WATER TREATMENT BY ENHANCED COAGUATION AND OZONATION-BIOFILTRATION

INTERMEDIATE REPORT ON OPERATION OPTIMIZATION PROCEDURES AND TRIALS
TECHNEAU

WP5.3 Operation of water treatment facilities – Optimization efforts and modelling of unit process operation
Colophon

Title
WATER TREATMENT BY ENHANCED COAGULATION
AND OZONATION-BIOFILTRATION
Intermediate report on operation optimization procedures and trials

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1 Introduction

1.1 Why is water treatment plant operation optimization important?

Sub-optimal operation of water treatment facilities may seriously compromise safety, sustainability and cost-efficiency of water supply systems. Even more serious, it may compromise public health.

Therefore, it is important to identify major operational status and challenges, optimization potentials and needs, and best operation practices of water treatment facilities.

It is very likely that sub-optimal operation of water treatment facilities is a widespread phenomenon. The reasons for this may be several, including missing focus on operational issues and challenges in general; lack of driving forces for optimization efforts; suboptimal treatment technologies and improper process design; a large number of small scale water supply systems with limited resources; under-reporting of water-borne diseases; rapid changes in raw water quality and correspondent operational difficulties; lack of robust and reliable sensors for process control purposes; lack of – or too complicated - unit process operation models; more long-term effects of climate change on raw water quality and quantity, e.g. increasing NOM; greater quality variations due to more severe droughts and floods; lack of operational competence and knowledge on optimization potentials and possibilities; etc.

NOM in water is a major concern and should be removed from drinking water for a number of reasons, including that NOM:

- affects organoleptic properties of water (colour, taste and odour);
- reacts with most disinfectants used in water treatment, thus reducing their disinfection power;
- influences disinfectant demand, and disinfection process design, operation and maintenance;
- produces disinfection by-products (DBPs) of various kinds;
- affects stability and removal of inorganic particles;
- influences heavily on coagulant demand;
- may control coagulation conditions and coagulation performance;
- affects corrosion processes;
- affects biostability and biological regrowth in distribution systems;
- forms complexes with and increase mobility of most chemical substances found in nature;
- fouls membranes;
- reduces adsorption capacity of GAC/PAC by pore blocking
- competes with taste and odour for adsorption sites in GAC/PAC
Contrary to conventional coagulation processes aimed primarily at turbidity removal, enhanced coagulation implies the use of elevated coagulant dosages and strict control of pH. The implications of this shift in treatment target and operating conditions includes elevated sludge production rates, increased solids load to subsequent separation processes (i.e. settling, flotation and/or filtration units), use of inorganic acids for pH-control, increased focus on operation and optimization issues, possible conflicts in optimum conditions for various target parameters like turbidity, NOM and micro organisms. In addition, coagulated NOM will form loose flocs and lead to early filter breakthroughs, i.e. shortened filter runs compared with conventional coagulation and filtration processes for the removal of turbidity. Bursill et al (2002) stated that NOM of microbial, animal and vegetable origin in reservoir catchments is the key factor influencing most, if not all water treatment processes. Edzwald and Tobaison (1999) stated that NOM is a key parameter with respect to coagulation process operation because it will control coagulation processes in most cases.

Despite the important impacts of NOM on water quality and treatment issues and the trends towards increasing NOM levels that are observed in many countries, the EU drinking water directives do not reflect the importance of NOM-related parameters and NOM removal issues to the same extent as the American and Australian regulations. However, several European countries have adopted specific and strict national regulations with respect to NOM and NOM control.

Because NOM is known to control coagulation processes and to significantly affect the operation, control and performance most water treatment processes (membrane filtration, activated carbon adsorption, ozonation and biofiltration, disinfection, etc.), an adequate characterization of NOM will constitute a good basis for further evaluations on treatability, process performance and operation optimization. On this background, NOM is a key target parameter in this report.

### 1.2 Report scope and objective

The main focus of this research activity is operation of existing water treatment facilities employing: 1) enhanced coagulation-separation processes, and/or 2) ozonation-biofiltration processes.

The major objectives of this report are to identify:

- Operational status at existing water treatment facilities
- Optimization recommendations and optimization procedures
- Best operation practices (BOP) for enhanced coagulation-separation, and for ozonation-biofiltration processes
- Links between water characteristics/characterization methods, water treatability and BOP
In addition, treatment process operation models will be tested and verified experimentally.

Integration, e.g. linking raw water characteristics with water treatability, treatment process control, risk reduction, etc. is a major objective within the Techneau project. For successful implementation of optimization procedures at existing water treatment facilities, it is therefore important to establish good links to other work areas, including climate change/changing raw water qualities, monitoring technologies, treatment technologies, risk assessment and risk management during water treatment and demonstration activities. For that reasons, IHE-Delft and S:can (SME) are included as partners in WP5.3 to strengthen the water (NOM) characterization efforts.

This preliminary report addresses water treatment plant operation optimization, focussing on two specific treatment processes: 1) Enhanced coagulation-separation, and 2) ozonation-biofiltration. As part of this, water quality characterization routines and optimization procedures are identified, described and tested in lab, pilot and full-scale facilities.

The primary objectives of this report and this part of the Techneau R&D-activity can be summarized in the following five principal questions:

1. How can actual operation performance and sub-optimal operating conditions be identified at existing water treatment facilities?
2. What procedures can be applied to identify operational bottlenecks and optimization potentials?
3. What procedures can be applied to optimize treatment plant operations and reveal operation optimization benefits?
4. How can we better link treatability, treatment performance and operation optimization to water (NOM) characteristics, i.e. how can optimization efforts benefit from improved NOM characterization?
5. How can best operation practices (BOPs) be identified and implemented, and how can the obtained optimization benefits be presented?

1.3 Approach

Literature reviews and state-of-the-art on characterization methods, operation challenges, optimization needs and best operation practices was reported in 2006 (D5.3.1 A and B).

Following the state-of-the-art report, the next phase of the project (on-going) is to test selected characterization and optimization procedures in pilot and full-scale treatment plants, and to identify optimization benefits and best-operation practices (BOPs). In addition, the experimental activities aim to improve the basis for the development of user-friendly operational models, and provide input to the development of a treatment process simulator (WP5.4).
This preliminary report from the experimental phase covers selected NOM characterization and fractionation methods, novel biodegradability column tests, and preliminary tests of selected process optimization procedures in pilot as well as full-scale facilities.

Dedicated pilot treatment plants and full-scale plants in Norway (Trondheim) and Latvia (Riga) are used for the experiments. In addition, full-scale trials that are performed in cooperation with Techneau end-users are included as case studies. In summary, these activities indicate that the optimization potentials are very significant.

1.4 Terms and definitions

**AOC** - Assimilable Organic Carbon is part of organic carbon which is converted to biomass by specified bacteria or consortium of bacteria

**BDOC** - Biologically Degradable Organic Carbon is the fraction of DOC that is consumed by a community of natural bacteria in favourable conditions during a certain period of time (normally less then one month)

**Biofiltration** - A process in which water is filtered though media populated with microorganisms capable to treat water. Ozonation is usually used prior to biofiltration and then the process is termed an ozonation biofiltration process (OBP)

**BOM** - Biodegradable Organic Matter is the fraction of DOC that could be converted by bacteria to energy or biomass

**CHA** - Charged hydrophilics: The fraction of NOM (DOC) that is retained by the anion exchange resin IRA-958

**Contact filtration**: A process where coagulated water is treated in a filter step without any separate flocculation, settling or flotation steps prior to the filter unit. Thus, the coagulation/destabilization processes will to a great extent occur within the filter bed in close contact with the filter media grains. Capture and storage of captured substances (NOM, particles, bacteria, viruses, protozoa, etc.) will have to take place in the filter bed. Because coagulant species like metal hydroxides may be effective adsorbents, particles, micro organisms, NOM may adsorb to precipitated coagulant species and deposits in the filter bed. Thus, adsorption may be an additional and relevant removal mechanism in contact filtration processes

**Conventional filtration**: A process with coagulation, a separate flocculation step, and pre separation units (sedimentation or flotation) prior to the filtration step
**Direct filtration:** A process with coagulation, and a separate flocculation step before the water is filtered directly without any settling or flotation steps prior to the filter unit

**DOC** - **Dissolved Organic Carbon:** The concentration of organic carbon in a water sample after 0.45 μm pre filtration

**DOM** - **Dissolved Organic Matter:** The total concentration of organic substances in a water sample after 0.45 μm pre filtration

**EBCT** - **Empty Bed Contact Time** is the theoretical contact time associated with the volume that is displaced by the bulk media in the filter. It is calculated as total volume of the filter bed divided by the water flow through the filter

**GAC** - **Granular Activated Carbon**

**HPI** - **Hydrophilic fraction:** The fraction of NOM (DOC) that is passing, i.e. not sorbed on XAD-8 or XAD-4

**HPO** - **Hydrophobic fraction:** The fraction of NOM (DOC) that is retained, i.e. sorbed on XAD-8

**HPON** - **Hydrophobic neutrals:** The fraction of NOM (DOC) that is retained and eluted from XAD-8 with organic solvents such as acetonitrile, CH₃CN

**NEUT (NEU)** - **Neutral hydrophilics:** The fraction of NOM (DOC) that is passing, i.e. not sorbed on DAX-8, XAD-4 and IRA-958

**NOM** - **Natural Organic Matter** is a chemically complex and heterogeneous mixture of organic substances produced from vegetative decay processes. NOM is a ubiquitous constituent of all drinking waters, and is known to control the coagulation process in many cases. NOM may also interfere with adsorption and disinfection processes and cause fouling of membranes

**OBP** - **Ozonation-Biodegradation Process:** A water treatment process in which ozonation is combined with rapid filtration though media populated with bacteria.

**Particle counts:** is a measure of particle number and (and size) in water sample (or other liquid or gas). Particle counts are determined by (Liquid) Particle Counter. Three methods are commonly used for detecting and measuring particles (though many exist); Light Blocking, Light Scattering and the Coulter principle. Most commonly used is the Coulter principle that states that particles pulled through an orifice, concurrent with an electrical current, produce a change in impedance that is proportional to the size of the particle traversing the orifice

**RDOC** - **Refractory dissolved organic carbon:** The fraction of DOC which are not degraded by bacteria

**SEC** - **Size exclusion chromatography**
SHA -  **Slightly hydrophobic acids:** The fraction of NOM (DOC) that is retained, i.e. adsorbed by XAD-4

**SUVA (or SUVA\textsubscript{254}):** **Specific UV Absorbance:** UV absorbance at 254 nm (1/m) divided by the concentration of dissolved organic carbon (mg C/L). The unit of SUVA is commonly expressed as L mgC\textsuperscript{-1} m. TSUVA is defined similarly, with DOC replaced by TOC

**TPH:**  **Transphilic fraction:** The fraction of NOM (DOC) that is passing XAD-8, but retained, i.e. sorbed on XAD-4

**TPHA:**  **Transphilic acids:** The fraction of the TPH that is eluted from XAD-4 with NaOH at pH 13

**TPHN:**  **Transphilic neutrals:** The fraction of TPH that is eluted from XAD-4 with organic solvents such as acetonitrile CH\textsubscript{3}CN

**Turbidity:** Turbidity is cloudiness or haziness of water (or other fluid) caused by individual particles (suspended solids and colloids) that are generally invisible to the naked eye. Turbidity standard is measured in nephelometric turbidity units (NTUs). Turbidity is usually measured using an optical instrument in a laboratory called a nephelometric turbidimeter. The term Nephelometric refers to the way the instrument estimates how light is scattered by suspended particulate material in the water.

**VHA:**  **Very hydrophobic acids:** The fraction of NOM (DOC) that is retained, i.e. adsorbed by DAX-8

**XAD (4 or 8):** The trade names of a series of proprietary resins, which are useful for the characterization/fractionation of NOM.
2 Water characterisation and treatability

An adequate first step in a treatment process and NOM removal optimization activity is to characterise the water to be treated (Bèle et al, 2006).

This report focuses on general and selected characterisation methods for NOM and biodegradability. In addition, attempts are made to link water and NOM characteristics to treatability evaluations and best operation practices.

2.1 NOM and biodegradability characterisation in general

2.1.1 Colour and UV-absorption
Visible and ultraviolet absorbance has been widely used to characterize raw waters in general. Because of the good correlation to dissolved organic carbon, colour and UV-absorption (UV-abs) are also used as surrogate parameters to DOC.

2.1.2 TOC and DOC
Total and dissolved organic carbon is measured indirectly from the CO₂ produced by UV-oxididation or combustion of the organic matter in a water sample.

2.1.3 Specific UV-absorption (SUVA)
Specific UV absorbance (SUVA or SUVA₂₅₄), is defined as the UV absorbance at 254 nm (1/m) divided by the concentration of dissolved organic carbon (mg C/L). The unit of SUVA is commonly expressed as L/mgC m.

Specific UV-absorption (SUVA) correlates well with the aromaticity and the hydrophobicity of the organic carbon. High hydrophobicity is associated with good treatability by coagulation. Therefore, SUVA can be used to indicate raw water treatability by coagulation and to predict the removal of organic carbon by coagulation.

2.1.4 Assimilable organic carbon (AOC)
This parameter was developed by van der Kooij (1992). It is based on culturing two bacterial strains (Pseudomonas fluorescens P-17 and Spirillum sp. Strain NOX) in the water under investigation and matching the maximum number of cells obtained with a calibration curve produced by using an easily assimilated nutrient such as sodium acetate. An AOC value of 10µg L⁻¹ or less is recommended for a biologically stable water. The AOC level is considered to indicate the quantity of carbon in a water sample that can easily be assimilated by bacteria. Lately several improvements which allow a significant decrease in the time requirement of the AOC analysis has been suggested (Hemmes and Egli, 2005).
2.1.5 Biological regrowth potential (BRP)

In the BRP method the sample is prepared by sterile filtration through 0.2 μm pore size filters, and a nutrient salt medium is added. Bacterial proliferation is then monitored as turbidity at 12°C by forward scattering. From the curves of turbidity increase over time the growth rate is calculated by fitting a Monod type growth function. Usually a regrowth factor is given as a result, i.e. the turbidity plateau reached after some time is divided by the initial turbidity.

Sometimes the concentration of assimilated organic carbon is calculated from a regression of regrowth factors for water samples spiked with acetate. It is often claimed that an advantage of the BRP method is the use of a mixture of autochthonous bacteria which may be better adapted to the substrates than the specific strains applied in the AOC method. However, the amount of bacteria available from the sample may often be too small. Then bacteria from other environments (e.g. from GAC filter effluents of drinking water treatment plants) may be added.

