and after aerobic and anoxic biodegradation studies, respectively. Objectives and results of these studies are presented in detail in the following section “Biodegradation studies”. However, is this section the SEC results of Clear Creek biodegradation studies are presented in contrast to the SEC results of the ED membrane studies.

Figure 4.12 presents the molecular weight distribution prior to and after 5-day aerobic and anoxic biodegradation tests. It was found that the fraction of polysaccharides was preferentially degraded by the microorganisms, indicated by a significant peak

decrease at elution time 1,600-2,500 seconds. The 5-day aerobic test showed a slightly higher reduction of polysaccharides compared to the anoxic test. According to Figure 4.12 no biodegradation of humic substances occurred. This was expected, since humic substances are refractory by definition and hence are relatively resistant to biodegradation, depending on the degree of humification (Huber, 1996). Beyond biodegradation of polysaccharides a slight reduction of low molecular weight acids (elution time >3,600 seconds) was observed. Similarly to the fraction of polysaccharides, generally good bioavailability is expected for the low molecular weight acids fraction (Huber, 1996).

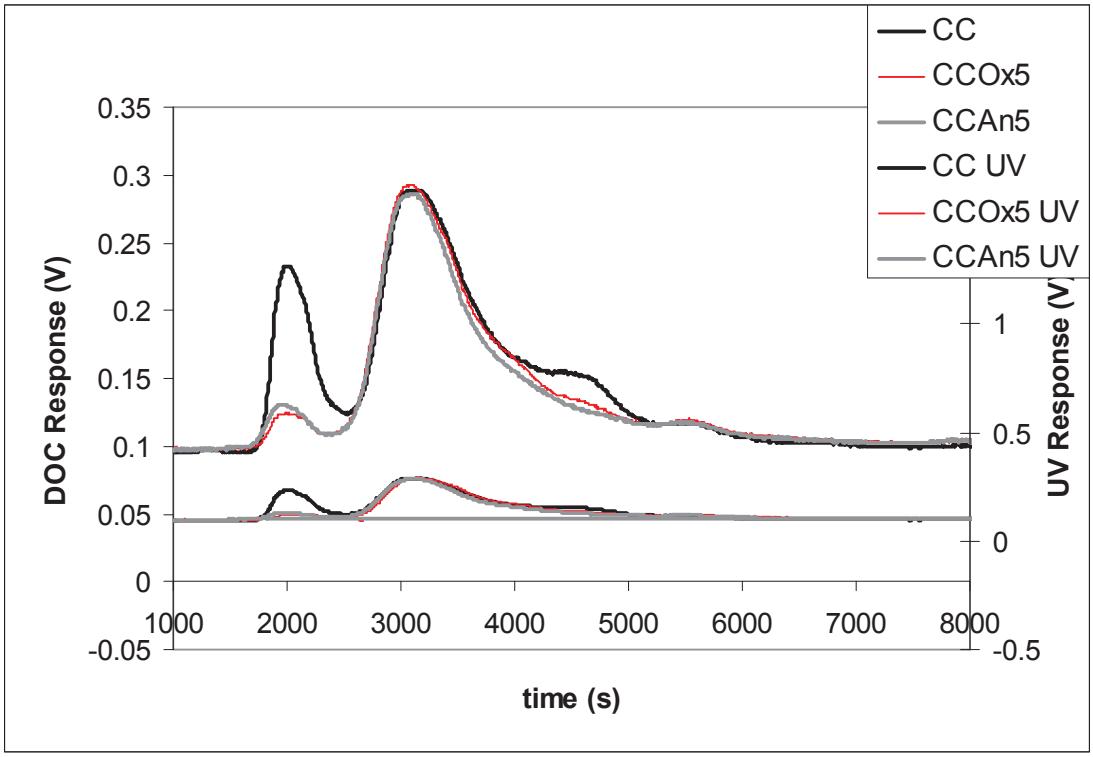

Figure 4.12: SEC chromatogram of the Clear Creek water biodegradation tests
CC = desalted Clear Creek RO concentrate
Ox5 = 5-day aerobic
An5 = 5-day anoxic

4.3.5 Biodegradation Studies

Biodegradation studies were conducted using batch reactors with microbiologically acclimated sand. Desalted RO concentrate from Clear Creek and Boulder secondary effluent served as feed water. Five different dilutions of each sample were investigated. The goal of the BDOC tests was to determine the amount of DOC

degraded by microbial activity or adsorption onto the soil in order to assess the bioavailability of organic carbon in samples of high DOC concentration and low salt content. Optimum system adjustment provided, it was hypothesized that biodegradation is not only influenced by the type of DOC but also by its initial concentration. To be able to compare effects of initial organic carbon concentration on biodegradation of DOC, the reactors were dosed with undiluted RO concentrate (C_0), undiluted raw water, RO concentrate diluted by factor two ($C_0/2$), and RO concentrate diluted by factor ten ($C_0/10$). An additional reactor was run with undiluted RO concentrate, spiked with sodium azide to investigate the role of adsorption. The initial DOC concentrations in the reactors can be found in Table 4.4. All samples were run in duplicate.

Based on the initial and final DOC levels in all samples, DOC reduction ranged from 10% to 45% over a period of 11 and 17 days, respectively (see Table 4.4). Figures 4.13 and 4.14 present the DOC removal of the BDOC batch tests using Clear Creek water and Boulder secondary effluent, respectively. Most intense DOC removal was observed during the first five days of the experiment. The figures show strong correlation between DOC concentrations and the extend of DOC reduction. It was found that samples with high initial DOC concentrations showed higher removal than highly diluted samples. This trend was observed for Clear Creek water as well as Boulder effluent and is indicated in Figure 4.13 and Figure 4.14 with an arrow. It is likely that the concentration of DOC is limiting for biodegradability. For example, the 1:9 dilutions of Clear Creek and Boulder effluent concentrate had DOC concentrations of 1.3 mg/L and 3.9 mg/L, respectively. It seems that microbial activity is substantially decreased due to lack of available substrate at these low concentrations of DOC. BDOC tests using undiluted raw water with similar initial DOC concentrations, at least in case of the Clear Creek sample, (Clear Creek water:1.9 mg/L, Boulder effluent: 9.1 mg/L) showed similar DOC reduction. Therefore, it can be concluded that matrix effects due to dilution (e.g. change in ionic strength) did not affect biodegradation significantly. Table 4.4 summarizes the initial DOC concentrations and the achieved DOC reduction. BDOC experimental results were calculated as the difference between the initial and final concentration of DOC at the start and end of the BDOC experiment, respectively. DOC concentrations reported are average values of duplicate tests.

Table 4.4: Biodegradability of Clear Creek samples and Boulder effluent samples

Sample	Initial DOC [mg/L]	DOC* removed [%]	**Sample**	Initial DOC [mg/L]	DOC* removed [%]
CC-raw water	1.4	29 ! 3.1	**B-raw water**	9.1	37 ! 0.2
CC-C_0	14.2	36 ! 1.2	**B-C_0**	38.0	45 ! 0.6
CC-C_0/2	7.1	40 ! 0.7	**B-C_0/2**	19.2	42 ! 0.4
CC-C_0/10	1.3	22 ! 0.8	**B-C_0/10**	3.9	30 ! 0.3
CC-C_0+NaN_3	14.1	10 ! 0.4	**B-C_0+NaN_3**	37.8	12 ! 0.1

* Mean and standard deviation from duplicate tests
CC = Clear Creek sample
B = Boulder secondary effluent sample
C_0 = concentration of undiluted RO concentrate

With the exception of sample "CC-C_0/2", which showed a slightly higher DOC reduction than sample "CC-C_0", both DOC types (NOM, EfOM) were degraded in a similar pattern. DOC reduction in the Clear Creek samples was surprisingly high. As shown in Table 4.4 DOC removal ranged from 22% to 40%. These results were surprising, since organic carbon in such isolates were expected to be essentially refractory. Nevertheless, the Clear Creek water contained a high portion of BDOC. The results confirm also good acclimation of the microbial population due to the rapid degradation of organic carbon in samples with high initial DOC concentrations.

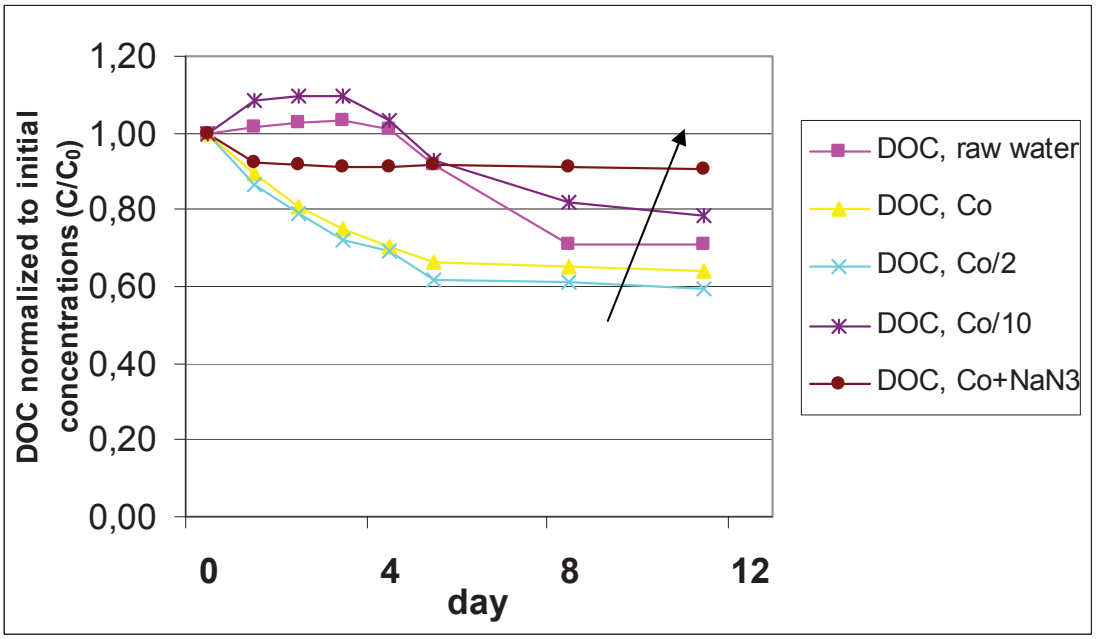

Figure 4.13: DOC reduction in the Clear Creek samples

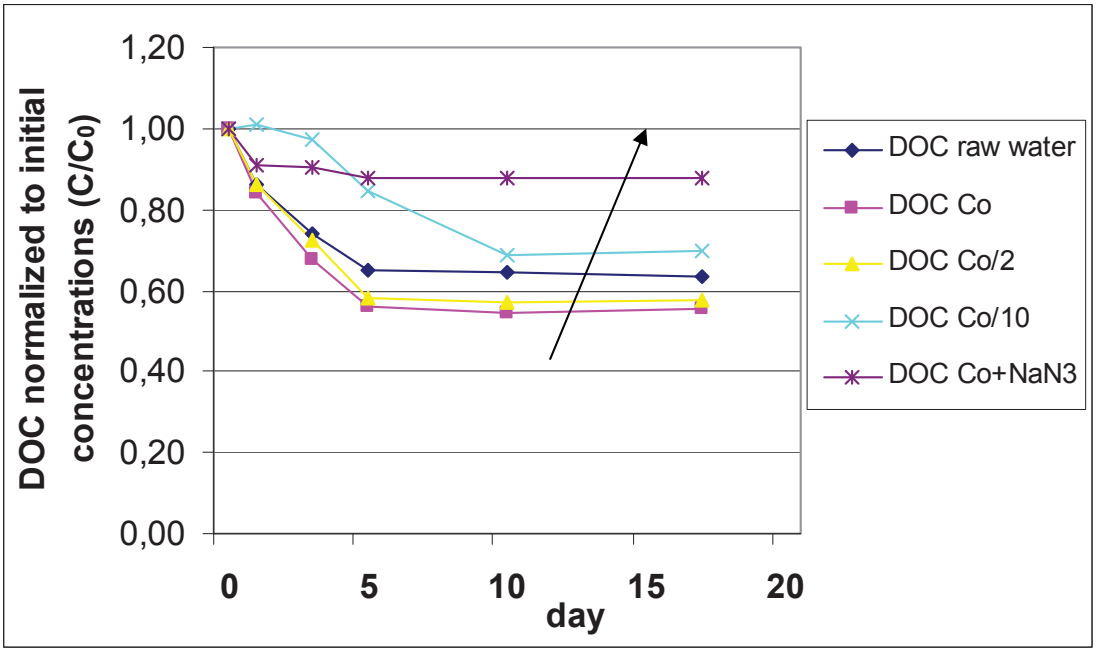

Figure 4.14: DOC reduction in the Boulder effluent samples

Figure 4.13 indicates signs of bacterial decay occurring in the samples with the lowest initial DOC concentrations. These samples are “CC-raw water” and “CC-C_0/10” with initial DOC concentrations of 1.4 mg/L and 1.3 mg/L, respectively. DOC levels of this two samples were increasing during the first three days of the test by approximately 10%. It is likely that this increase in DOC was the result of microbial decay that was caused by a very low food to microorganism ratio, since all Clear Creek batch reactors were acclimated using undiluted RO/ED concentrate with a starting DOC concentration of approximately 14 mg/L. When acclimation of the sand was fully achieved some of the reactors were dosed with samples of a much lower DOC content, such as the “CC-raw water” and the “CC-C_0/10” sample. These two samples did not provide enough substrate for the existing microbial population. Due to lack of available substrate, breakdown and lysis of biofilm microorganisms occurred. After that an equilibrium between the microbial population and available nutrients was achieved and the DOC levels started to decrease. Matrix effects due to dilution effecting ionic strength, pH or nutrient concentrations causing the bacterial lysis can be excluded since the undiluted raw water sample “CC-raw water” showed almost the same behavior than sample “CC-C_0/10”.