Disadvantages of the BRP method includes the fact that the amount of inoculum needed is relatively large in comparison to the AOC method (about 5·10⁴ cells mL⁻¹). Thus a large increase in bacterial concentration has to be found to be reflected in the regrowth factor. Furthermore, the risk of contamination of the sample with biodegradable carbon is higher during sterile filtration compared to pasteurization, and the equipment used is relatively expensive.

2.1.6 Biodegradable dissolved organic carbon (BDOC)

The sample to be analysed for BDOC is placed in contact with a native mixed biomass. Monitoring of DOC over time enables the degradation of the organic matter to be observed, with a corresponding increase in the levels of carbon dioxide and bacterial cells. When the degradation has reached a plateau, the residual DOC value obtained is described as refractory dissolved organic carbon (RDOC). The difference between the initial DOC and the RDOC enables the BDOC to be calculated in mg L⁻¹. A 30 day incubation time is normally used. For faster results more biomass should be used in the experiments. This can be accomplished by adding sand with biomass to the sample or by filtration of the water sample though a column (2 hours) in which stable biofilm has developed. It has been found that biologically stable waters contained less than 0.25 mg L⁻¹ of BDOC (Niquette et al. 2001).

2.1.7 Dissolved organic nitrogen (DON)

Both low and high molecular weight molecules containing organic nitrogen (e.g. simple amino acids, algal-derived organic substances) have been observed to implicate as disinfection by-product precursors and membrane foulants. In spite of this, relatively minor attention has been put on dissolved organic nitrogen (DON) in water. Westerhoff et al (2006) studied the occurrence of DON in raw and finished drinking waters and provided information on its chemical characteristics and reactivity towards metal hydroxides and oxidants/disinfectants. They developed an accurate DON quantification method for drinking water, quantified DON removal by
coagulation and activated carbon adsorption, and defined the role of DON in DBP formation.

2.2 Characterization methods selected for further testing
In the first phases of the optimization experiments, two characterization methods are being tested:

1) Rapid NOM fractionation, and
2) Column-based biodegradability tests

2.2.1 Rapid NOM fractionation
From simplicity and practical applicability evaluations, we have applied a rapid and simplified fractionation technique (RFT) based on measuring DOC concentrations before and after contact with the resins DAX-8, XAD-4 and IRA-958. The method is adapted from the Australian Water Quality Centre (AWQC) and described by Chow et al. (2000).

The rapid characterization technique is specifically designed to study water treatment processes, and is based on the full-scale fractionation scheme reported by Croué et al. (1994) and Bolto et al. (1999). Based on subtractions of the DOC concentrations of subsequent resin effluents, the organic carbon concentrations of four fractions of NOM can be determined:

- Very hydrophobic acids, VHA (adsorbed by DAX-8)
- Slightly hydrophobic acids, SHA (adsorbed by XAD-4)
- Charged hydrophilics, CHA (bound to the anion exchange resin IRA-958)
- Neutral hydrophilics, NEUT (passed through all columns)

The details of the DOC calculations are presented below (Chow et al 2004):

\[
\begin{align*}
VHA &= \text{Raw} - (\text{DAX-8 effluent}) \\
SHA &= (\text{DAX-8 effluent}) - (\text{XAD-4 effluent}) \\
CHA &= (\text{XAD-4 effluent}) - (\text{IRA-958 effluent}) \\
NEUT &= (\text{IRA-958 effluent})
\end{align*}
\]

Results can be presented as actual DOC concentrations of each fraction or as a relative percentage. VHA and SHA is predominantly composed of higher molecular weight humic and fulvic acids, CHA is ascribed to proteins, amino acids and anionic polysaccharides, and the NEUT fraction is ascribed to carbohydrates, aldehydes, ketones and alcohols. These are typically small molecular weight components such as polysaccharides and proteins and are often indicative of biologically derived material (Leenheer, 1981, van Leeuwen et al 2004, Buchanan et al 2005). Specifics of the technique and definitions have been described elsewhere (Chow et al 2004).

The order for ease of removal by coagulation is generally VHA > CHA=SHA > NEUT (Leeuwen et al 2002; Chow et al 2004). It has been demonstrated that
the removal of particular fractions is dependent upon treatment conditions such as applied coagulant dose, pH, etc. and that treatment conditions can be optimized based on the character of the organic matter present in the raw water (Chow et al 2004). A wide range of alum doses (30-180 mg/L of alum) was used to simulate situations of under-dosing, conventional alum treatment, enhanced coagulation treatment, and extreme coagulant over-dosing. The results show that the NEU fraction was hardly removed by alum coagulation. The CHA fraction was readily removed in the under-dosing and in the extreme over-dosing situations. In the intermediate dose range covering conventional to enhanced coagulation, both the SHA and the VHA fractions were preferably removed. It was stated that the rapid fractionation technique could be applied as a tool in the operation of treatment plants and for guidance of treatment operators to control and monitor the treatment process in in order to optimise NOM removal.

Fabris et al (2006) stated that the rapid fractionation technique could also be used to identify situations where treatment was not effective for DOC removal, either due to lack of optimisation or problems with normal operation.

2.2.2 Column-based biodegradability testing

In recent years, attention has been put on the carbonaceous organic matter that can be used by microorganisms as a source of nutrients. This fraction of DOC is called biodegradable organic matter (BOM).

BOM is mainly composed of non-humic substances, though lately it is reported that 10 to 20% of the humic substances in rivers and lakes can be biodegradable and thus also contribute to BOM. In the drinking water industry, two measurement-specific BOM subsets are widely used. Biologically degradable organic carbon (BDOC) is the fraction (10-20%) of the DOC that can be mineralised by heterotrophic bacteria (Servais et al, 1987), whereas assimilable organic carbon (AOC) is the fraction of DOC (1-10%) that can be converted to cell mass by either a single organism or a consortium of bacteria (van der Kooij et al, 1992). The bacterial regrowth potential can also be determined by the BRP method (biological regrowth potential). The BRP method is not primarily aimed at identifying the utilizable organic carbon concentrations, but more on the question how the bacteria originally present in the water sample can multiply.

Excessive growth of bacteria in the distribution network is not desirable because of the sludge this may produce. In addition, some of these bacteria are potentially pathogenic (e.g. *Legionella* and *Mycobacterium avium*). Bacterial growth in the distribution network is mainly occurring in biofilms on the pipe surfaces. The biofilm is an environment where invertebrates can develop and where pathogens may be protected from the effects of disinfectants. To reduce these problems, the BOM levels in drinking water leaving the treatment plant should be as low as possible. Water in which bacteria cell are not multiplying is called biologically stable.
BDOC is analytically defined as the decrease of DOC in a water sample as a result of contact with biomass. Several methods for measuring of BDOC exist, however often two approaches are used: 1) incubation of a water sample in batch with added biomass (suspended or immobilised on carriers), and 2) filtration of a water sample though a column filled with porous media covered with biomass. With the former approach results usually are available after more than two weeks, whereas with the latter within 2 hours.

In several cases however, when the BDOC degradation rate is slow (e.g. in humic waters after ozonation) not only the total amount but also the kinetics of DOC degradation should be evaluated.

An approach to determine changes of BDOC within minutes was developed by Digiano et al (2001). In this approach the water sample is recycled though a BDOC column with an EBCT of about a minute and the DOC concentration is determined after each cycle. From this approach the degradation rate (related to the amount of biomass in the column) could be determined.

Another factor which should be taken into account in BDOC measurements is the adaptation of biomass when shifting from one water sample to another. This issue has not been properly addressed in BDOC measurements before. Our analyses show that columns should be adapted to a new sample for at least 24 hours prior to sampling and analysis (Figure 2.1) by recycling of the water samples through the BDOC measurement columns. Otherwise BDOC values are significantly underestimated.

Figure 2.1 BDOC values of water samples (1,2 – after biofilters, 3 - river water 4 - drinking water ) from Daugava WTP after measurements with “adapted” (water samples were circulated 24 hours through the columns before measurement), and “not adapted” BDOC columns
2.2.3  **Advanced NOM characterization**
From 2007/2008, additional and more advanced NOM characterisation measurements will be performed by IHE-Delft: 1) Fluorescence excitation-emission matrix (EEM) and 2) Size-exclusion chromatography with dissolved organic carbon detection (SEC-DOC).

Both EEM and SEC-DOC can provide quantitative as well as qualitative information. The EEM allows one to track humic-like NOM, effectively removed during coagulation, and protein-like NOM, amenable to removal by biofiltration. SEC-DOC allows one to track biopolymers, potentially removable by biofiltration, low molecular weight acids, significantly removable by biofiltration, and humic substances, effectively removed by enhanced coagulation processes.

2.3  **NOM properties and treatability evaluations**
For raw waters with minor variations in NOM concentration and composition, a stoichiometric relationship is often found between NOM concentration and coagulant demand. In such cases, simple coagulant demand prediction models based on raw water colour, UV-abs. and/or DOC can be applied with good results, and coagulant dosage can be controlled by on-line monitoring of these parameters.

For raw waters where NOM concentration and composition varies significantly over the year, coagulant dose predictions should be based on a more comprehensive NOM characterisation (e.g. SUVA, NOM fractionation, charge/zeta potential measurements, etc).

2.3.1  **Specific UV-absorption - SUVA and treatability**
According to Edzwald and Tobiason (1999) SUVA values of 4 and higher indicate that NOM controls the coagulation process, and that good NOM removal can be expected (> 50 %). In this case, NOM is dominated by high molecular weight, hydrophobic humic acid fractions.

For SUVA values in the range of 2-4, NOM is normally dominated by a mixture of hydrophobic and hydrophilic fractions of different molecular weights, humic and fulvic acids, as well as other NOM (algae and algae residues, etc). Here NOM influences coagulation, and fair to good DOC removals can be expected (25-50 %).

For raw waters with SUVA below 2, NOM is normally dominated by mostly non-humic, low molecular weight substances with low hydrophobicity. NOM has little influence on coagulation performance, and poor DOC removal can be expected (< 25 %).
Table 2.1. SUVA as an indicator of raw water treatability by coagulation (Edzwald and Tobiason, 1999)

<table>
<thead>
<tr>
<th>SUVA</th>
<th>Composition</th>
<th>Coagulation</th>
<th>DOC Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 4</td>
<td>Mostly Aquatic Humics, High Hydrophobicity, High MW</td>
<td>NOM Controls, Good DOC Removals</td>
<td>&gt; 50 % for Alum, Little Greater for Ferric</td>
</tr>
<tr>
<td>2-4</td>
<td>Mixture of Aquatic Humics and Other NOM, Mixture of Hydrophobic and Hydrophilic, Mixture of MWs</td>
<td>NOM Influences, DOC Removals Should be Fair to Good</td>
<td>25-50 % for Alum, Little Greater for Ferric</td>
</tr>
<tr>
<td>&lt; 2</td>
<td>Mostly Non-Humics, Low Hydrophobicity, Low MW</td>
<td>NOM has Little Influence, Poor DOC Removals</td>
<td>&lt; 25 % for alum, Little Greater for Ferric</td>
</tr>
</tbody>
</table>

Parsons et al (2007) review coagulation performance data from a number of studies, and found good correlation between SUVA and DOC removal efficiency (Figure 2.2). By grouping data with SUVA values below 2.5 and above 4, significant differences in DOC removal performance was identified (Figure 2.3). From this, good DOC removal (50-80 %) will normally be achieved in waters that are strictly hydrophobic in nature (SUVA > 4), while far less removal can be expected in waters (NOM) that are hydrophilic in nature (SUVA < 2.5).

Figure 2.2. Effect of raw water SUVA levels on DOC removal efficiency (After Parsons et al 2007, based on results from Bell-Ajay et al. 2000; Singer and Bilyk 2002; Volk et al. 2000; Croué et al. 1993; Owen et al. 1993; Crozes et al. 1995; Chow et al. 1999; Edzwald 1993.)
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Based on USEPA Information Collection Rule (ICR) database analysis, Archer and Singer (2006) proposed an enhanced coagulation matrix with TOC removal requirements based on raw water SUVA (Table 2.2). Compared to SUVA, TSUVA uses TOC instead of DOC.

Table 2.2 Proposed enhanced coagulation matrix with TOC removals based on raw water TSUVA from IRC database analysis (Archer and Singer, 2006).

<table>
<thead>
<tr>
<th>Raw water TSUVA (L/m·mg)</th>
<th>TOC removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 1.0-2.0</td>
<td>35</td>
</tr>
<tr>
<td>&gt; 2.0-3.0</td>
<td>40</td>
</tr>
<tr>
<td>&gt; 3.0-4.0</td>
<td>40</td>
</tr>
<tr>
<td>&gt; 4.0</td>
<td>55</td>
</tr>
</tbody>
</table>

TSUVA = UV-abs/TOC

2.3.2 Treatability of NOM fractions

The different NOM fractions exhibit different properties in terms of treatability by coagulation. It has been reported that high molecular weight, hydrophobic NOM fractions can be removed efficiently while low molecular weight hydrophilic fractions are not removed to any great extent. Furthermore, the different NOM fractions exhibit different coagulant demand and show different chlorine and ozone reactivity and by product formation.

An illustrating example is presented in Figure 2.4, showing percentage removals of the different DOC-fractions VHA, SHA, CHA, and NEUT in two Australian raw waters by alum coagulation at pH 6 in jar tests.
Figure 2.4 Percentage removals of DOC fractions by alum coagulation at pH 6 from: a) Mt.Zero, and b) Moorabool raw waters (van Leeuwen et al 2002).

These results are supported by Sharp et al (2006, 2006b, 2006c) who investigated how the NOM fractions influenced on coagulation performance. They found that the hydrophilic non-adsorbed fraction was least amenable to removal by conventional coagulation, attributed to a negligible charge density. The hydrophobic fulvic acid fraction most readily resembled the bulk raw water operational characteristics in relation to coagulation, such as floc size, strength, settling velocity, iso-electric point, generating small compact flocs and exerting the most influence on the charge balance of the system. The results demonstrate that simple fractionation (i.e. hydrophobic/hydrophilic balance of the water) could provide a fast and effective method for improved understanding of coagulation performance.

2.3.3 Colloidal charge and zeta potential

Sharp et al (2006c) reported that the majority of the total colloidal charge exists in the hydrophobic material, with values of 5.1±1.3, 3.6±0.7 and 1.0±0.6 meq/gDOC for the humic, the fulvic and the hydrophilic acid fractions, respectively. Humic and fulvic waters typically exhibit charge densities of 5-15 meq/gDOC (Edzwald, 1993; Tipping, 1993; Collins et al 1986). The charge densities of the hydrophilic fractions are generally very low (Edzwald, 1993).