The initial DOC concentrations of the Boulder effluent samples were much higher compared to the Clear Creek samples. This might be the reason why bacterial decay was not an issue during the Boulder BDOC tests. Only a slight increase in DOC was examined in the B-C_0/10 sample within the starting period of the test (Figure 4.14). Biodegradation efficiencies, listed in Table 4.4, ranged from 30% to 45% and showed the same trend as observed in studies of the Clear Creek isolates: High initial DOC concentrations were accompanied by high removal rates. This observation further supported the hypothesis that biodegradability of organic carbon is obviously influenced by the concentration of these organics. Furthermore it was observed that higher DOC reduction could be achieved compared to the Clear Creek BDOC tests. These results were expected, since there are substantial differences in chemical character between NOM and EfOM, which consists usually of a higher portion of biodegradable organic carbon than NOM.

Based on the model for kinetics of biological growth proposed by Monod (as discussed in Section 2.3.1) the effects of different initial DOC concentrations on substrate utilization rates (q), were plotted (Figures 4.15 and 4.16). Substrate utilization rates were calculated by subtracting the portion of adsorption from the single DOC reduction rates in order to include only BDOC in the plot.

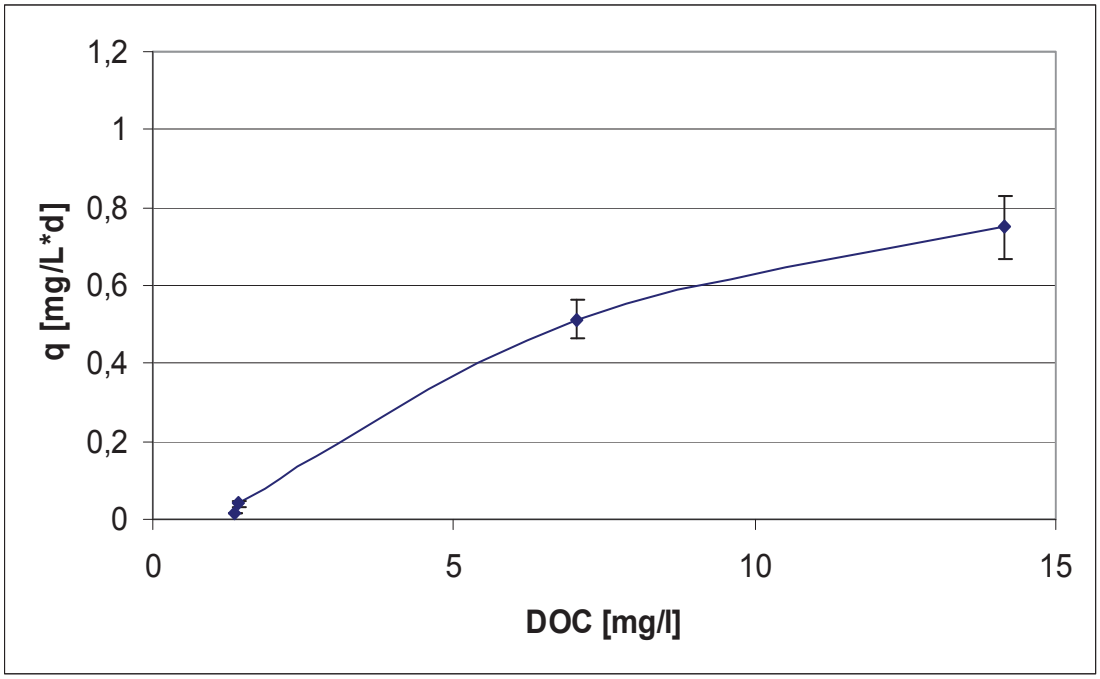

Figure 4.15: Substrate utilization rates in the Clear Creek sample

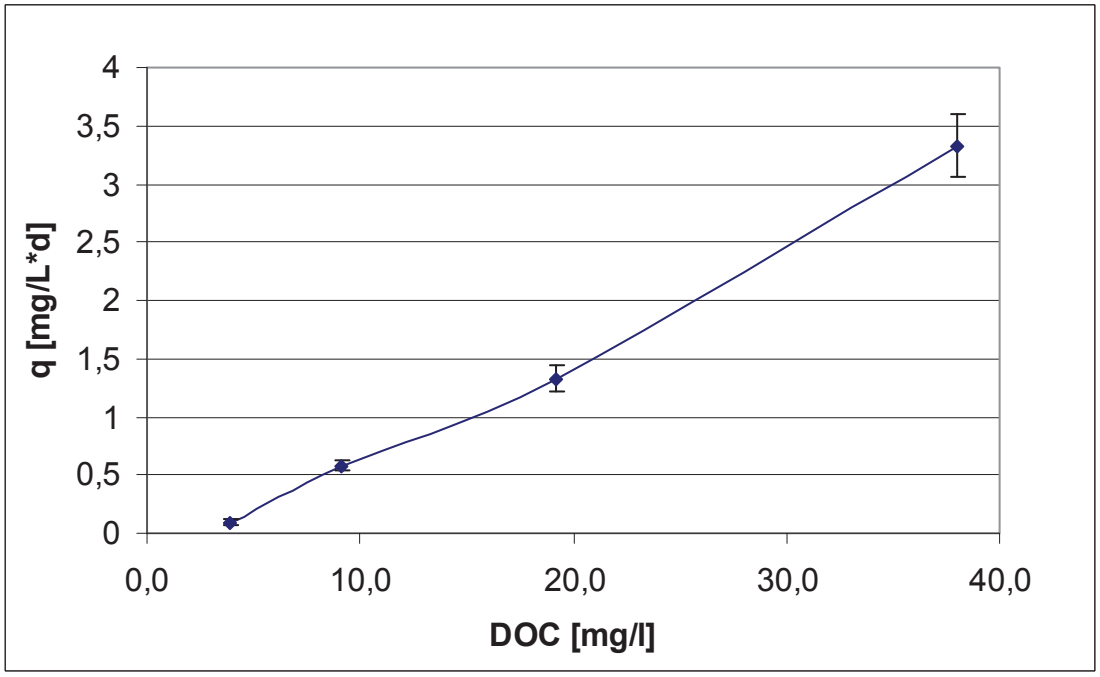

Figure 4.16: Substrate utilization rates in the Boulder effluent sample

Figures 4.15 and 4.16 demonstrate also the relationship between initial DOC concentrations and biodegradation rates. Higher levels of biodegradation are possible using the same substrate supplied at higher concentrations. In Figure 4.16 it can be observed that the relationship between initial DOC concentration and substrate utilization is almost linear. A typical shaped Monod curve is approaching a maximum utilization rate asymptotically, as suggested schematically in Figure 2.4. Due to the lack of samples with DOC concentrations higher than 14 or 38 mg/L it was not possible to determine the maximum substrate utilization rates of both samples, Clear Creek and Boulder secondary effluent, respectively.

4.3.5.1 DOC Adsorption

To address the impact of adsorption on the overall DOC reduction in the batch reactors, the sand was rinsed with 0.15 M NaCl and 1mM $MgCl_2$ solution after biodegradation has come to an end point. The amount of adsorbed DOC was determined by analyzing the rinse solutions for DOC and UVA_{254}. Average percentage of adsorption was found to be 8.7% (Clear Creek samples) and 10.2% (Boulder effluent samples). Furthermore, a strong correlation between initial DOC concentration and specific adsorbance was determined.

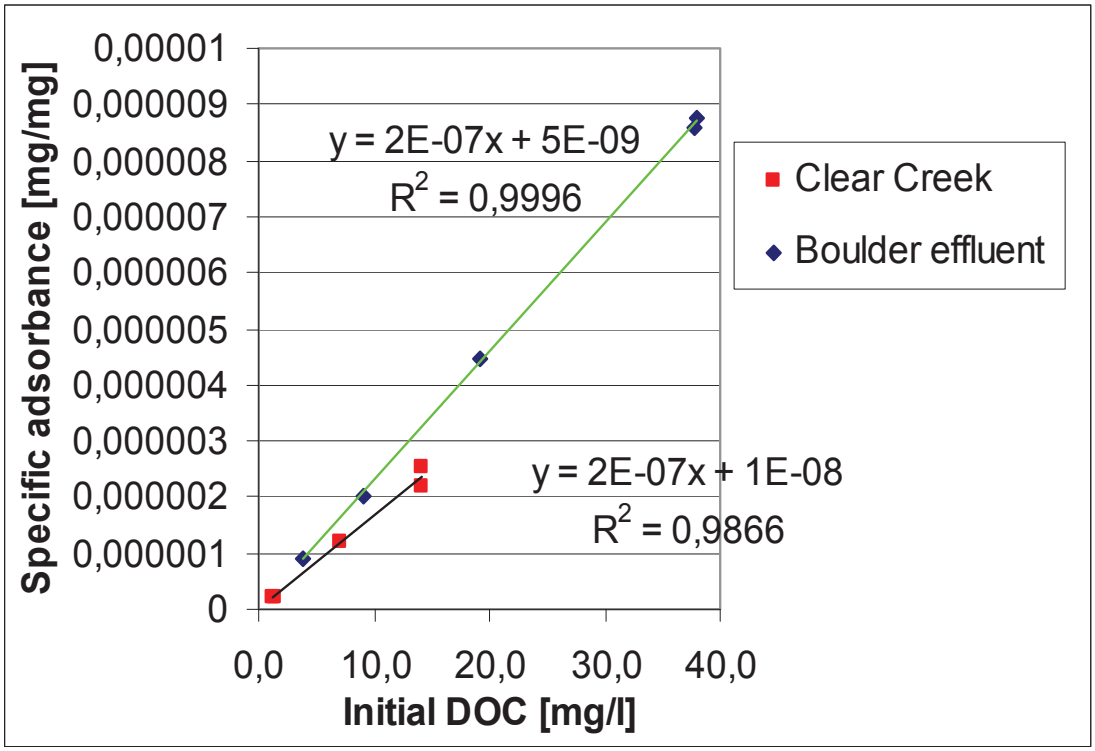

Figure 4.17: Correlation between initial DOC and specific DOC adsorbance

Specific adsorbance was calculated by multiplying the mass DOC adsorbed with the remaining sample volume and dividing the product by the mass of adsorbent (Figure 4.17). In addition to analyses of the rinse solutions containing the desorbed organic carbon, two reactors were spiked with 2mM sodium azide to eliminate microbial activity in order to determine DOC reduction caused only by adsorption processes. These tests were performed only with undiluted RO/ED concentrates of Clear Creek water and Boulder secondary effluent. The results of these tests, presented in Table 4.4, showed slightly higher DOC adsorption compared to the previously discussed adsorption tests. For the Clear Creek concentrate, adsorption of 10% (compared to 8.7%) of its initial DOC was examined and the Boulder RO/ED concentrate showed adsorption of 12% (compared to 10.2%). The sodium azide experiment demonstrated that the saline solution of NaCl and $MgCl_2$ is not able to desorb all DOC from the sand and therefore this method is not appropriate to gain reliable adsorption data.

4.3.5.2 Specific Absorbance

The $SUVA_{254}$ values for the Clear Creek samples and the Boulder secondary effluent samples are presented in Table 4.5. It was observed that the $SUVA_{254}$ of NOM samples were increasing while the EfOM samples showed decreasing $SUVA_{254}$ values. In Table 4.5 the percentage of deviation from the initial values is also listed.

Table 4.5: $SUVA_{254}$ results of the BDOC tests

Sample	Initial $SUVA_{254}$ [L/mg m]	Percent deviation[3]	Sample	Initial $SUVA_{254}$ [L/mg m]	Percent deviation[4]
CC[1]-raw water	1.64	+13.3	**B[2]-raw water**	1.57	-8.5
CC-C_0	2.11	+11.1	**B-C_0**	1.71	-11.5
CC-C_0/2	1.99	+14.8	**B-C_0/2**	1.72	-15.2
CC-C_0/10	3.03	+2.1	**B-C_0/10**	1.79	-10.4
CC-C_0+NaN_3	2.08	+0.9	**B-C_0+NaN_3**	1.75	-8.8

[1]Clear Creek sample
[2]Boulder secondary effluent sample
[3]after a test period of 11 days
[4]after a test period of 17 days

The different behavior of the $SUVA_{254}$ values can be explained with the different characters of the two types of DOC. NOM is more refractory in character compared to EfOM. As shown in the biodegradation tests, the EfOM sample contained a larger

fraction of biodegradable DOC. The increase in $SUVA_{254}$ during the biodegradation studies is probably due to the preferential degradation of aliphatic structures in NOM.

Calculated $SUVA_{254}$ values of the rinse solutions, which were used to investigate the influence of adsorption, showed that UV-activity was slightly higher in desorbed DOC compared to the initial EfOM samples. These results suggest that aromatic compounds were preferentially adsorbed onto the sand and therefore a negative deviation from the initial $SUVA_{254}$ values (see Table 4.5) was possible. Table 4.6 presents the $SUVA_{254}$ values of the rinse solutions.

Table 4.6: $SUVA_{254}$ values of the rinse solutions with desorbed DOC

Sample	**$SUVA_{254}$** [L/mg m]	**Sample**	**$SUVA_{254}$** [L/mg m]
CC*-raw water	1.61	**B**-raw water**	1.63
CC-C_0	1.97	**B-C_0**	1.89
CC-C_0/2	1.91	**B-C_0/2**	1.84
CC-C_0/10	2.92	**B-C_0/10**	1.82
CC-C_0+NaN_3	1.97	**B-C_0+NaN_3**	1.91

* Clear Creek sample, ** Boulder secondary effluent sample

5 Conclusions

This study was performed to gain further insight into the separation mechanisms of a novel reverse osmosis/electrodialysis approach for isolation of organic carbon. The new approach is intended to be utilized as an alternative DOC isolation method to the commonly used XAD resin fractionation. The first research goal was to optimize the RO/ED system in terms of improving DOC recoveries in order to apply it to NOM and EfOM samples. Another objective was to investigate the bioavailability of concentrated organic carbon in RO/ED isolates.

ED membrane tests revealed that for this special application the highly crosslinked, monoselective membranes (ACS/CMS) of Asahi Glass performed best of all tested membranes. With these membranes it was possible to achieve DOC rejection of approximately 92% in the bench-scale test and they were therefore selected and applied in the subsequent experiments using polyethylene glycol, NOM and EfOM as DOC sources.