Sharp et al (2006) studied seasonal variation in DOC. They calculated charge concentrations and showed that the majority of the charge load comes from the hydrophobic fractions (e.g. 0.0266, 0.0263 and 0.0280 meq/L for April 2002, January 2004 and August 2004 samples, respectively). The charge density or carboxylic acidity of a fraction is likely to affect the coagulant demand. Higher charges are associated with the larger MW fractions. The charge load of each NOM-fraction shows seasonal variation, and it was concluded that coagulant demand cannot be calculated based solely on bulk parameters such as DOC in the specific raw waters. The zeta potential values at a pH of greater than 4 were -13±3.7, -17±0.3, and -25±2.2 mV for the fulvic
acid fraction, the raw water, and the humic acid fraction, respectively. In contrast, the zeta potential for the hydrophilic fractions was substantially lower and decreased with pH. Sharp et al (2006) concluded that it is the hydrophobic fractions which appear to be critical in determining the resultant charge properties of the coagulant-NOM system and hence the subsequent coagulant dose requirements. At the coagulation pH of normal operation (pH 5-7), the hydrophilic fractions possess a negligible or slightly positive charge, leading to poor removal and values as low as 16% were reported by Fearing et al (2004).

Sharp et al (2006c) performed bench scale and pilot scale coagulation experiments on three source waters: two from UK moorland catchments and one from a US snow melt source. From this they presented an overview and a discussion of the links between NOM character and treatability by coagulation. Their work demonstrated the importance of the polarity balance and the charge density of the NOM. NOM composition can vary both temporarily and spatially, with increased DOC concentrations associated with both an increase in hydrophobic content and charge density. The hydrophobic content controls the coagulant demand such that variation in the demand between sources or sampling periods can be accounted for by changes in the hydrophobic content and charge density of the NOM. The raw water hydrophilic content, and specifically the non-acid fraction, provides an indicator of the achievable residual. A clear relationship was revealed between zeta potential and residual DOC. For each source an optimum operational zeta potential exists, in the range between −10 and +3 mV for the investigated raw waters, thus providing a useful guide range for operational control of enhanced coagulation processes.

Ratnaweera et al (1999) performed jar tests to study the coagulation behaviour of eight natural Norwegian water samples containing NOM. They found that the optimum coagulant dose and the colloidal charge were both proportional to the initial colour, and that DOC and UV-absorbance was well correlated with colour. Zeta potentials at optimum coagulation conditions deviated from zero, indicating that other coagulation mechanisms than charge neutralization are relevant. From this, they considered it difficult to use zeta potential as the only tool for online dosing control.

Henderson et al (2006) investigated surface characteristics and floc properties of three common systems: NOM, algae and clay. They demonstrated that difficulties arise when coagulation is not optimized for the dominant substance/particle. Charge density and specific surface area were important parameters with respect to coagulant demand for charge neutralization of all three systems. Extra-cellular organic matter (EOM) affected the coagulant demand of algae to such an extent that it could dominate the coagulation process. Algal flocs were much weaker and required five times the flocculation period to reach steady-state floc size compared to NOM and clay flocs. Despite similarities between algae and NOM in terms of organic content and coagulant demand, the fact that algae is a dynamic, biological system creates numerous problems for the coagulation/flocculation processes.
Qin et al (2006) studied NOM removal by enhanced coagulation at a water works in Singapore. From jar tests using different coagulation pHs and alum dosages the optimum conditions were observed at a pH of 5.2 and a alum dose of 5 mg Al/L. Under optimal conditions, turbidity and DOC removals of 97% and 45% were obtained, respectively. The DOC removal obtained with conventional coagulation at pH 7.2 was only 35%. It was concluded that control of coagulation pH was critical for NOM removal in treatment of reservoir water.

Jarvis et al (2005) studied how the NOM floc structure was affected by increased organic fraction in the floc. It was observed that when the organic floc fraction went significantly over a mass ratio of 1 mg DOC to 1 mg of Fe (coagulant), the floc size, settling velocity, fractal dimension, and strength were seen to decrease even when the NOM removal during coagulation remained high. These effects were proposed to result from adsorption of NOM on primary particle surfaces (i.e. coagulant precipitates). The operational significance of these results suggests that a correct coagulant dose must be applied and that coagulant under-dosing should be avoided to provide a good floc structure for separation.

Sharp et al (2006b) stated that a number of UK and US water utilities have been experiencing operational difficulties associated with increased DOC levels during the autumn and winter periods, resulting in increased coagulant demand and increased production of DBPs. During a 3-year study period a seasonal change in NOM composition was observed, with the hydrophobic, fulvic acid fraction increasing from 36% in September to 61% in November. A reduction in treatment performance was not simply due to an increased organic carbon concentration (from 4.3 to 14.5 mg DOC/L), but is also to a change in the charge density of the NOM. Hydrophilic NOM fractions were found to possess a negligible charge density (< 0.06 meq/g DOC), they were less amenable to removal by coagulation, and were therefore likely to indicate the DOC residual remaining after treatment. On the other hand, it was the hydrophobic NOM fractions, the fulvic acid fraction in particular, that exert the greater dominance on coagulation control. Understanding the seasonal changes in NOM composition and character and their reactivity with the coagulants should lead to a better optimisation of the coagulation process and a more consistent treated water quality.

2.3.4 NOM and seasonal variability
NOM composition and properties, and thereby treatability, may vary with place (location) and time. Sharp et al 2004 fractionated raw water samples from Albert WTP by XAD resin adsorption into the hydrophobic (HPOA) and hydrophilic (HPIA) components. The HPOA fractions were then separated into the humic acid fraction (HAF) and the fulvic acid fraction (FAF). The non-adsorbed fraction was categorised as hydrophilic non-acid (HPINA). Their results showed that the make up of the water varied throughout the year even during a period of relatively stable total DOC (Figure 2.5).
As the DOC increases the majority of the additional organic matter is considered likely to be hydrophobic (Malcolm, 1985). Sharp et al. (2006, 2006b, 2006c) reported that during certain periods, particularly following initial periods of heavy rainfall, there is not only an increase in hydrophobic material as reported by Owen et al. (1993); Ratnaweera et al. (1999) but also an additional increase in the hydrophilic content of the water. This is in accordance with the findings by Scott et al. (1998) who observed variations in the hydrophilic content of 20-80% during a four-year study of water from a UK upland peat catchment system. The seasonal variations are often explained in relation to a microbially driven mechanism of DOC release (Scott et al. 2001). The soil microbes are more active during the warmer and often drier periods in the summer/early autumn, but the result of this is not seen until the organic matter is transported from the watershed to the water source during the first rainfall.

Figure 2.5. Seasonal variations in NOM fraction contribution to DOC in Albert WTP raw water, expressed as mg DOC/L (a) and percentage of raw water DOC (b) (Sharp et al. 2004).
Liu et al (2006) studied the effects of pre-ozonation on organic matter removal by coagulation. From the differences between the UV$_{254}$ and DOC removals, the results indicated that pre-ozonation changed the molecular structure of the organic matter. Fractionation results showed that the organic material was more low molecular weight and more hydrophilic after pre-ozonation, thus impairing the removal of DOC in the following coagulation.

Liu et al (2006 b, 2005) studied NOM removal by enhanced coagulation and polymer aided coagulation through jar tests, pilot and full-scale experiments in southern China. Both processes were able to remove UV-absorbing organic matter to 90 % or more. Enhanced coagulation was more effective with respect to removal of hydrophobic fractions, while the hydrophilic NOM fractions were better removed using polymer aided coagulation (poly acrylamide).

### 2.3.5 Coagulant dose requirements

For raw waters where NOM is dominated by hydrophobic humic fractions and the variations in NOM concentration and composition is only marginal, simple coagulant demand prediction models based on a stoichiometric relationship with raw water colour, UV-abs. and/or DOC can be applied (Figure 2.6). The absolute minimum dose is the minimum dose required to comply with the regulations, while the practical minimum dose is set 25 % higher in order to widen the pH-window for optimal performance.

![Figure 2.6 Simple prediction model for determination of minimum practical (D$_{Prak}$) and absolute (D$_{Min}$) coagulant dose levels needed to comply with relevant Norwegian water quality standard values (TOC < 3 mg/L; Colour < 5 mgPt/L; Turbidity < 0.2 NTU, Residual Al < 0.15 mg/L).](image)

For raw waters where NOM concentration and composition vary significantly over the year, coagulant dose prediction models based on more sophisticated NOM characterization (e.g. SUVA, NOM fractionation, zeta potential, etc) should be used. With significant seasonal variations in DOC, SUVA, NOM fraction concentrations, charge/zeta potentials, etc., the coagulant demand...
may vary substantially with time and space and can no longer be predicted from simple DOC, colour or UV-abs. concentrations.

Chow et al (2005) collected raw and treated water samples (prior to chlorination) on a monthly basis from two Australian WTPs for an 18-month period in 2001 and 2002. They calculated the ‘specific alum demand’ to evaluate DOC removal performance, defined as the required alum dose divided by the concentration of DOC removed by the treatment process. The required alum dose was the plant alum dose subtracted by the dose required to remove turbidity (i.e. 1 mg/L of alum per 0.48 NTU). From this approach, the great seasonal variation in specific alum coagulant demand is well illustrated (Figure 2.7).

In addition, Figure 2.7 shows that despite of the increase in raw water DOC levels near the end of 2001, the specific alum demand was significantly reduced. Fractionation studies revealed that the increase in DOC was mainly an increase of the VHA fraction, a fraction that is typically considered easily removable by alum coagulation. This correspond well with the differences in coagulant demand among the NOM fractions presented before (Fig. 2.4).
The results presented in Figure 2.7 illustrate well the challenges in coagulant dosage control imposed by the seasonal variation in NOM concentration and character.

2.3.6 NOM and climate change
With the current trends forecasting an increase in DOC concentrations, an increased understanding of the treatment system and the involved mechanisms is vital, especially as the potential consequences of increasing NOM concentration levels are likely to impact dramatically on the water industry in terms of optimal WTP design, operation and process control systems (Figure 2.8).

![Figure 2.8 Impacts of increasing raw water NOM content (i.e. colour) on major coagulation-contact filtration operational characteristics. Alum coagulation, filtration rate 7.5 m/h (Eikebrokk et al 2004).](image)

The above considerations on NOM characterization and treatability across different source waters, seasons and coagulants should be employed more actively in a proactive strategy to achieve a safer and more robust, less resource and energy demanding as well as a more cost-effective water treatment plant operation performance. The optimisation potentials are without doubt significant in general, and during problem periods in specific.
3 Operation optimization procedures

An adequate first step in a treatment process optimisation activity is to characterize the water and the target compounds (Ch. 2).

3.1 Design and operation of enhanced coagulation-separation processes

3.1.1 Design of enhanced coagulation processes

Figure 3.1 shows an example of a treatment process including enhanced coagulation, pH- and corrosion control, dissolved air flotation (DAF), sand filtration, granular activated carbon (GAC) filters, and chlorine disinfection.

![Treatment process scheme](image)

Figure 3.1. Treatment process scheme of the Rusko WPT (Jokela, et al 2006)

A less complex enhanced coagulation – contact filtration process scheme with integrated corrosion control (lime and CO₂), and post-disinfection by chlorination is presented in Figure 3.2. Except for the fact that numerous chlorination systems have been replaced by UV-disinfection, this process is widely used in Norway for treating soft and NOM-laden raw waters with low turbidity and low alkalinity. With the inclusion of UV, the process also provides two treatment barriers against parasites.

Figure 3.2 illustrates an alternative filter bed design where an alkaline filter layer (CaCO₃) is applied as a third medium below the sand layer, a layer also capable of collecting possible metal coagulant residuals from the anthracite-sand layers, thus ideally allowing a reduction in coagulant dosage. This design is made for integrated NOM and corrosion control purposes, and may some advantages at small and medium size facilities. The alkaline filter layer could also be designed a separate post filter unit.
Figure 3.2 Scheme of an enhanced coagulation-contact filtration plant. Dual media anthracite-sand filtration, lime/CO₂ for pH and corrosion control, and chlorine disinfection.

Figure 3.3 Illustration of a 3-M anthracite-sand-CaCO₃ filter design used for integrated NOM and corrosion control purposes.

Conventional filtration, direct filtration and contact (in-line) filtration concepts have all proven effective for controlling NOM as well as protozoa in water, provided optimum or near-optimum coagulation and filtration conditions and management.

In most cases filtration is the final and separation step. Filters should be backwashed at the right time and with sufficient power to avoid solids accumulation over time. Continuous monitoring of turbidity or particle content from every filter unit is recommended in order to control the filtration efficiency including filter ripening and breakthrough, to identify malfunctioning filters, and to start backwash at the correct time. Filter head loss should also be measured, as well as head loss distribution within the filter bed that can give valuable information of the interactions between the filter bed and the water that is filtered.

Figure 3.4 illustrates well the typical phases of a filter run, with initial ripening, a period with good and stable filtrate quality, and finally a
breakthrough of particles/turbidity. Compared to conventional turbidity removal, enhanced coagulation systems with elevated NOM and coagulant dosages typically yield short filter runs, i.e. more frequent backwash is required due to loose flocs and increased solids loads creating early breakthroughs and more rapid head loss development.

The importance of monitoring head loss and turbidity from each filter unit is well demonstrated in Figure 3.4. These are the parameters that terminate the filter run length and decide when backwash should be initiated.

![Figure 3.4. Typical filter ripening, and development of filter effluent turbidity and head loss (H) during filtration. The detected turbidity pattern is explained from water initially present in the underdrains (TU), within the pores of the filter media (TM), and from the backwash remnant water above the media (TB). Total time of ripening is TR. Adapted from Amirtharajah, 2002.](image)

3.1.2 Operation challenges

Some major design and operational challenges in enhanced coagulation facilities are:

- Adequate characterization of the water to be treated
- Selection of a proper coagulant type, dose and pH level;
- Application of process control systems that are well adapted to variations in raw water quality;
- Filter beds that are well adapted to the water to be filtered;
- Monitoring systems that controls filter effluent turbidity from each filter unit, including head loss development and head loss distribution within the filter bed;
- Hydraulic control systems that avoids peaks in filtrations rates as a result of demand variations, backwashing of parallel filter units, return flows from sludge treatment, too small buffer volumes/clean water tank, etc.
- Adequate filter backwash techniques, and filter bed inspection routines that are able to detect potential problems related to insufficient cleaning (mud ball formation, biofilms, inorganic precipitates, trends towards shortened filter run times, increasing initial head loss and increasing rates of head loss development, etc.)