ED laboratory-scale experiments using polyethylene glycol of different molecular weights as feed solution were conducted employing two different sets of membranes (ACS/CMS of Asahi Glass and AMX/CMX of Tokuyama). Lessons learned from these experiments are that the molecular cut-off of both membrane combinations is lower than 200 Dalton. The ACS/CMS combination showed slightly higher DOC recoveries of approximately 96% compared to 89% of the AMX/CMX membrane combination.

The overall DOC recovery of the RO/ED system was found to be 86.7% for the NOM sample and 86.8% for the EfOM sample. During RO-concentration about 7% of the initial DOC in the NOM sample and 2% in the EfOM sample were lost into the permeate. Calculations of the $SUVA_{254}$ revealed that non UV-active compounds were preferentially transported into the permeate. In the subsequent desalination process the previously tested ACS/CMS membranes of Asahi Glass showed very high DOC rejection, ranging between 95% and 97%. Furthermore the ED membranes did not show signs of irreversible fouling. All DOC adsorbed during the process could be recovered by rinsing the system with 0.1 N HCl. It was found that aromatic compounds were preferentially adsorbed onto the membranes. Ion chromatographic analyses confirmed that the ACS/CMS membranes are less permeable for multivalent ions than for monovalent ions. Between 60% and 90% of the sulfate and phosphate ions could not be removed from the feed. However, the main disadvantage in terms of the selected membranes were the relatively poor desalination efficiency, which did not exceed 80%. The results of size exclusion

chromatography showed almost no loss of organics during ED treatment and hence confirmed the DOC mass balances of the desalination process.

Biodegradation batch tests performed on NOM and EfOM isolates showed DOC removal of up to 33%. DOC reduction was slightly higher in the EfOM samples. The proposed hypothesis that the concentration of organic carbon in water samples might influence the degree of DOC reduction was validated by experimental results. It was observed that higher initial DOC concentrations resulted in higher degradation. The decreased biodegradation efficiency in highly diluted samples was most likely caused by a lack of available substrate. These results suggest that substrate concentration may be the limiting factor controlling biologically catalyzed oxidation of DOC. Furthermore, bioavailability of DOC is impacted by many factors such as the presence of capable microorganisms or the accessibility and mobility of the different fractions of DOC to the microbial population. Additionally conducted adsorption tests showed that DOC reduction due to adsorption was varying between 10% and 12% of the initial DOC concentration.

These findings suggest that the reverse osmosis/electrodialysis approach is a capable tool to isolate organic carbon from water samples. The main advantage of this technique in comparison to the conventional XAD resin adsorption chromatography is the minimum chemical alteration of the sample. No addition of chemical reagents is necessary and only slight pH changes occur during the isolation process. The selected Asahi Glass ACS/CMS ED membranes improved significantly DOC recoveries in comparison to previously performed studies. Furthermore, it became obvious that selection of an appropriate membrane is a key factor to achieve high DOC recoveries, in the ED- as well as in the RO-system.

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7 Appendix

7.1 Measuring Data of the ED Membrane Tests

Table 7.1: Data of the AM-2/CM-3 experiment

Time [min]	**0**	**110**
Current [A]	1.18	0.21
Feed conductivity [mS/cm]	6.81	0.89
CEC conductivity [mS/cm]	14.63	15.06
AEC conductivity [mS/cm]	14.85	19.40
Feed UVA [1/m]	64.94	41.87
CEC UVA [1/m]	0.02	0.97
AEC UVA [1/m]	0.07	12.65
Feed DOC [mg/L]	37.7	27.8
CEC DOC [mg/L]	0.3	1.6
AEC DOC [mg/L]	0.4	6.9

Table 7.2: Data of the ACS/CMS experiment

Time [min]	**0**	**180**
Current [A]	0.82	0.25
Feed conductivity [mS/cm]	6.85	1.03
CEC conductivity [mS/cm]	14.97	18.60
AEC conductivity [mS/cm]	14.89	25.10
Feed UVA [1/m]	64.94	56.33
CEC UVA [1/m]	0.02	0.71
AEC UVA [1/m]	0.07	7.80
Feed DOC [mg/L]	37.7	34.5
CEC DOC [mg/L]	0.3	0.8
AEC DOC [mg/L]	0.4	5.4

7.2 Measuring Data of the PEG Experiments

Table 7.3: Data of the PEG 200 experiment employing AMX/CMX membranes

Time [min]	**0**	**20**	**40**	**60**
Current [A]	2.05	0.89	0.39	0.19
Feed conductivity [mS/cm]	4.90	2.14	0.93	0.39
Conc. conductivity [mS/cm]	4.63	7.19	7.99	8.40
Rinse conductivity [mS/cm]	5.34	5.53	5.48	5.47
Feed pH	6.1	6.7	7.1	7.2
Concentrate pH	6.1	5.8	5.8	5.8
Rinse pH	6.1	5.9	5.8	5.7
Feed DOC [mg/L]	19.4	18.6	17.8	17.0
Concentrate DOC [mg/L]	0.2	1.0	1.4	1.8
Rinse DOC [mg/L]	0.1	0.3	0.3	0.4

Table 7.4: Data of the PEG 600 experiment employing AMX/CMX membranes

Time [min]	**0**	**20**	**40**	**60**
Current [A]	1.99	0.83	0.36	0.18
Feed conductivity [mS/cm]	4.89	2.05	0.81	0.35
Conc. conductivity [mS/cm]	4.74	7.17	7.78	8.01
Rinse conductivity [mS/cm]	5.33	5.31	5.30	5.39
Feed pH	6.0	6.7	7.0	7.2
Concentrate pH	6.0	5.7	5.7	5.7
Rinse pH	6.0	5.8	5.7	5.6
Feed DOC [mg/L]	19.1	18.3	17.5	16.7
Concentrate DOC [mg/L]	0.1	0.6	0.9	1.1
Rinse DOC [mg/L]	0.1	0.3	0.4	0.4

Table 7.5: Data of the PEG 6000 experiment employing AMX/CMX membranes

Time [min]	**0**	**20**	**40**	**60**
Current [A]	2.01	0.87	0.36	0.18
Feed conductivity [mS/cm]	4.93	2.29	0.89	0.37
Conc. conductivity [mS/cm]	4.72	7.09	7.99	8.22
Rinse conductivity [mS/cm]	5.35	5.57	5.57	5.46
Feed pH	5.9	6.5	7.0	7.2
Concentrate pH	6.0	5.6	5.6	5.6
Rinse pH	5.9	5.7	5.6	5.6
Feed DOC [mg/L]	19.1	18.4	17.6	17.1
Concentrate DOC [mg/L]	0.1	0.6	0.7	1.0
Rinse DOC [mg/L]	0.1	0.2	0.2	0.3

Table 7.6: Data of the PEG 200 experiment employing ACS/CMS membranes

Time [min]	**0**	**20**	**40**	**60**
Current [A]	2.12	0.77	0.33	0.13
Feed conductivity [mS/cm]	5.21	2.19	0.86	0.29
Conc. conductivity [mS/cm]	4.92	8.29	9.03	9.35
Rinse conductivity [mS/cm]	5.84	5.85	5.88	5.94
Feed pH	6.0	6.8	7.2	7.7
Concentrate pH	6.1	5.4	5.4	5.4
Rinse pH	6.0	6.0	6.0	5.9
Feed DOC [mg/L]	18.9	18.2	17.6	17.2
Concentrate DOC [mg/L]	0.2	1.1	1.4	1.7
Rinse DOC [mg/L]	0.1	0.3	0.3	0.4