### 3.1.3 Optimum coagulation conditions (coagulant type, coagulant dosage and pH)

Deviations from optimum coagulation conditions (i.e. coagulant dose and pH) can seriously affect treatment performance with respect to residual coagulant concentrations, turbidity, particle counts, NOM, and microorganisms. A proper control of coagulant dosage and coagulation pH are the most important operation challenges. Rapid and large variation in raw water quality, with optimal adjustment of the coagulation conditions to the actual raw water quality (e.g. DOC, colour, etc.), represents major operational challenges.

Edzwald and Tobison (1999) summarized principles for alum coagulation of NOM as follows: negatively charged NOM creates a coagulant demand for positively charged Al species resulting in a stoichiometric relationship between the alum dosage and the raw water DOC that is pH dependent. They addressed coagulation in a broader view than enhanced coagulation, termed multiple objectives coagulation. This includes maximization of particle, turbidity, TOC, and DBP precursor removal, and minimization of residual coagulant, sludge production and operating costs. Based on full-scale plant data they also demonstrated a dual coagulation strategy of alum and cationic polymer that reduces sludge production and overall operating costs compared to alum alone.

Edzwald (1993) presented a review on coagulation in water treatment, emphasizing the importance of raw water chemistry, NOM concentration and type, and the chemistry of coagulants. NOM rather than particles in water supplies can control coagulant dosage and selection. The removal of NOM with Al coagulants can involve hydrolysis, complexation, precipitation, and adsorption reactions. SUVA can be used to estimate whether the NOM is high or low in hydrophobic acids and to estimate removals of DOC by coagulation.

O’Melia et al (1999) stated that adsorption of NOM on oxides depends significantly on complex formation reactions between specific sites on oxide surfaces and functional groups on the NOM. Coagulation requirements can and often are set by the TOC concentration in a water source. Frequently there is a stoichiometric relationship between the required coagulant dosage and the TOC of the water to be treated. Other important factors include pH and the concentration of divalent cations.

Gray (1991) performed laboratory and pilot scale direct filtration experiments to study the influence of particles and NOM on filtration performance. He concluded that raw water NOM determined the coagulant dose and filtration performance to a far greater extent than turbidity. Below a certain particle
concentration limit the filter ripening may be extremely slow, and even low turbidity waters with moderate NOM concentrations require relatively high coagulant doses.

Eikebrokk (1996, 1999, 2001) demonstrated in contact filtration pilot experiments with aluminium and iron based coagulants that compliance with the total residual coagulant concentration standard of 0.15 mg Me/L was the determining factor with respect to identifying the minimum coagulant demand when treating low turbidity surface waters with NOM-concentrations measured as colour and TOC in the range of 15-50 mg Pt/L and 2-6 mg TOC/L, respectively. Compliance with the turbidity (<0.2 NTU) and colour standard values (<5 mgPt/L) could be obtained with lower coagulant doses. The great importance of controlling the coagulation pH within strict limits was clearly demonstrated. The width of the optimum “pH-window” increased with increasing coagulant dose level, indicating the relationship between coagulant dosage and ease of operation from the operator’s point of view. Therefore a distinction was made between absolute and practical minimum doses; the difference being that for the absolute minimum dose level the maximum residual metal concentration of 0.15 mg Me/L could be obtained only within a very narrow pH-window. When using the 25% higher “practical minimum” dosage, the pH window for optimum process performance and compliance with the water quality standards can be obtained within a wider range of pH. The carbon specific alum and ferric coagulant dose requirements were in the range of 0.43-0.70 mg Al per mg C, and 0.89-1.45 mg Fe per mg C, respectively. As an illustrating example, raw water with a specific UV-absorption (SUVA) of 4.8 and a TOC of 5 mg/L would require a minimum dose of 3.5 mg Al/L and 7.25 mg Fe/L to cope with the residual metal standard of 0.1 mg Me/L. The correspondent reductions in colour and TOC would be in the range of 90 and 50-60 %, respectively. For the organic coagulant chitosan (derived from shrimp and crab shells) a dose of 4.5 mg/l would be required to obtain colour and TOC reductions in the range of 60 and 20-35 %, respectively.

The optimum range of pH (measured on-line in filter effluent water) for the different coagulants were as follows:

- ALG pH 5.8-6.6
- JKL pH 4.0-5.5
- Chi pH 5.0-6.5

For chitosan it should be noted that an increase in colour and TOC removal was observed with decreasing pH in some cases. Coagulation at a pH below 4-5 may however interfere with turbidity removal and is not likely to be cost-effective.

The specific coagulant dose requirements presented above agree well with data presented by Pernitsky and Edzwald (2006) who tested coagulation requirements for raw waters with different NOM, turbidity and alkalinity levels. For all waters examined, they found that 0.5-0.8 mg Al per mg of TOC
in the raw water was required, which is in accordance with stoichiometric estimates presented by Van Benschoten and Edzwald (1990) and Edzwald (1993).

The dosage requirements also agree well with data from the Information Collection Rule (ICR) database, the largest nationwide water quality survey ever conducted in the U.S.A. Archer and Singer (2006) presented data on enhanced coagulation performance for water treatment facilities. They examined the relationship between SUVA and the amenability of water to coagulation for NOM removal, and demonstrated that the removal of TOC, UV-absorbing organics, and DBP precursors was a function of the raw water SUVA (UV-abs to DOC) or TSUVA (UV-abs to TOC) value.

TSUVA values decreased as a result of coagulation, and the low alkalinity raw waters experienced the largest reductions. These results indicate that coagulation preferentially removes UV-absorbing, aromatic organic carbon, and imply that raw waters with high alkalinity and hardness, and corresponding low TSUVA values, are comprised primarily of hydrophilic organic carbon that is less susceptible to coagulation.

Figure 3.5 shows a frequency distribution plot for the applied specific alum coagulant dosage, i.e. mg Al applied per mg TOC in raw water. The mean value for the 1571 records is 0.7 mg Al/mg TOC. Some of the variability of the specific coagulant dosage is related to high alkalinity raw waters. The results in Figure 3.5 agree well with the results presented above.

Figure 3.5 Frequency distribution plot for specific coagulant dosage (mg Al/mg TOC) based on ICR database (Archer and Singer, 2006).

river water they concluded that NOM removal was a function of coagulant type, coagulant dose, and pH of coagulation. Ferric chloride was consistently more effective than alum in removing NOM. Coagulation pH appeared to be a determining factor for maximum NOM removal, and the removal of DBP precursors was significantly enhanced at pH 5.5 in comparison with the initial pH of the water. Pre-adjustment of pH with sulphuric acid reduced the required coagulant dosage and thus the production of sludge.

Pernitsky and Edzwald (2006) presented guidelines for the selection and use of poly aluminium chloride (PACl) and alum in terms of raw water quality and treatment method. NOM was identified as the most important parameter affecting coagulant dose. The nature of NOM, as measured by SUVA, was useful for predicting the degree of NOM removal expected. Raw water turbidity and NOM did not influence the type of coagulant that was most effective. As it relates to pH of coagulation, raw water alkalinity is important for choosing one coagulant type over another. The basicity of the PACl should be matched to raw water alkalinity, so that coagulation pH is as close as possible to the pH of minimum solubility of the coagulant. PACls containing sulphate were found to have the best settling characteristics, but showed the highest head loss rates in direct filtration applications. Dissolved air flotation performance was relatively insensitive to coagulant type.

Jiang and Graham (1996) studied the consequences of enhanced coagulation, i.e. the use of excess coagulant and lowering the coagulation pH in order to improve NOM removal, including increased sludge production and increased treatment costs, and the need for chemical storage and feed facilities to be changed. They stated that the use of various types of pre-polymerized coagulants that have been developed in recent years can improve NOM and trihalomethane formation potential (THMFP) removals at relatively lower dosages, and thereby reduce the operational and economic consequences of enhanced coagulation.

Gao and Yue (2005) studied turbidity and NOM removal by poly-aluminium-chloride sulphate (PACS) coagulation. The coagulant was synthesized using AlCl₃·6H₂O, Al₂(SO₄)₃·18H₂O and Na₂CO₃ as raw materials. They found that the coagulation performance of PACS in water treatment was affected by the PACS particle size distribution and zeta potential which were both affected by the basicity [(OH⁻)/[Al³⁺]] and the sulphate to aluminium molar ratio (SO₄²⁻/Al³⁺) of the coagulant. They concluded that PACS achieved an optimum NOM and turbidity removal when the coagulant was prepared with a basicity of 2.0 and a sulphate to aluminium molar ratio of 0.0664. Gao and Yue (2005b) studied NOM coagulation performance of PACS with this composition and compared it with PACl, FeCl₃ and alum. They found optimum coagulant dose and pH values of 5.0 mg Al/L and pH 5.0-8.2 for PACS and PACl, 7.0 mg Fe/L and pH 5.0-6.0 for ferric, and 7.0 mg Al/L and pH 5.0-7.0 for alum. At optimum conditions, the selected PACS achieved the best NOM removal, followed by PACl, ferric, and then alum. Under the optimum coagulant conditions with PACS and PACl, the residual aluminium concentration in treated water was 115 µg/L.
Matilainen et al (2005) compared the efficiency of aluminium and ferric sulphate coagulants for NOM removal during coagulation/flotation of drinking water in Finland. Approximately 95% of high molar mass organic substances (HPSEC) were removed with both coagulants. The greatest difference between the coagulants occurred in the removal of organic compounds having molar masses of 1000-4000 g/mol, which were removed 25% more efficiently with the iron-based than the aluminium-based coagulant. Low molar mass material was poorly removed regardless of the coagulant (10%). In terms of overall NOM removal, iron was 10% more efficient than aluminium. However, turbidity removal during coagulation-flotation was more efficient with aluminium, especially during the winter period. Turbidity was effectively removed during filtration.

Matilainen et al (2002) studied the removal of NOM in the different stages of the water treatment process at Rusko WTP in Tampere, Finland. The treatment process steps include coagulation, flocculation, clarification by sedimentation or flotation, activated carbon (GAC) filtration and disinfection. They used high-performance size exclusion chromatography (HPSEC) to determine changes in NOM character (molecular size) during the treatment steps, and measured water quality in terms of TOC, KMnO₄-number and UV-absorbance. Significant correlation was established among these parameters. The results showed that high MW organic matter was clearly easier to remove in coagulation and clarification than low MW matter. Depending on the regeneration status, the GAC filters were able to reduce the amount of low MW organics to some degree, but were not able to remove most of these substances.

Fearing et al (2004) reported that over 70% removal of hydrophobic and hydrophilic acid fractions, while only 16% of the hydrophilic non-acid fraction was obtained using conventional coagulation treatment during elevated NOM loadings at a treatment facility. From jar tests on isolated NOM fractions, it was concluded that increased removal of the hydrophilic fractions could be obtained when conditions were optimized. From this, an optimized two-stage coagulation process was proposed to increase the removal of recalcitrant fractions of NOM.

To gain more insight into the types of NOM that are recalcitrant to removal by coagulation, van Leeuwen et al (2002) studied alum coagulation of two Australian water sources. They used a simplified fractionation technique (Chapter 2) to isolate four DOC fractions: VHA, SHA, CHA, and NEUT. The isolated fractions were then treated by alum coagulation. The fractions were characterized by a number of different methods: high performance size exclusion chromatography (HPSEC), bacterial regrowth potential (BRP), trihalomethane formation potential (THMFP), pyrolysis gas-chromatography mass spectrometry (Py-GC-MS), and thermochemolysis. The highest removal of DOC by alum coagulation was obtained in samples spiked with the CHA fractions while the NEUT fractions were the most recalcitrant. The CHA fraction contained the highest MW organic matter, and the NEUT fraction
contained the lowest MW material. The NEUT fractions had the highest relative proportion of saccharide derived organic material, and showed considerable variety in BRP, and thereby in the ability to support microbial growth.

Wang et al (2002) studied the effectiveness of enhanced alum coagulation for removal of NOM at various alum dosages and pH conditions for three source waters in Taiwan. Jar tests were performed with alum dosages ranging from 60-120 mg/L of alum, and pH values from 5.0 to 8.0. DOC removals of up to 50 % were achieved, depending on raw water DOC and alkalinity levels.

Freese et al (2001) performed laboratory and pilot scale tests to compare the effectiveness of enhanced coagulation with ozonation and granular activated carbon adsorption in treating various types of raw water in South Africa. Reductions of up to 50% in trihalomethane formation potential and 50-70% in organic carbon and colour were obtained using enhanced coagulation, which compared favourably with ozonation and GAC filtration. The latter process was especially effective in the removal of micro pollutants, generally being in excess of 70%. Inorganic coagulants were found to be more effective than polymeric coagulants for organic matter removal, and the addition of inorganic acids to depress pH allowed for increased organics removal at lower coagulant doses.

Bell-Ajay et al (2000) studied conventional and optimized (enhanced) coagulation for NOM removal in jar tests of raw water samples from 16 US water utilities and two water treatment plants in Pennsylvania. Results showed that enhanced coagulation can enhance the removal of TOC, DBP precursors, particles, and turbidity compared with conventional coagulation. The effectiveness of the optimized treatments depended on the pH of coagulation and the type and dosage of the coagulant.

Fearing et al (2004) investigated NOM control options related to seasonal periods of high rainfall that was shown to cause elevated NOM loadings at treatment plants and correspondent difficulties in removing sufficient NOM to meet water quality standards (i.e. THM) in the UK. Three treatment options for improved NOM removal were studied, either by: 1) optimising current coagulation processes, 2) pre-coagulation, and 3) post-coagulation. From NOM fractionation into hydrophobic and hydrophilic fractions it was shown that certain fractions were more recalcitrant to treatment during the times of high rainfall and high NOM loadings. By optimising coagulation for these fractions a staged coagulation was proposed. Although no significant increase in the removal of DOC or UV-adsorption could be observed as a result of the optimisation, filter run times were significantly increased.

Furthermore, the combination of ferric coagulation and magnetic ion exchange (MIEX®) showed that although the DOC in treated water was not significantly reduced, the THM formation potential was reduced by more than 50% for the lower MW compounds that are known to be untreated by conventional coagulation. Finally the addition of a range of adsorbents
including carbons, hydroxides and clays to both raw water and the isolated low MW fractions of NOM showed that an increase in DOC and UV254 removal was achievable.