Table 7.7: Data of the PEG 600 experiment employing ACS/CMS membranes

Time [min]	**0**	**20**	**40**	**60**
Current [A]	2.01	0.88	0.36	0.15
Feed conductivity [mS/cm]	5.28	2.48	0.91	0.32
Conc. conductivity [mS/cm]	5.26	8.28	9.21	9.42
Rinse conductivity [mS/cm]	6.01	5.97	5.96	5.99
Feed pH	6.2	6.7	7.5	7.7
Concentrate pH	6.3	6.3	5.3	5.3
Rinse pH	6.0	6.0	6.0	6.0
Feed DOC [mg/L]	19.1	18.3	17.9	17.6
Concentrate DOC [mg/L]	0.1	0.6	0.9	1.3
Rinse DOC [mg/L]	0.1	0.2	0.2	0.2

Table 7.8: Data of the PEG 6000 experiment employing ACS/CMS membranes

Time [min]	**0**	**20**	**40**	**60**
Current [A]	2.08	0.78	0.32	0.14
Feed conductivity [mS/cm]	5.50	2.18	0.80	0.26
Conc. conductivity [mS/cm]	5.57	8.45	9.13	9.26
Rinse conductivity [mS/cm]	5.94	5.99	5.97	5.99
Feed pH	5.6	6.6	7.5	7.7
Concentrate pH	5.8	5.4	5.4	5.4
Rinse pH	5.9	6.0	6.0	5.9
Feed DOC [mg/L]	19.1	18.4	18.1	17.9
Concentrate DOC [mg/L]	0.1	0.3	0.4	1.1
Rinse DOC [mg/L]	0.1	0.1	0.1	0.2

7.3 Measuring Data of the RO Concentration Process

Table 7.9: Data of the Clear Creek RO sample

Time [min]	**0**	**20**	**40**	**60**	**80**	**100**	**120**	**130**
Volume concentrate [L]	190	165	135	105	80	50	25	15
Conductivity conc. [mS/cm]	0.441	0.502	0.610	0.735	0.974	1.48	3.35	4.95
Conductivity perm. [mS/cm]	0.003	0.006	0.006	0.006	0.007	0.008	0.011	0.014
Flow rate conc. [GPH]	67	67	68	68	69	70	72	75
Flow rate perm. [GPH]	23	23	23	22.5	22	22	21	20
pH concentrate	7.0	7.1	7.2	7.4	7.7	8.0	8.4	8.4
pH permeate	4.9	4.7	4.7	4.7	4.7	4.8	5.1	5.3
DOC concentrate [mg/L]	1.4	-	-	2.5	-	-	-	14.6
DOC permeate [mg/L]	-	-	-	0.04	-	-	-	0.1
UVA_{254} concentrate [1/m]	2.45	-	-	4.41	-	-	-	30.19
UVA_{254} permeate [1/m]	-	-	-	0.08	-	-	-	0.19
Pressure feed [psi]	180	180	180	180	180	180	180	180
Pressure conc. [psi]	150	150	150	150	150	150	150	150
Temperature conc. [°C]	16.1	17.1	18.2	19.1	20.3	21.8	24.5	25.9
Temperature perm. [°C]	17.2	18.1	18.5	19.0	19.5	20.1	20.6	20.8

Table 7.10: Data of the Boulder RO sample

Time [min]	**0**	**15**	**30**	**45**	**55**
Volume concentrate [L]	111	85	60	35	22
Conductivity conc. [mS/cm]	0.775	0.982	1.43	2.11	3.47
Conductivity perm. [mS/cm]	0.017	0.018	0.020	0.026	0.033
Flow rate conc. [GPH]	66	66	67	68	69
Flow rate perm. [GPH]	23	23	23	22	21
pH concentrate	7.0	7.0	7.2	7.4	7.6
pH permeate	5.1	4.8	4.8	5.1	5.2
DOC concentrate [mg/L]	9.0	-	15.8	-	39.9
DOC permeate [mg/L]	-	-	0.1	-	0.2
UVA_{254} concentrate [1/m]	13.95	-	25.2	-	71.9
UVA_{254} permeate [1/m]	-	-	0.12	-	0.22
Pressure feed [psi]	180	180	180	180	180
Pressure conc. [psi]	150	150	150	150	150
Temperature conc. [°C]	20.8	21.3	22.7	23.8	25.4
Temperature perm. [°C]	21.0	21.5	21.9	22.4	22.7

7.4 Measuring Data of the ED Desalination Process

Table 7.11: Data of the Clear Creek ED sample

Time [min]	**0**	**20**	**40**	**60**	**100**	**150**
Current [A]	0.79	0.35	0.21	0.17	0.09	0.08
Conductivity feed [mS/cm]	4.95	3.24	2.17	1.62	1.27	1.03
Conductivity conc. [mS/cm]	1.37	3.29	4.21	4.79	4.98	5.16
Conductivity rinse [mS/cm]	6.40	6.15	6.17	6.17	6.17	6.18
pH feed	8.4	7.7	7.5	7.3	6.6	6.3
pH concentrate	5.7	6.1	6.5	6.7	6.8	7.0
pH rinse	6.1	5.9	6.0	6.1	6.1	6.1
DOC feed [mg/L]	14.6	-	-	-	-	14.1
DOC concentrate [mg/L]	0.0	-	-	-	-	0.7
DOC rinse [mg/L]	0.0	-	-	-	-	0.1
UVA_{254} feed [1/m]	30.19	-	-	-	-	28.21
UVA_{254} concentrate [1/m]	0.00	-	-	-	-	2.52
UVA_{254} rinse [1/m]	0.00	-	-	-	-	0.48

Table 7.12: Data of the Boulder ED sample

Time [min]	**0**	**20**	**40**	**60**	**120**
Current [A]	1.01	0.34	0.24	0.18	0.09
Conductivity feed [mS/cm]	3.35	2.33	1.79	1.37	1.02
Conductivity conc. [mS/cm]	2.46	3.52	4.11	4.42	4.88
Conductivity rinse [mS/cm]	5.80	5.81	5.83	5.85	5.81
pH feed	7.6	6.9	6.5	6.3	5.9
pH concentrate	5.3	5.8	6.1	6.3	6.6
pH rinse	6.4	6.4	6.3	6.4	6.4
DOC feed [mg/L]	39.9	-	-	-	38.1
DOC concentrate [mg/L]	0.0	-	-	-	2.4
DOC rinse [mg/L]	0.0	-	-	-	0.4
UVA_{254} feed [1/m]	70.98	-	-	-	69.49
UVA_{254} concentrate [1/m]	0.00	-	-	-	5.29
UVA_{254} rinse [1/m]	0.00	-	-	-	0.84