Bose and Reckhow (2007) fractionated NOM from a surface water source and identified fulvic acids and hydrophilic neutrals as the two most abundant fractions. Adsorption affinity of these fractions on preformed aluminium hydroxide flocs was found to increase with increasing charge of the fractions, except for the two most highly charged fractions, fulvic acids and hydrophilic acids, which showed less adsorption affinity than expected from their specific organic charge. Preozonation of the raw water resulted in a decline in DOC removal by alum coagulation with increasing ozone dosages. It appeared that ozone applied to raw water reacted preferentially with the humic fractions of NOM, resulting in the detrimental effects of ozonation on the subsequent NOM removal by alum coagulation being magnified. Ozonation of the isolated NOM fractions showed that prior ozonation of the fulvic acid fraction resulted in a decline in adsorption affinity on aluminium hydroxide surface. For the hydrophilic neutral fraction however, adsorption affinity increased as a result of preeozonation. Ozonation of pre-coagulated water demonstrated beneficial effects of ozonation on the removal of non-humic fractions of NOM through alum coagulation. In order to maximize DOC and UV254 removal for raw waters containing both humic and non-humic NOM, a staged coagulation treatment with intermediate ozonation was proposed.

Korth et al (2004) reported an increase in NOM in some German drinking water reservoirs during the past 10-15 years, and that the impacts of such a change on the drinking water quality were almost unknown although this represents a serious concern for the water industry. A research project that was carried out at several drinking water reservoirs and water works indicate that the NOM increase is predominately caused by an increasing input to the reservoir of high and intermediate MW humic substances from the catchment area. During water treatment, the fractions of the high MW humic substances and polysaccharides were significantly reduced. In contrast, low removal efficiencies were detected for the low and intermediate MW fractions. In summary, the increased raw water NOM concentration resulted in a correspondent increase in the NOM concentration of the treated water. In addition, the concentration of biodegradable substances (BDOC) in treated water also increased with the raw water NOM content. No relationship was found between treated water AOC and raw water NOM. However, AOC concentrations increased significantly during snowmelt and the circulation periods in the reservoir.

As stated above, it is important to apply a minimum coagulant dosage or higher to comply with the water quality standard. On the other hand, coagulant overdosing resulted in excessive sludge production, need for more chemicals for pH and corrosion control, early filter breakthrough and increased rate of head loss development.
The negative effects of increased filtration rates on filtered water turbidity due to increased hydraulic loading when parallel filter units were taken out of operation to be backwashed were also clearly demonstrated in the experiments.

3.1.4 **Optimum operation and multiple treatment objectives**

From the above considerations, it is obvious that NOM control the coagulation process and determine optimal coagulation conditions. An adequate coagulant dose is required in order to control the levels of NOM (DOC), UV-abs., residual coagulant and particles in treated water.

It is however also important to bear in mind that optimum coagulation conditions are required in order to secure an efficient treatment barrier against pathogens like *Cryptosporidium* and *Giardia*.

In addition, an adequate coagulation process is essential for good clarification and filtration performance and for the control of pathogens (e.g. *Giardia, Cryptosporidium*) and disinfection by-products. Improper coagulation can cause high residual coagulant residuals in treated water and post-treatment precipitation of particles causing turbidity, deposition and coatings of pipes in the distribution system. Minimizing of solids residuals (sludge) from coagulation has also become a more important part of utility operations due to increased disposal costs and landfilling restrictions Fernitsky and Edzwald (2006). Thus, coagulant over-dosing should be avoided from economic as well as process related reasons (excessive sludge production, increased solids load to separation units, reduced direct and/or contact filter run lengths, increased backwash water consumption, etc).

These issues have put additional pressure on utilities to optimize coagulation to meet the multiple treatment objectives (modified after Edzwald and Tobaison, 1999): 1) to maximize the removal of particles, turbidity and microorganisms/pathogens by downstream solid-liquid separation, 2) to maximize TOC and DBP removals, 3) to minimize residual coagulant concentrations, 4) to minimize solid residuals (sludge) production, and 5) to minimize operating costs.

Budd et al (2004) stated that optimization of coagulation is central to the drinking water industry’s ability to meet goals for particulate (turbidity) and NOM removal. They stressed the importance of adopting a holistic view of treatment objectives when considering possible changes to the coagulation process, and highlight the necessity of evaluating coagulation as a multiple-input process that can be fine-tuned through adjustment of two fundamental parameters - pH and coagulant dose. Changes that might be undertaken include trying a different coagulant dose and pH, using alternative coagulants, and adding coagulants in a different sequence. Their recommendations were based on coagulation evaluations performed at a number of US water treatment facilities over the past 15 years.
Gregory and Carlson (2003) studied the impact of coagulation pH, zeta potential and floc formation kinetics on particle removal during settling and filtration. They concluded that higher coagulation pH – and thus higher alum coagulant doses – could be advantageous during periods of rapidly changing water quality conditions, such as high-NOM runoff events. The rate of floc formation measured immediately following coagulant addition could be indicative of overall process performance.

Pernitsky and Edzwald (2006) presented guidelines for the selection and use of polyaluminium chloride (PACl) and alum coagulants in terms of raw water quality and treatment method. The concentration of NOM was found to be the most important parameter affecting coagulant dose. SUVA was useful for characterizing the nature of the NOM, and thus for predicting the degree of NOM removal expected. Raw water turbidity and NOM did not influence the type of coagulant that was most effective. Raw water alkalinity, as it related to the pH of coagulation in cases where independent pH control is not used, was found to be very important for choosing one coagulant type over another. PACl basicity should be matched to raw water alkalinity, so that coagulation pH is as close as possible to the pH of minimum solubility of the coagulant. The solids separation process used was also found to be important for coagulant selection. Raw waters coagulated with PACls containing sulphate was found to have the best settling characteristics, but showed the highest headloss rates in direct filtration applications. Dissolved air flotation performance was relatively insensitive to coagulant type.

Coagulant dosage and coagulation pH is traditionally determined according to results from jar-tests or operator’s experience, which often lead to coagulant overdosing or insufficient dosing, reduced water treatment performance and increased treatment costs.

Eikebrokk (1996, 1999) showed how residual metal (Al, Fe) determined the coagulant dosage requirement in order to meet the relevant Norwegian drinking water quality standards for treatment plants applying coagulation (i.e. Residual Al or Fe < 0.15 mg/L; Turbidity < 0.2 NTU, Colour < 5 mg Pt/L, and TOC < 3 mg/L).

The example of pilot investigation results using ferric coagulation-contact filtration presented in Figure 3.6 illustrates well that although TOC removal in excess of 60% was obtained with a coagulant dosage of 5 mg Fe/L, a dosage of 6.5 mg/L was required to comply with the residual Fe standard of 0.15 mg/L. With 5 mg/L of Fe, a residual Fe concentration in excess of 0.4 mg/L was detected. In addition, the figure demonstrates well how an increase in coagulant dosage level is able to widen the pH-range of optimal treatment performance. With the 5 mg Fe/L dosage, the optimum pH-range is very narrow (4.9-5.2). With 6.5 mg Fe/L however, more than 60% TOC removal was achieved within a wide range of pH (3-6). However, even 6.5 mg Fe/L was close to the minimum dosage required in order to comply with the 0.15 mg residual Fe/L standard within a reasonably wide pH-range (5.0-5.5).
Similar curves and relationships were obtained with alum and polyaluminium chloride, but the optimal pH-values were higher with these coagulants (pH 5.5-6.5).

As discussed above, total residual metal coagulant concentrations often determine the coagulant dosage needed in order to comply with the water quality standards.

Srinivasan et al (1999) analysed data from the Buffalo Pond WTP in Saskatchewan, Canada, in order to examine seasonal variations and factors influencing residual aluminium concentrations. Analysis of eight-year data showed that the DOC present in the raw water played a major role in controlling efficacy of alum coagulation. They found that when alum/DOC ratio was less than 7, insufficient alum addition led to incomplete coagulation resulting in colloidal material mostly consisting of organic aluminium in particulate form. Hence particulate aluminium increased in treated water. But this increase in residual aluminium did not increase the turbidity of treated water. This indicated that an adequate alum dose in response to dissolved organic carbon is important in minimising residual aluminium in treated water. The plant data also showed that when freshly regenerated GAC contactors were used, peaks of dissolved aluminium occurred as a result of alkaline metal (calcium and magnesium) oxides present in the regenerated GAC that shifted the pH of filtered water to alkaline range with consequent formation of soluble aluminium species like Al(OH)₄⁻.

Srinivasan and Viraraghavan (2004) conducted aluminium speciation experiments in a pilot scale water treatment plant using different alum doses. In addition, they conducted jar tests at various alum/DOC ratios. They concluded that an alum/DOC ratio of at least 7.3 should be maintained in order to meet the operating guidelines of 100 µg/L of total aluminium proposed by Health Canada given that finished water soluble aluminium levels may be in the range of 35-40 µg/L. For lower alum/DOC ratios (1.37 and 5.3) most of the total aluminium in filtered water was in the form of
particulate aluminium, and soluble organic aluminium increased compared to the level in raw water.

Jekel (1986) investigated the interactions of humic acids and aluminium coagulants and reported that at low coagulant dosages, i.e. less than 10 mmol of $\text{Al}^{3+}$/g DOC in raw water (i.e. 0.27 mg Al/mg DOC), high residual aluminium levels were found and low amounts of DOC were removed. He concluded that the minimum dosage of aluminium should be in the order of 20-40 mmol $\text{Al}^{3+}$/g DOC (i.e. 0.54-1.08 mg Al/mg DOC) to overcome the complexing and coagulation problem and to achieve low aluminium residuals.

As discussed before, residual coagulant concentrations normally determine coagulant dosage requirements in enhanced coagulation processes. In addition to the ability of increasing pH, calcium and alkalinity levels, a main benefit of the alkaline filter layer is the ability of reducing the residual metal coagulant concentrations. A combination of enhanced coagulation and corrosion control by alkaline post filtration may therefore reduce the coagulant demand, the sludge production, and the solids load to the filters. This in turn will increase filter run times and increase the applicability of direct and contact filtration processes in the direction of raw waters with higher than recommended NOM levels.

Emelko (2003) investigated the removal by alum coagulation of viable as well as formalin-inactivated *Cryptosporidium parvum* oocyst in bench-scale dual- and tri-media filters. Her results indicated that formalin-inactivated oocysts were suitable surrogates for viable oocysts. She also found that poor coagulation conditions severely compromised removal of viable and inactivated oocyst by dual- and tri-media filters compared to stable operating conditions and filter ripening, emphasizing the importance of optimized coagulation for the successful removal of oocysts during filtration. During filter ripening, the *C. parvum* removals were moderately lower (approximately 0.5-1-log) than during stable operation, while during coagulation failure conditions the *C. parvum* removal capacity of both dual- and tri-media filers was severely decreased (by more than 3-log) relative to both ripening and stable (optimised) conditions (Figure 3.7). Tri-media (3-M) filters offered only marginally higher oocyst removals than dual-media (2-M) filters.
Although a sub-optimal coagulant dose may result in excessive residual metal concentrations, reduced removal of pathogens like *Giardia* and *Cryptosporidium*, and non-compliance with the water quality standards, coagulant overdosing should be avoided. In conventional filtration applying pre sedimentation the negative effects of overdosing is normally limited to increased costs, excessive sludge production, etc. However, restabilization may occur, resulting in poor treatment performance.

The negative consequences of coagulant overdosing are however significantly larger in direct and contact filtration processes where the filter has to cope with the excessive amount of sludge formed. The example shown in Figure 3.8 illustrates the negative effects of alum coagulant overdosing in contact filtration processes. The figure demonstrates the negative effects of coagulant overdosing on filtration performance in terms of breakthrough and head loss development, and thereby also on dual media filter run time and treatment capacity/net water production. From an optimum coagulant dosage of 1.0 mg Al/L, a dose increase to 1.8 and further to 3.1 mg Al/L, increases the solids load to the filter and reduces the filter run time from about 15 hours to about 7.5 and 6 hours, respectively. The head loss increase as a result of coagulant overdosing is also significant, from 6.3 cm/hr at the optimum dosage of 1.80 mg Al/L to 9.2 and 12.8 cm/hr at alum doses of 1.8 and 3.1 mg Al/L, respectively. The applied filtration rate was 7.5 m/hr.
Figure 3.8 Effects of coagulant dosage level on filter run time, i.e. terminated by breakthrough and/or head loss. (Contact filtration with alum; 2-M filter; 7.5 m/hr). Eikebrokk, 1999.

If pH is lowered to improve coagulation and organic removal, it is typically necessary to raise pH in the final effluent from the plant to provide a less corrosive finished water. The pH may be adjusted at one or more points in the treatment, including rapid mixing, prefiltration and postfiltration. In case of enhanced coagulation it is recommended to readjust the pH after the filtration process as compared to prefiltration. This is due to the fact that some organic matter may be adsorbed onto the floc that may carry over from the clarification process, and any prefiltration pH adjustment may then result in “release” of that organic matter, which could pass through the filters and contribute to subsequent DPB formation.

One of the greatest practical problems faced in removing soluble NOM from low turbidity waters is inability to produce an acceptable floc (Gregor et al 1997). Natural turbidity provides a ready source of nucleating sites for floc development, and once present, these flocs act as adsorption sites for soluble NOM. For low turbidity waters, these essential floc nuclear sites can be provided by lime that is used for pH and alkalinity correction, provided the lime is added in sufficient quantity and at the point where it retains some particulate nature. If pH adjustment with lime is not needed, bentonite clay or activated silica can be used as a coagulant aid.

States et al (2002) studied the influence of enhanced coagulation and decreased coagulation pH levels on the removal of Cryptosporidium oocysts, TOC, turbidity and particle counts. A series of pilot-plant trials were performed with commonly used coagulants (ferric chloride, alum, and poly aluminium chloride) at various pH levels to treat river water spiked with large numbers of Cryptosporidium oocysts. The results show that TOC removal is significantly enhanced by coagulation at lower pH levels and that all three coagulants are effective in removing Cryptosporidium oocysts (mean removal = 4.3 log units). However, turbidity and particle counts appeared to be unreliable indicators of oocyst removal. The investigation suggested that lowering coagulation pH does not interfere with removal of Cryptosporidium.
Dai and Hozalski (2002) performed experiments in bench-scale 0.25 m deep rapid filters with 0.55 mm glass beads to study how the removal of Cryptosporidium oocysts by filtration was effected by NOM and biofilms. They found that the oocyst removal efficiency was decreased as a result of presence of NOM and biofilm-coatings in the filter bed, indicating that water treatment facilities employing biologically active filters have a greater potential for oocyst breakthrough and proper coagulation is critical for effective removal of oocysts in the filters. Oocysts pre-equilibrated with NOM were more hydrophobic and significantly more negative than those obtained for untreated oocysts. Fortunately, the use of alum for coagulation was able to neutralize the surface charge of the NOM-coated oocysts and provide high removal efficiency.

Xagoraraki and Harrington (2004) evaluated the removal of viable Cryptosporidium parvum oocysts and changes in zeta potential during alum coagulation and sedimentation. The removal of oocysts and their zeta potential was evaluated at three raw water DOC concentration levels and a wide range of alum doses and coagulation pH values. The study showed that the NOM content of the raw water, i.e. the initial DOC concentration affected the removal and zeta potential of the oocysts. Charge neutralization was not considered a relevant removal mechanism for oocysts under the conditions used in this study. Sweep coagulation appeared to be the primary removal mechanism at the lowest DOC concentration tested. For the highest DOC concentration used in this study, optimal coagulation for oocyst removal coincided with optimal coagulation conditions for NOM removal, suggesting that NOM plays a key role in the interaction between oocysts and the aluminium hydroxide precipitate.

Logsdon (2000) stated that deviations from optimum or near-optimum coagulation and improper management of filtration rate increases can severely deteriorate filtration performance for removal of protozoa. Likewise, improper backwash water recycling can disrupt coagulation.

Continuous monitoring of coagulation and filtration is an aid to effective management of the treatment process. Production of filtered water having a turbidity of 0.1 NTU or lower should be the goal if effective control of cysts and oocysts is to be attained. However, no concentration of cysts could be associated with a specific value of filtered water turbidity.

Hamilton et al (2002) concluded that if oocysts are present in a work’s raw water, there is strong evidence to suggest that minimising treated water turbidity/particle count will reduce Cryptosporidium risk. However, neither particle counters nor turbidimeters are able to detect Cryptosporidium oocyst or reliably predict their occurrence in treated waters. Particle counters have demonstrated some benefits in three areas, namely:

a) higher sensitivity to changes in water quality at low turbidities (<0.1 NTU)
b) higher sensitivity changes associated with larger particle sizes (e.g. filter breakthrough events)  
c) the ability to monitor changes in particle size distribution

Logsdon (2000) reviewed five pilot plant investigations, treating raw waters with turbidity generally below 10 NTU:

- Logsdon et al (1981) investigated *Giardia* removal (seeded cysts) in direct filtration pilot trials with a dual media anthracite and sand filter, a filtration rate of 10 m/hr, and a coagulant dose of 10 mg/l alum (i.e. approx. 0.9 mg Al/l). Operational variations tested included sub-optimal and very inadequate coagulation, filtration rate increases, and turbidity breakthrough with high head loss.

- DeWalle et al (1984) investigated *Giardia* removal (seeded cysts) in a dual media anthracite and sand filter. Filtration rates were typically 10 m/hr, with variations within 4.3-10 m/hr. Alum at a dosage of 12 mg/l (i.e. approx. 1.1 mg Al/l) was used in most runs, with some testing of sub-optimal coagulation.

- Hendricks et al (1999) investigated *Giardia* and *Cryptosporidium* removal in two types of contact (in-line) filters: 1) a dual media anthracite-sand filter, and 2) a monomedium anthracite filter. An alum dosage of 26 mg/l (i.e. 2.4 mg Al/l) was generally used, with some runs at a sub-optimum dosage of 13 mg/l (i.e. approx. 1.2 mg Al/l).

- Ongerth and Pecoraro (1995) investigated *Giardia* and *Cryptosporidium* removal in direct mixed media filtration (anthracite over sand and garnet). The filtration rate was 12 m/h, and the optimum alum dosage was about 10 mg/l (i.e. approx. 0.9 mg Al/l) at a pH of 6.4-6.6. In a sub-optimal coagulation run, an alum dosage of 5 mg/l (i.e. approx. 0.4-0.5 mg Al/L) was tested.

- Patania et al (1995) investigated *Giardia* and *Cryptosporidium* removal in conventional filtration, and a filtration rate of 15 m/h. Ferric chloride was used as the coagulant, typically at a dosage of 15 mg/l with or without Cat-Floc T at 1 mg/l. They evaluated filtration at optimum coagulation conditions during filter ripening and later in the filter runs when stable filtered water quality had been attained.

Logsdon (2000) concluded from the review that at optimum coagulation conditions when filtered water turbidity was 0.1 NTU or lower, removal of cysts and oocysts was more effective than when turbidity was above 0.1 NTU. Sub-optimal coagulation resulted in filtered water turbidity in the range of 0.1-1 NTU. Higher concentrations of cysts and increased filtered water turbidity were observed during filter ripening. Filtration rate increases ranging from 50% to 150% in 10 seconds did not cause filtered water turbidity to increase when flocs were strengthened with a non-ionic polymer (Logsdon
et al 1981). When alum was used with no polymer, a filtration rate increase from 10 m/hr to 27 m/hr for a period of two minutes caused turbidity to increase from 0.3 to 1.0 NTU, and the *Giardia* cysts concentration increased 25-fold. When the filtration rate was decreased to 10 m/hr, both turbidity and *Giardia* cyst concentration returned to levels observed before the rate increase.

The results also showed that turbidity breakthrough at the end of a filter run can be accompanied by a massive discharge of microorganisms. Recycling of filter backwash water by returning it to the influent raw water will normally increase the concentration of suspended solids and microorganisms in the influent water, and it may upset the coagulation chemistry.

Enhanced coagulation using metal coagulants normally produce relatively short filter runs due to loose flocs and early breakthroughs. Because larger particles like protozoa breaks through earlier than the bulk of particles (turbidity), there is reason to be careful in the pre-breakthrough phase. Some facilities therefore initiate backwash before turbidity or particle breakthrough can be detected, i.e. after a certain filter run time or volume of water treated. In this way a safety factor can be included to avoid breakthrough of protozoa.

The application of filter aid polymers in small quantities (0.05-0.2 mg/L) have proven very effective in order to increase floc strength, increase attachment and/or decrease particle detachment within the filter bed and thereby prolong the filter run times. This allows for the use of higher filtration rates and thereby an increased treatment capacity. However, there is some variability in the level of success of polymer use, and there seem to be a need for more research on this issue.

Poor quality raw waters may need pre separation of solids prior to filtration in order to secure adequate performance and filter run times. In such cases, conventional filtration with pre-settling) or pre-flotation may be better alternatives than direct or contact filtration processes.

**Conventional filtration**

In conventional filtration systems applying flocculation and sedimentation prior to filtration, a large proportion of the solids (sludge) is removed during sedimentation. The solids loads to the filter is reduced as a result of the pre-settling, and relatively long filtration times can be obtained before breakthrough or head loss terminates the filter run.

However, sub-optimal coagulant dosage will result in inadequate treatment performance with respect to NOM and pathogens, filtered water turbidity, and residual coagulant concentrations.

On the other hand, coagulant overdosing may reduce treatment performance due to restabilization of colloids in some cases. In addition, coagulant overdosing will inevitably result in excessive sludge formation and increased chemicals and residuals management costs. However, it can also increase the floc volume fraction, and thus increase flocculation and separation efficiency.
For high alkalinity raw waters, coagulant overdosing may be a practical alternative to supplemental acid addition to depress coagulation pH to optimum values.

For low alkalinity raw waters however, coagulant overdosing can create an additional need for base addition to prevent pH form being reduced to sub-optimal values. Polymeric coagulants with high basicity may be suitable in such situations.

**Dissolved air flotation (DAF)**
Enhanced coagulation followed by dissolved air flotation (DAF) and filtration processes may be a good treatment alternative for NOM removal, especially when NOM levels are too high for direct and contact filtration applications, and where algae removal is required. DAF requires good coagulation so that the air bubbles can attach to the floc particles. Permitsky and Edwald (2006) found that DAF was relatively insensitive to coagulant selection. However, high-basicity PACls were more effective at lower doses and/or over a broader range than alum or other PACls for some waters.

**Direct and contact (in-line) filtration**
Enhanced coagulation and direct or contact filtration has proved a cost-efficient treatment alternative for raw waters with a low to moderate coagulant demand, thus minimizing sludge production and solids load to the filters. These processes are considered feasible for raw waters with turbidity less than 10 NTU, colour less than 40 mg Pt/L and algae biomass less than 10 µg/L as chlorophyll-a (Janssens and Buekens 1993), i.e. for raw waters with a relatively low coagulant demand.

Coagulant overdosing is normally not a good strategy in direct or contact filtration applications, because filter run times are sensitive to solids loading. Thus, coagulant overdosing will normally result in early filter breakthrough, increase in the rate of head loss development and thus reduced filter run times and reduced treatment capacity. Treatment performance may also be compromised because of the increased frequencies of filter backwash and filter ripening.

Due to the relatively short filter run times normally obtained in enhanced coagulation followed by direct- or contact filtration processes, it is particularly important to avoid coagulant overdosing in such processes. The use of a polymer as filter aid in order to increase floc strength and/or attachment forces within the filter bed has proven to be an efficient tool to increase filter run times, and/or to allow for the use of higher filtration rates while still maintaining reasonable filter run times. However, the results from filter aid polymer applications appear inconsistent; In some cases the filter run times can be increased 2-3 times compared to the use of a coagulant alone (Eikebrokk, 1982), while in other cases the effects are rather small. The reasons for this do not seem well known or described in literature.
Due to the high coagulant dosage requirements, and the increased sludge production and solids loading to the filters, filter run time and treatment capacity considerations are of specific interest for enhanced coagulation applied in direct- and contact filtration processes.

Regardless of the type and degree of separation prior to the filter unit, optimal enhanced coagulation conditions are required to optimize the overall treatment performance. Major challenges seem to exist regarding optimum treatment process performance and operation, related in specific to residual coagulant concentrations, turbidity, NOM, pathogens removal (e.g. *Giardia* and *Cryptosporidium*), filter run times, and treatment capacity.

### 3.2 Optimization procedures – Coagulation and filtration profiles

Eikebrokk (2004b) suggested a systematic on-site approach to identify the “coagulation profile” for a specific raw water/water treatment plant (Fig. 3.9). For a reasonable number of different coagulant dosage levels (normally 3-4), coagulation pH is varied in a step-wise manner within each dosage level, and filter effluent samples are analyzed after steady-state performance is established after every change in coagulation conditions. In this way not only the optimum pH and coagulant dosage can be identified, but also the interrelationship between dose and pH, e.g. a higher coagulant dosage normally widens the “pH-window” for optimum treatment performance.

Similarly, a “filtration profile” can be identified by running tests with different filtration rates, thereby identifying the effects of filtration rate – and thereby solids load rates - on filter run times determined by breakthrough or head loss (Fig. 3.9). These tests should be performed under optimal coagulation conditions found during the coagulation profile identification tests described above. Coagulation and filtration profile identification tests should be performed during selected periods during the year, covering the range of seasonal variations in raw water quality. This will give operators very valuable information and insight into the optimum operation conditions of their water treatment facility, and how these optimal conditions are affected by variations in the raw water quality.
Thus, a step-wise optimisation procedure is suggested for existing WTPs:

1. Characterisation of raw water and NOM
2. Compare coagulant dose model predictions to actual (applied) dose levels
3. Perform optimisation trials (identify coagulation and filtration profiles) according to Fig. 3.9.
4. Identify optimisation potentials and evaluate operation adaptations
5. Identify optimisation benefits in terms of process performance and cost efficiency

3.3 Optimization procedures for ozonation-biofiltration processes

The total BOM in raw water and ozonated water contains numerous compounds with different biodegradation kinetics. The biodegradation kinetics of BOM depends among other factors on the raw water characteristics and the applied ozone dose. Therefore, the degradation rates of DOC are often different for different waters even when the total BDOC-values are the same. The contact time in biofiltration is normally within the range of 5 to 20 minutes, while BDOC during the bioassay is determined over a time period of several days (the more biomass the shorter time of the test). Therefore not all BDOC will be removed in the biofilter, and the DOC degradation kinetics should be determined in order to predict biofilter performance.

To address this problem some authors have suggested a classification of BDOC in several fractions depending of their degradation rates (Carlson and Amy, 2001). Two classes were suggested: 1) BDOC\textsubscript{rapid}, which is the fraction of BDOC that is rapidly degraded (i.e. within 60 min), and 2) BDOC\textsubscript{slow}, which is the fraction of BDOC that is degraded over a time period from 1 hour to
the end of the BDOC test (30 days). They found that BDOC\textsubscript{rapid} is similar for several water sources, representing about 12% of the total DOC when a minimum ozone dose was applied (> 1 mg\textsubscript{O}_3 mg\textsubscript{DOC}\textsuperscript{-1}), while BDOC\textsubscript{slow} varied significantly, from 5 to 25% depending on the water source. Most likely BDOC\textsubscript{rapid} will be removed in the biofilter while BDOC\textsubscript{slow} will enter the distribution network and will be slowly degraded by the bacteria living there.

Yavich et al (2004) using the same approach divided BDOC into 3 classes: “fast” BDOC, “slow” BDOC and “non” BDOC. Klevens \textit{et al.} (1996) operationally defined the distinction between “fast” and “slow” BDOC by bisection the extreme tangent lines at the beginning and at the end of the biodegradation curve (Figure 3.10). From this mathematical interpretation the maximum rate of biodegradation of “fast” BDOC can be calculated, and the value was found to vary from 0.08 to 0.46 mg DOC L\textsuperscript{-1} min for ozonated water. Also Digiano \textit{et al.} (2001) developed a method for the determination of the biodegradation kinetics of BDOC.

Figure 3.10 Illustration of an approach for the quantification of biodegradation rates of BDOC fractions (Yavich et al 2004)

On this background optimisation of biofiltration processes requires: 1) adjustment of the ozonation conditions so that the formation of fast BDOC is maximised and the formation of slow BDOC is minimised, or 2) adjustment of the biofilter operation so that as much slow BDOC as possible is removed in the biofilter.

In practice it is time consuming to obtain enough data points from column tests to draw accurately a degradation curve like the one presented in Figure
3.7. Therefore, a step-wise optimization procedure is proposed for existing ozonation-biofiltration facilities:

1) Evaluation of the total BDOC content from column experiments. Prior to the DOC measurements the columns should be seeded with biomass for at least 2 months and adapted for 24 hours with the actual water sample.

2) In humic-rich waters (also after ozonation) DOC biodegradability and biodegradation kinetics should be determined (Digiano et al 2001)

3) The ATP concentration (pg/g) of the biofilters (upper 10 - 30 cm) should be measured.

4) Expected BDOC removal efficiency should be predicted from a simple model (Section 6.1.3). Before application the models should be verified in columns used for BDOC determination.