7.5 Measuring Data of the IC Analyses

Table 7.13: Data of the Clear Creek anion IC analyses

Sample	**Cl** [mg/L]	**F** [mg/L]	**NO_3** [mg/L]	**SO_4** [mg/L]	**PO_4** [mg/L]
Filtered	18,3822	0,5198	1,5392	88,0670	0,0000
Softened	18,7399	0,5741	1,6042	87,9911	0,0000
RO permeate	2,1326	0,0000	0,1580	0,8278	0,0000
RO concentrate	280,9826	8,4144	20,8377	1070,7669	0,0000
ED feed 150	4,2495	0,2108	0,0534	640,4799	0,0000
ED concentrate 0	329,4013	0,0050	0,0315	0,0133	0,0000
ED concentrate 150	656,1775	9,2046	18,8163	282,3374	0,0000
ED rinse 0	0,8571	0,0000	0,0000	3104,8004	0,0000
ED rinse 150	0,2596	0,0000	0,0166	3213,2015	0,0000

Table 7.14: Data of the Clear Creek cation IC analyses

Sample	**Na** [mg/L]	**K** [mg/L]	**Mg** [mg/L]	**Ca** [mg/L]
Filtered	21,6697	4,8929	7,7746	30,1277
Softened	10,8191	119,9866	0,0628	0,1783
RO permeate	0,7689	2,8156	0,0077	0,0461
RO concentrate	152,2224	1887,0456	0,4695	0,9077
ED feed 150	13,8795	85,1692	0,1721	0,3727
ED concentrate 0	229,3176	3,4871	0,0179	0,1176
ED concentrate 150	343,7342	1238,9958	0,1909	0,4108
ED rinse 0	1568,5343	4,8044	0,0440	0,5372
ED rinse 150	1513,5438	199,4511	0,0430	0,3613

Table 7.15: Data of the Boulder anion IC analyses

Sample	**Cl** [mg/L]	**F** [mg/L]	**NO_3** [mg/L]	**SO_4** [mg/L]	**PO_4** [mg/L]
Filtered	43,9655	1,0973	73,7042	76,6753	9,3961
Softened	44,0354	1,1721	73,9120	77,3105	9,3414
RO permeate	1,9444	0,0000	8,3176	0,6555	0,0000
RO concentrate	215,0584	6,7873	349,8878	412,9039	46,8796
ED feed 120	1,9248	0,7207	21,0406	279,2922	43,6847
ED concentrate 0	337,8754	0,0069	0,0487	0,0247	0,0000
ED concentrate 120	604,2413	5,8347	318,1821	25,3164	8,8611
ED rinse 0	0,7591	0,0000	0,0000	3279,4974	0,0000
ED rinse 120	1,5415	0,0000	1,3099	3691,9293	0,0000

Table 7.16: Data of the Boulder cation IC analyses

Sample	**Na** [mg/L]	**K** [mg/L]	**Mg** [mg/L]	**Ca** [mg/L]
Filtered	52,5217	11,3901	10,4669	34,3654
Softened	61,9807	122,5539	0,2006	0,7360
RO permeate	2,9831	4,2142	0,0064	0,0428
RO concentrate	289,2641	553,4162	0,0957	0,1771
ED feed 120	12,7861	11,3687	0,0000	0,1469
ED concentrate 0	235,9875	3,6987	0,0125	0,1587
ED concentrate 120	532,7004	299,3734	0,0416	0,1945
ED rinse 0	1608,5343	1,8044	0,0540	0,5572
ED rinse 120	1351,7944	79,8225	0,3665	2,9106

7.6 Measuring Data of the BDOC Batch Tests

Table 7.17: Data of the Clear Creek BDOC tests

Day, Sample	pH	DOC [mg/L]	UVA_{254} [1/m]
0, raw water (1/10)	7,8	1,4	2,29
0, raw water (2/10)	7,8	1,4	2,31
0, C_o (3/10)	5,9	14,2	29,71
0, C_o (4/10)	6,0	14,1	29,89
0, C_o/2 (5/10)	6,0	7,1	13,98
0, C_o/2 (6/10)	6,0	7,0	14,09
0, C_o/10 (7/10)	7,3	1,4	3,21
0, C_o/10 (8/10)	7,2	1,3	3,95
0, C_o+NaN_3 (9/10)	6,1	14,2	28,99
0, C_o+NaN_3 (10/10)	6,0	14,0	29,78
1, raw water (1/10)	7,8	1,4	2,10
1, raw water (2/10)	7,7	1,4	2,07
1, C_o (3/10)	6,5	12,8	25,65
1, C_o (4/10)	6,4	12,5	25,44
1, C_o/2 (5/10)	6,6	6,1	12,08
1, C_o/2 (6/10)	6,5	6,1	12,44
1, C_o/10 (7/10)	7,2	1,5	3,75
1, C_o/10 (8/10)	7,2	1,5	3,52
1, C_o+NaN_3 (9/10)	6,5	12,9	27,01
1, C_o+NaN_3 (10/10)	6,6	13,1	27,46
2, raw water (1/10)	7,8	1,4	2,01
2, raw water (2/10)	7,8	1,5	2,02
2, C_o (3/10)	6,6	11,5	23,18
2, C_o (4/10)	6,6	11,4	24,01
2, C_o/2 (5/10)	6,7	5,6	11,54
2, C_o/2 (6/10)	6,6	5,5	11,81

Table 7.17 continued: Data of the Clear Creek BDOC tests

Day, Sample	pH	DOC [mg/L]	UVA_{254} [1/m]
2, C_o/10 (7/10)	7,2	1,5	3,41
2, C_o/10 (8/10)	7,2	1,5	3,38
2, C_o+NaN_3 (9/10)	6,6	12,9	27,18
2, C_o+NaN_3 (10/10)	6,7	12,9	27,16
3, raw water (1/10)	7,8	1,4	1,95
3, raw water (2/10)	7,8	1,5	1,93
3, C_o (3/10)	6,7	10,8	22,09
3, C_o (4/10)	6,6	10,5	22,84
3, C_o/2 (5/10)	6,7	5,1	11,06
3, C_o/2 (6/10)	6,7	5,0	11,17
3, C_o/10 (7/10)	7,2	1,5	3,04
3, C_o/10 (8/10)	7,2	1,5	3,09
3, C_o+NaN_3 (9/10)	6,7	12,8	26,84
3, C_o+NaN_3 (10/10)	6,7	12,9	27,49
4, raw water (1/10)	7,8	1,4	1,93
4, raw water (2/10)	7,8	1,4	1,89
4, C_o (3/10)	6,7	10,1	21,61
4, C_o (4/10)	6,7	9,8	22,08
4, C_o/2 (5/10)	6,8	4,9	10,59
4, C_o/2 (6/10)	6,7	4,8	10,72
4, C_o/10 (7/10)	7,2	1,4	2,97
4, C_o/10 (8/10)	7,2	1,4	2,91
4, C_o+NaN_3 (9/10)	6,8	12,9	26,99
4, C_o+NaN_3 (10/10)	6,7	12,8	27,21
5, raw water (1/10)	7,8	1,3	1,90
5, raw water (2/10)	7,8	1,3	1,85
5, C_o (3/10)	6,9	9,3	21,05
5, C_o (4/10)	6,7	9,4	21,45