5) Ozone transfer efficiency (and ct-values) should be identified from water sampling along the length of the ozone contactor

6) The overall ozonation- biofiltration efficiency should be identified on the basis of:
   a. NOM and BDOC removal efficiencies (with different ozone doses, EBCTs)
   b. Residual BDOC and regrowth potentials
   c. Turbidity removal
   d. Treatment barrier evaluations
4 NOM characterisation and biodegradability results

4.1 Inter-laboratory comparison of TOC measurement methods

4.1.1 Rationale
Uncertainties in operation evaluations of water treatment plants may result from inaccurate measurements and the application of analytical methods (e.g. BDOC and NOM-fractionation) still under development and not yet standardized.

This chapter presents the BDOC and NOM-fractionation methods and activities used in the pilot and full scale studies.

Total organic carbon (TOC) is a standard method. However, measurements are done with different types of equipment and different standards. The tested waters were also very different in terms of TOC, alkalinity, and inorganic carbon concentration levels. Therefore it was considered necessary also to include TOC measurements in the inter-laboratory comparisons (i.e. round-robin tests).

4.1.2 Methodology for TOC round-robin test
The following laboratories were involved in the Round-robin test for the measurement of the (TOC):

1) RTU, Latvia
2) EAWAG, Switzerland
3) SINTEF, Norway

The protocols of TOC used by the laboratories are summarized in Table 4.1 below.

Inter-laboratory calibration was done for synthetic and drinking water samples with TOC levels in range of 2 - 6 mg/l. Samples were prepared by each laboratory and sent to the other laboratories by courier in dark glass bottles without preservatives added. The logistic of sample sending is presented in the scheme below. Two samples (150207A and 150207B) were prepared by RTU and sent to SINTEF. SINTEF analyzed the samples and forwarded them to EAWAG. EAWAG then returned the two samples back to RTU after analysis. This procedure allowed a determination of the effects of sample storage during transport, which was around 2 months for these two samples. Two other samples (060207A and 060207B) were prepared by SINTEF and sent to RTU. These samples were however lost in the postage on the way back to SINTEF. Samples EAWAG3 and EAWAG2 were prepared by EAWAG and sent to RTU only.
Table 4.1  TOC measurement data for the laboratories involved in the study

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Standard used</th>
<th>Principle of the method</th>
<th>Apparatus used</th>
<th>Accuracy according to manual</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTU, Latvia</td>
<td>LVS EN 1484:2000 equal to EN 1484:1997</td>
<td>Total carbon (TC) conc. is determined from CO₂ concentration (infrared detector) after catalytic sample oxidation at 680 °C. Inorganic carbon (IC) is determined from CO₂ conc. after degassing of acidified sample with phosphoric acid. TOC = TC-IC</td>
<td>Shimadzu 5000A</td>
<td></td>
</tr>
<tr>
<td>EAWAG, Switzerland</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SINTEF, Norway</td>
<td></td>
<td>Combustion Analyzer with infrared (NDIR) detector.</td>
<td>Tekmar Dohrmann Apollo 9000 HS TOC Analyzer</td>
<td></td>
</tr>
</tbody>
</table>

4.1.3  Results from TOC round-robin test

Results from the inter-laboratory calibration are summarized in Table 4.2. For comparison of results, statistical significance assays of the differences (Student’s t-test and a procedure for computing one-way ANOVA) were done, with paired samples when possible. Statistical analyses of the data reported by the laboratories show that the TOC results were comparable, with the exception of the samples where the retention time during sample sending exceeded two weeks (Table 4.3, Figure 4.1-4.3).
### Table 4.2 Summary of TOC results (mg/l) from each laboratory

<table>
<thead>
<tr>
<th>Sample label</th>
<th>RTU</th>
<th>SINTEF</th>
<th>EAWAG</th>
<th>RTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>060207A</td>
<td>2.708</td>
<td>2.6725</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.820</td>
<td>2.6786</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.445</td>
<td>2.6637</td>
<td></td>
<td></td>
</tr>
<tr>
<td>060207B</td>
<td>5.349</td>
<td>5.0219</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.720</td>
<td>4.9895</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.979</td>
<td>5.0812</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150207A</td>
<td>3.119</td>
<td>3.3085</td>
<td>1.951*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.173</td>
<td>3.2852</td>
<td>2.892</td>
<td>1.896*</td>
</tr>
<tr>
<td></td>
<td>2.936</td>
<td>3.3324</td>
<td>1.941</td>
<td></td>
</tr>
<tr>
<td>150207B</td>
<td>4.720*</td>
<td>5.7543</td>
<td>5.696</td>
<td>3.97*</td>
</tr>
<tr>
<td></td>
<td>4.890*</td>
<td>5.7258</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.470*</td>
<td>5.7338</td>
<td>4.10</td>
<td></td>
</tr>
<tr>
<td>EAWAG3</td>
<td></td>
<td>2.825</td>
<td>2.716</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.675</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.722</td>
<td></td>
</tr>
<tr>
<td>EAWAG2</td>
<td></td>
<td>5.011</td>
<td>4.854</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.942</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.833</td>
<td></td>
</tr>
</tbody>
</table>

*The difference in mean of the mass is statistically significant.

### Table 4.3 Repeatability and reproducibility of data from the TOC inter-laboratory calibration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Repeatability, absolute (mg/l)/relative (%)</td>
</tr>
<tr>
<td></td>
<td>RTU</td>
</tr>
<tr>
<td>060207A</td>
<td>0.193/7.2</td>
</tr>
<tr>
<td>060207B</td>
<td>0.316/6.3</td>
</tr>
<tr>
<td>150207A</td>
<td>0.124/4.0</td>
</tr>
<tr>
<td>150207B</td>
<td>0.393/7.8</td>
</tr>
<tr>
<td>EAWAG3</td>
<td></td>
</tr>
<tr>
<td>EAWAG2</td>
<td></td>
</tr>
</tbody>
</table>

*
**Figure 4.1** Results from inter-laboratory measurements for samples 060207A (A) and 060207B (B). Dotted lines show the confidence interval defined by two (…) and three (- - -) standard deviations of the measured value. Labs: 1-RTU, 2-SINTEF.

**Figure 4.2** Results from inter-laboratory measurements for samples EAWAG3 (A) and EAWAG2 (B). Dotted lines show the confidence interval defined by two (…) and three (- - -) standard deviations of the measured value. Labs: 1-RTU, 2-EAWAG.

**Figure 4.3** Results from inter-laboratory measurements for samples 150207A (A) and 150207B (B). Dotted lines show the confidence interval defined by two (…) and three (- - -) standard deviations of the measured value. Labs: 1-RTU, 2-SINTEF, 3-EAWAG.
4.1.4 Conclusions on the applicability of TOC measurement method

Regardless of the TOC apparatus and laboratory protocols used the results from the inter-laboratory trials with synthetic and natural drinking water samples were statistically similar with one exception when sample travel time did not exceed a few weeks.

4.2 Comparison of BDOC analytic methods

4.2.1 Rationale

BDOC is the fraction of the dissolved organic carbon (DOC) that can be metabolized and assimilated by heterotrophic microflora (or bacteria) within a period of a few days to a few months. BDOC is often used to evaluate the regrowth potential of microorganisms in water distribution networks.

While TOC can be measured by chemical methods, BDOC measurements require biological systems. This makes results more dependent on local conditions.

The aim of this part of the study was to compare several BDOC measurement methods and to select the optimal technique to be used in further studies (i.e. shortest, simplest and with the highest sensitivity). The following methods were compared:

I. Batch BDOC test with suspended inoculum (Method 1)
II. Batch BDOC test with attached biofilm (Method 2)
III. Dynamic BDOC column test with attached biofilm (Method 3)

4.2.2 Methodology used for comparison of BDOC methods

Sample collection and preparation
All the glass bottles/flasks used in these experiments were preheated for 6 hours at 265 °C in order to avoid organic carbon release. The filtration systems were sterilized for 20 minutes at 121°C. The filters used were carefully rinsed, first with distilled water (1000 ml) and then with the actual water sample (200 ml). Raw water (S2) and drinking water (S1) samples were collected from Daugava WTP in Riga (Latvia). In addition, synthetic solution samples (S3) containing miners and sodium acetate were prepared in the laboratory.

Description of method 1
200 ml of water sample was sterilized by filtration through a 0.45 µm membrane (Millipore, sterile, USA). Then 2 ml of inoculum containing Pseudomonas fluorescens bacteria was added. Incubation of the inoculated sample was performed at 21±2 °C in the dark for 28 days. 5 ml subsamples were collected for DOC determination at the beginning of the incubation
period (just after addition of the bacteria) and after 1, 2, 5, 7, 9, 15, 21, and 28 days of incubation.

**Description of method 1A**
The same as above, the only difference being that 2 ml of inoculum containing cells from biofilm was added (biofilm was cultured on glass carrier beads, $\varnothing=6$ mm, for 3 months).

**Description of method 2**
In this method, BDOC was determined by use of a fixed biofilm cultured on glass carrier beads ($\varnothing=6$ mm, Assistant, Germany) by incubating a mixture of one-third of river water (prefiltered in 1.2 µm pore diameter membrane filters) and two-thirds of drinking water (after biofiltration). 100 g of the biofilm carriers were filled in 500 ml glass bottles, and the bottles were filled with the water mixture and shaken on a horizontal orbital shaker with 150 rpm (Biosan, Multi-Shaker PSU 20, Latvia). To adapt the microorganisms, the carriers were stored for 4 weeks at $21\pm2$ °C in the dark (weekly water exchange).

For BDOC determination the carriers were washed three times with the sample water. After that the bottle was filled with the sample water and incubated in the dark on a horizontal shaker at $21\pm2$ °C. Samples for DOC analysis were taken at the beginning of the incubation period and after 1, 2, 5, 7, 9, 15, 21, and 28 days of incubation.

**Description of method 2A**
The same as above, except that inorganic nutrients were added to the water sample (100 µl to 100 ml water sample of an AOC solution containing 4.55 g $(\text{NH}_4)_2\text{SO}_4$, 0.2 g KH$_2$PO$_4$, 0.1 g MgSO$_4\times7\text{H}_2\text{O}$, 0.1 g CaCl$_2\times2\text{H}_2\text{O}$ and 0.2 g NaCl in 1000 ml deionized water (11)).

**Description of method 3**
Two glass columns ($H=29$ cm, $\varnothing=2.5$ cm, Chromaflex, USA) was filled with 200 g of 6 mm diameter glass carrier balls with a surface area of 3.76 cm$^2$/g. The water samples were continuously pumped upward through the columns by a peristaltic pump (Masterflex L/S, Cole-Parmer, USA) at an optimal flow of 3-5 ml/min, representing a compromise between the required retention time (1h/column) and the speed of the assay. Biofilm was cultured by incubation using a specific mixture of waters (see Method 2). To adapt the microorganisms, the carriers were stored for 16 weeks at $21\pm2$ °C in the dark (with weekly water exchange). The columns were considered ready for BDOC tests when the ATP concentration (after about 4 weeks) was in range of 0.5 to 100 ng/cm$^2$.

The BDOC value corresponds to the difference ($\Delta\text{DOC}$) between the inlet DOC and the DOC of the outlet of the second column (after 2h).
Bacterial biomass determination
The amount of active biomass in the water and on the surface of the carriers was determined by measurements of adenosine triphosphate (ATP) (CCK-2S Contamination Control Kit Hygiena, USA). The concentration of ATP was calculated from the RLU value using a conversion factor determined in the calibration measurements. High-energy sonification at a power input of 40 W for 2 min was applied to the samples (5 g carrier beads in 25 ml deionized water) for detachment of biomass. All samples were tested in triplicate and the mean value was used for BDOC calculation.

DOC determination
The samples were filtered thought 0.45 µm pore size membrane filters (Sartorius, Minisart, sterile, Germany) that were carefully pre-rinsed with 100 ml of deionized water (Elga labwater, Purelab ultra, USA) and then with 10 ml of the actual water sample. DOC measurements were performed with a TOC-5000A Analyzer (SHIMADZU, Japan). Every sample was tested in duplicate and the mean value was calculated (CV≤2%). A blank and control solution was analyzed within each sample series in order to verify the accuracy of the obtained results.

Statistic analysis
To compare the results obtained with the different BDOC methods, one-way ANOVA assays with paired samples (when possible) were used.

4.2.3 Results from BDOC comparison tests
The results from comparison of the various BDOC methods applied to drinking water samples (Table 4.4), river Daugava samples (Table 4.5) and sodium acetate solution samples (Table 4.6) are presented below. The results showed DOC values in the range of 1.52-4.06 mg C/l, with BDOC fractions in the range of 45-59% in the drinking water. In the river water DOC ranged from 10.46-14.26 mgC/l, with BDOC fractions in the range of 14-19%. In the sodium acetate solution (6 mg C/l) used in the experiments, the measured DOC concentrations ranged from 5.51-6.29 mg C/l, with BDOC fractions of 90-94%.

Anova tests were applied to compare the difference in mean values between the samples. The test showed that there is no statistically significant difference between the BDOC methods used for testing of drinking water (F_{3,8}=8.8746;P<0.05), river water (F_{3,11}=1.6800;P<0.05) and sodium acetate solution samples (F_{3,8}=2.7868;P<0.05).
Table 4.4 DOC and BDOC values obtained by the different methods for drinking water.

<table>
<thead>
<tr>
<th>Method</th>
<th>DOC, mg/l</th>
<th>Mean DOC, mg/l±SD</th>
<th>BDOC, mg/l</th>
<th>Mean BDOC, mg/l±SD</th>
<th>(BDOC/DOC)×100 ±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.56</td>
<td>2.34</td>
<td>2.23</td>
<td>2.49±0.13</td>
<td>1.3±0.10</td>
</tr>
<tr>
<td>1a</td>
<td>2.84</td>
<td>2.68</td>
<td>3.01</td>
<td>2.84±0.17</td>
<td>1.62±0.10</td>
</tr>
<tr>
<td>2</td>
<td>2.6</td>
<td>2.52</td>
<td>2.34</td>
<td>2.49±0.13</td>
<td>1.3±0.10</td>
</tr>
<tr>
<td>2a</td>
<td>3.93</td>
<td>4.24</td>
<td>4.06</td>
<td>4.08±0.16</td>
<td>2.39±0.10</td>
</tr>
<tr>
<td>3</td>
<td>1.52</td>
<td>1.9</td>
<td>2.06</td>
<td>1.93±0.28</td>
<td>0.69±0.10</td>
</tr>
</tbody>
</table>

Table 4.5 DOC and BDOC values obtained by the different methods for river water.