Table 7.17 continued: Data of the Clear Creek BDOC tests

Day, Sample	pH	DOC [mg/L]	UVA_{254} [1/m]
5, C_o/2 (5/10)	6,9	4,5	10,12
5, C_o/2 (6/10)	6,8	4,3	9,49
5, C_o/10 (7/10)	7,1	1,3	2,93
5, C_o/10 (8/10)	7,2	1,2	2,84
5, C_o+NaN_3 (9/10)	7,0	12,9	26,72
5, C_o+NaN_3 (10/10)	6,9	12,9	27,09
8, raw water (1/10)	7,8	1,0	1,91
8, raw water (2/10)	7,8	1,0	1,81
8, C_o (3/10)	6,8	9,2	20,62
8, C_o (4/10)	6,8	9,3	21,16
8, C_o/2 (5/10)	6,9	4,4	10,09
8, C_o/2 (6/10)	6,8	4,3	9,40
8, C_o/10 (7/10)	7,1	1,2	2,98
8, C_o/10 (8/10)	7,2	1,1	2,84
8, C_o+NaN_3 (9/10)	7,0	12,8	26,84
8, C_o+NaN_3 (10/10)	6,9	12,9	27,01
11, raw water (1/10)	7,8	1,0	1,91
11, raw water (2/10)	7,8	1,0	1,80
11, C_o (3/10)	6,9	9,0	20,83
11, C_o (4/10)	6,8	9,1	21,45
11, C_o/2 (5/10)	7,0	4,3	10,04
11, C_o/2 (6/10)	6,9	4,1	9,19
11, C_o/10 (7/10)	7,1	1,1	2,95
11, C_o/10 (8/10)	7,2	1,0	2,80
11, C_o+NaN_3 (9/10)	7,0	12,8	27,47
11, C_o+NaN_3 (10/10)	7,0	12,7	26,18

Table 7.18: Data of the Clear Creek BDOC rinse solutions with desorbed DOC

Sample	**DOC** [mg/L]	**UVA_{254}** [1/m]
CC-raw water (1/10)	0.11	0.19
CC-raw water (2/10)	0.13	0.19
CC-C_o (3/10)	1.12	2.22
CC-C_o (4/10)	1.12	2.20
CC-C_o/2 (5/10)	0.63	1.19
CC-C_o/2 (6/10)	0.59	1.15
CC-C_o/10 (7/10)	0.10	0.35
CC-C_o/10 (8/10)	0.14	0.35
CC-C_o+NaN_3 (9/10)	1.28	2.53
CC-C_o+NaN_3 (10/10)	1.30	2.55

Table 7.19: Data of the Boulder BDOC tests

Day, Sample	pH	DOC [mg/L]	UVA_{254} [1/m]
0, raw water (1/10)	7,1	9,1	14,28
0, raw water (2/10)	7,0	9,1	14,41
0, C_o (3/10)	6,8	37,9	65,24
0, C_o (4/10)	6,8	38,1	64,67
0, C_o/2 (5/10)	6,9	18,8	32,81
0, C_o/2 (6/10)	6,9	19,5	33,17
0, C_o/10 (7/10)	7,2	3,9	6,89
0, C_o/10 (8/10)	7,2	3,8	6,97
0, C_o+NaN_3 (9/10)	6,8	37,7	66,47
0, C_o+NaN_3 (10/10)	6,8	37,9	65,91
1, raw water (1/10)	7,5	7,8	12,48
1, raw water (2/10)	7,5	8,0	12,87
1, C_o (3/10)	7,1	31,9	54,12
1, C_o (4/10)	7,0	31,8	53,89
1, C_o/2 (5/10)	7,1	16,3	27,18
1, C_o/2 (6/10)	7,1	16,8	27,43
1, C_o/10 (7/10)	7,2	3,9	6,61
1, C_o/10 (8/10)	7,2	3,9	6,59
1, C_o+NaN_3 (9/10)	7,2	34,2	61,47
1, C_o+NaN_3 (10/10)	7,1	34,7	61,43
3, raw water (1/10)	7,6	6,7	10,32
3, raw water (2/10)	7,7	6,8	10,10
3, C_o (3/10)	7,4	25,7	41,33
3, C_o (4/10)	7,4	25,9	42,87
3, C_o/2 (5/10)	7,2	13,8	21,13
3, C_o/2 (6/10)	7,1	13,9	21,47
3, C_o/10 (7/10)	7,2	3,8	6,43
3, C_o/10 (8/10)	7,2	3,7	6,29

Table 7.19 continued: Data of the Boulder BDOC tests

Day, Sample	pH	DOC [mg/L]	UVA_{254} [1/m]
3, C_o+NaN_3 (9/10)	7,6	33,9	56,67
3, C_o+NaN_3 (10/10)	7,6	34,3	55,43
5, raw water (1/10)	7,6	6,0	8,54
5, raw water (2/10)	7,5	5,9	8,43
5, C_o (3/10)	7,4	21,5	32,84
5, C_o (4/10)	7,4	21,1	33,14
5, C_o/2 (5/10)	7,2	10,9	16,47
5, C_o/2 (6/10)	7,2	11,4	17,81
5, C_o/10 (7/10)	7,2	3,3	5,47
5, C_o/10 (8/10)	7,2	3,3	5,39
5, C_o+NaN_3 (9/10)	7,7	33,1	54,27
5, C_o+NaN_3 (10/10)	7,6	33,4	54,97
10, raw water (1/10)	7,6	5,9	8,17
10, raw water (2/10)	7,6	5,8	8,20
10, Co (3/10)	7,4	20,6	31,84
10, Co (4/10)	7,4	20,7	31,99
10, Co/2 (5/10)	7,2	10,7	16,18
10, Co/2 (6/10)	7,3	11,2	16,37
10, Co/10 (7/10)	7,2	2,7	4,51
10, Co/10 (8/10)	7,2	2,7	4,49
10, Co+NaN_3 (9/10)	7,8	33,0	53,78
10, Co+NaN_3 (10/10)	7,7	33,2	54,91
17, raw water (1/10)	7,6	5,8	8,27
17, raw water (2/10)	7,6	5,8	8,39
17, Co (3/10)	7,5	21,1	32,09
17, Co (4/10)	7,6	20,9	31,45
17, Co/2 (5/10)	7,3	10,9	15,99
17, Co/2 (6/10)	7,4	11,2	16,31

Table 7.19 continued: Data of the Boulder BDOC tests

Day, Sample	pH	DOC [mg/L]	UVA_{254} [1/m]
17, Co/10 (7/10)	7,3	2,7	4,43
17, Co/10 (8/10)	7,2	2,7	4,21
17, Co+NaN_3 (9/10)	7,8	33,2	54,20
17, Co+NaN_3 (10/10)	7,8	33,3	51,98

Table 7.20: Data of the Boulder BDOC rinse solutions with desorbed DOC

Sample	DOC [mg/L]	UVA_{254} [1/m]
CC-raw water (1/10)	0.91	1.46
CC-raw water (2/10)	0.89	1.47
CC-C_o (3/10)	3.92	7.39
CC-C_o (4/10)	3.88	7.35
CC-C_o/2 (5/10)	2.00	3.66
CC-C_o/2 (6/10)	1.96	3.62
CC-C_o/10 (7/10)	0.42	0.74
CC-C_o/10 (8/10)	0.40	0.74
CC-C_o+NaN_3 (9/10)	3.82	7.26
CC-C_o+NaN_3 (10/10)	3.80	7.27