<table>
<thead>
<tr>
<th>Method</th>
<th>DOC, mg/l</th>
<th>Mean DOC, mg/l±SD</th>
<th>BDOC, mg/l</th>
<th>Mean BDOC, mg/l±SD</th>
<th>(BDOC/DOC)×100 ±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.72</td>
<td>12.41</td>
<td>12.72</td>
<td>12.28±0.51</td>
<td>1.93±0.25</td>
</tr>
<tr>
<td>1a</td>
<td>12.05</td>
<td>11.80</td>
<td>12.02</td>
<td>11.96±0.14</td>
<td>1.85±0.10</td>
</tr>
<tr>
<td>2</td>
<td>11.32</td>
<td>11.62</td>
<td>11.61</td>
<td>11.52±0.17</td>
<td>1.87±0.10</td>
</tr>
<tr>
<td>2a</td>
<td>11.41</td>
<td>11.8</td>
<td>11.55</td>
<td>11.59±0.20</td>
<td>1.7±0.10</td>
</tr>
<tr>
<td>3</td>
<td>10.46</td>
<td>11.34</td>
<td>14.26</td>
<td>12.02±1.99</td>
<td>1.35±0.10</td>
</tr>
</tbody>
</table>

Table 4.6 DOC and BDOC values obtained by the different methods for a sodium acetate solution.

<table>
<thead>
<tr>
<th>Method</th>
<th>DOC, mg/l</th>
<th>Mean DOC, mg/l±SD</th>
<th>BDOC, mg/l</th>
<th>Mean BDOC, mg/l±SD</th>
<th>(BDOC/DOC)×100 ±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.804</td>
<td>5.923</td>
<td>5.699</td>
<td>5.81±0.11</td>
<td>5.487</td>
</tr>
<tr>
<td>1a</td>
<td>5.506</td>
<td>5.612</td>
<td>5.822</td>
<td>5.65±0.16</td>
<td>5.291</td>
</tr>
<tr>
<td>2</td>
<td>5.617</td>
<td>5.937</td>
<td>5.821</td>
<td>5.79±0.16</td>
<td>5.145</td>
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<tr>
<td>3</td>
<td>5.656</td>
<td>6.294</td>
<td>6.183</td>
<td>6.04±0.34</td>
<td>5.237</td>
</tr>
</tbody>
</table>

The kinetic analyses from the BDOC batch tests showed that the optimal time period is between 9 and 15 days. Shorter or longer periods will yield higher effluent DOC, i.e. lower BDOC values (Figure 4.4). Measurements of ATP in water and biofilm also showed that the highest activity of biomass was found in this period. The results are expressed as the mean values of three samples.
The DOC is higher in the river water, but the ratio of BDOC to DOC is higher in drinking water. Incubation period was 28 days for all methods.

Figure 4.4 DOC removal kinetics obtained in different BDOC batch tests with samples of acetate solution (A), drinking water (B), and river water (C).
4.2.4 Adaptation of BDOC column to changes of substrate

The experiments showed that before each measurement the water samples should be filtered through BDOC columns (with an EBCT of 2 hours) to adapt the biomass to different substrates. Figure 4.5 shows how the adaptation time affects the degradation of an acetate solution. After 6 hours of sample pumping the BDOC columns were well adapted, with a reduction in acetate concentration from 2 to about 0.3 mg/l. If the acetate concentration was 10 mg/l the column adoption period was about 1 day. After this period almost 100% of the acetate will be degraded by the BDOC column within an EBCT of 2 hours. Regardless of concentration the adaptation rate followed first-order kinetics.

Figure 4.5 Effects of bacteria adaptation times (0-24 hours) in BDOC columns used for degradation of 2 mg/l and 10 mg/l acetate solutions. The columns were initially used for measurement of BDOC in drinking water samples and then shifted to the acetate solution. The EBCT was 2 hours in all experiments.

4.2.5 Removal capacity of BDOC columns

The results showed that with adapted columns and DOC in the range of 0.5-7 mg/l, more than 90% of the easily degradable substances (acetate) are removed.
Table 4.7 Accuracy (Khan et al, 2003; 2005) of the BDOC determination relative to the DOC measurements for the acetate solution.

<table>
<thead>
<tr>
<th></th>
<th>DOC_in mg/l</th>
<th>DOC_in repeatability</th>
<th>DOC_out mg/l</th>
<th>DOC_out repeatability</th>
<th>Accuracy of BDOC/DOC_in</th>
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</thead>
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<tr>
<td>1</td>
<td>10.065</td>
<td>0.096</td>
<td>0.652</td>
<td>0.398</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>9.489</td>
<td>0.145</td>
<td>0.524</td>
<td>0.329</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
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<td>0.104</td>
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</tr>
<tr>
<td>4</td>
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<td>0.459</td>
<td>0.213</td>
<td>94</td>
</tr>
<tr>
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<td>0.487</td>
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<tr>
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<td>0.152</td>
<td>0.253</td>
<td>0.171</td>
<td>71</td>
</tr>
</tbody>
</table>

4.2.6 Conclusions about the applicability of BDOC methods

- Both batch and column BDOC methods generated similar results with respect to determination of BDOC concentrations
- The BDOC measurements period required in batch tests is within the range of 9-15 days
- The column method is much faster (about 2 hours) and therefore preferable
- Between measurements on different samples, the columns need to be adapted to the new substrate. Depending on the concentration and probably also the type of substrate the adaptation period needed for drinking water is about 6 hours
- The capacity of the BDOC columns exceeds 7 mg/l of easily degradable substrates (in 2 hours)
4.3 Resin fractionation of NOM

4.3.1 Methodology for NOM-fractionation

A rapid fractionation technique (RFT) developed by the Australia Water Quality Centre (AWQC) was used to characterize natural organic matter (NOM) (Fig. 4.6).

Figure 4.6 Scheme of the AWQC Rapid Fractionation Technique - RFT (Drikas 1999)

Recommendations for a 4-step RFT laboratory procedure are:

1) Pre-cleaning of virgin resins

   For all of the three applied resins DAX-8, XAD-4 and IRA-958:
   Clean the resins by mixing for 1 hr in HPLC grade methanol, then 1hr in HPLC grade acetonitrile, and finally 1hr in Milli-Q water. Resin fines have to be removed by decantation of the pre-cleaning solutions from the settled resins grains.

2) Running the sample (See Figure 4.6)

   Three 30 cm (length) x 15 mm internal diameter (ID) glass columns with DAX-8, XAD-4 and IRA-958 resins, respectively, are set up in series. The bed volumes should be 15 ml each. When the resins are not in use they must be kept in the columns; Sealed and with a reasonable amount of Milli-Q water head to maintain saturation. If a significant breakthrough occurs, the columns must be run through a full desorption/regeneration cycle again (Step 3), even if it was already done previously.
Filter 500 ml sample through a 0.45 um cellulose nitrate membrane filter. The filter must be washed with Milli-Q water (1000 ml) and sample (100 ml) before use.

**DAX-8**: Acidify the 500 ml filtered sample to pH 2 with HCl and pass it through the DAX-8 column at a rate of 3 ml/min (i.e. 0.2 bed volumes/min). Discard the first two bed volumes (30 ml) and collect the remaining effluent (470 ml). Collect a sub sample of 100 ml for DOC analysis.

**XAD-4**: The remaining effluent (370 ml) should be passed through the XAD-4 column at a rate of 3 ml/min. Discard the first two bed volumes (30 ml) and collect the remaining effluent (340 ml). Then collect a sub sample of 100 ml for DOC analysis.

**IRA-958**: Adjust the remaining effluent (240 ml) to pH 8 with NaOH and pump it through the IRA-958 column at a rate of 3 ml/min. Discard the two first bed volumes (30 ml) and collect the remaining effluent (210 ml) for DOC analysis.

Perform all pH adjustments using concentrated solutions to minimize dilution of the sample.

3) **Desorption and regeneration**

After each sample, desorption/ regeneration must be done for all the three resins. For DAX-8 and XAD-4 resins, use 0.1M NaOH for desorption, approximately 4 resin bed volumes (60 ml) at 0.2 bed volumes/minute (i.e. 3 ml/min). For regeneration use 0.1M HCl, same volume and flow as for NaOH.

Rinse with significant amounts of Milli-Q water between the acid and base solutions to prevent “salting out” due to reaction of the NaOH and HCl. Some more Milli-Q rinsing (60 ml) prior to running a sample is also recommended.

Being a strong anion exchange resin, IRA-958 requires stronger solutions and a chloride exchanger. Therefore 1M NaOH with 1M NaCl, and 1M HCl with 1M NaCl should be used with this resin. Again use 60 ml solution volumes and a flow through rate of 3 ml/min.

It is important to always use freshly made solutions to avoid DOC contamination. This is critical for maintaining good analysis performance and accuracy.

4) **Calculations**

\[ VHA = RAW - (DAX-8 \text{ effluent}) \]
SHA = (DAX-8 effluent) – (XAD-4 effluent)  
CHA = (XAD-4 effluent) – (IRA-958 effluent)  
NEU = IRA effluent

VHA = very hydrophobic acids  
SHA = slightly hydrophobic acids  
CHA = hydrophilic charged substances  
NEU = hydrophilic neutrals

4.3.2 Results for comparison of NOM-fractionation

For comparison, NOM-fractionation was performed by two laboratories (RTU and SINTEF) using the same procedures and experimental setup. A standard humic acid solution with a concentration of about 3 mg C/l was used. Results were rather comparable (Fig. 4.7), although the effects on DOC of a pH reduction to pH 2 were different. Our experience shows that rinsing of the columns between the samples is crucial for repeatability of results.

In addition to the standard humic acid solution, NOM-fractionation was also done for an acetate solution (Figure 4.8). Results were reasonable, with humic substances predominantly identified as very hydrophobic acids (VHA), and the acetate solution mainly identified as hydrophilic neutral (NEU) fractions.

Figure 4.7 Comparison between rapid NOM fractionation results obtained at RTU and SINTEF with a standard humic acid solution.
Figure 4.8 NOM fractionation results for a standard humic acid, for acetate, and for a mixture of both. VHA - very hydrophobic acids, SHA - slightly hydrophobic acids, CHA - hydrophilic charged, NEU - hydrophilic neutral
5 Results from pilot and full-scale optimisation studies

5.1 Process design and performance at Daugava WTP

Daugava water treatment plant (Fig. 5.1) is the largest plant in Latvia supplying about 50% of the drinking water for Riga city. The plant takes water from the River Daugava (from the reservoir of Riga hydroelectric power station). Upstream of the intake several villages and cities are located (in Russia, Belarusia and Latvia), therefore the raw water is influenced by wastewater discharges. To reduce the pollution risk of the drinking water the treatment process was upgraded with two stage ozonation in 2001. The watershed of the River Daugava is largely covered with swamps and forests; therefore, water in the river contains a high amount of humic substances (NOM). During a study period in 2006-2007 the concentration of DOC in the river varied between 9 and 26 mg/L. The average DOC concentration in River Daugava is close to 15 mg/l, and pH is within the range of 7.1-8.2, alkalinity 1.5-3 meq/L, and total hardness 2-3.5 meq/L.

To increase DOC removal and biostability, biofilters have been installed after the main ozonation (2nd stage ozonation). Ozone is also used prior to coagulation.

Figure 5.1 Process scheme of the Daugava water treatment plant in Riga. Newly added treatment steps are shown in red.

1- water intake; 2- ozonation; 3- coagulation (alum); 4- sedimentation; 5- pH correction; 6- filtration; 7- ozonation; 8- aeration; 9- biofiltration; 10- pH correction; 11- final disinfection; 12- clean water reservoir

About 50-60% of the DOC is removed by coagulation. Further removal of DOC in the biofilters is not occurring (Juhna and Rubulis, 2004).

The coagulant doses are in the range of 10-22 mg/l as Al₂O₃ (i.e. 5.2-11.4 mg Al/L. The average specific dosage is close to 0.5, with variations in the range of 0.44-0.58 mg Al/mg DOC. Ca(OH)₂ is used for pH-control after the sedimentation step, but no pH adjustment is possible before coagulant
addition. The coagulation pH is therefore within the range of pH 6.7-7.7. This is high compared to the pH level normally used in optimum enhanced alum coagulation applications.

The specific dosage applied at Daugava WTP falls within the lower range of TOC-specific alum coagulant dosages (i.e. mg Al per mg TOC) applied in American raw waters as presented by Archer and Singer (2006) on the basis of the Information Collection Rule (ICR) database. The mean value for the 1571 U.S. records was 0.7 mg Al/mg TOC (See Figure 3.5). Some of the variability of the specific coagulant dosage is related to high alkalinity raw waters, which is also the case at Daugava WTP. Because of the lack of pH control and the high pH of coagulation (7.1-8.2), the specific dose level seems relatively low. Therefore, future experiments will investigate the effects of decreased coagulation pH (i.e. pH control) and increased coagulant doses.

Parsons et al (2007) presented the relationship shown in Figure 5.2 between coagulant dose and raw water DOC concentration. The figure was based on results from Bell-Ajy et al. 2000; Singer and Bilyk, 2002; Volk et al. 2000; Croué et al. 1993; Owen et al. 1993; and Crozes et al. 1995). Although not specified, it is assumed that Figure 5.2 is valid for alum coagulation. Parsons et al (2007) further reported that the more hydrophilic water sources with SUVA values less than 3 achieved only 11-20 % DOC removal, while the more hydrophobic raw waters that realized greater than 70 % DOC removal tend to have SUVA values of 4.5 L m⁻¹ mg⁻¹ or above (See Fig. 2.3).

From Figure 5.2, the predicted coagulant dose range for Daugava WTP with a raw water DOC of 10 to more than 20 mg/L, falls within the range of 80 to more than 160 mg/L of alum, i.e. from about 7 to more than 15 mg Al/L.

Based on the results in Figures 3.5 and 5.2 and the fact that Daugava raw water is high in alkalinity and because no pH control is implemented in the coagulation step, the average alum dose range of about 0.5 mg Al/mg DOC (i.e. about 7.5 mg Al/L for a DOC of 15 mg/L) is considered low. For the highest raw water DOC levels (>20 mg/l), the applied coagulant dose level (11.4 mg Al/L) are significantly below what is considered the optimal enhanced coagulation conditions.
During ozonation, the humic substances are oxidized (split) which results in a significant reduction of UV\textsubscript{abs} and an increase of the BDOC value to 1-2 mg/L. The DOC concentration after treatment is in range of 2-8 mg/L, which is considered as high. As a result of this, chlorine consumption is high and there are bacterial regrowth problems in the distribution network.

It is reported that ozonation prior to coagulation may be detrimental to NOM removal by coagulation and may also increase residual aluminium concentrations (Bose and Reckhow, 2007). Eikebrokk (1995) tested the effect of preozonation on contact filtration. Preozonation in the range of 0.1-1 mg O\textsubscript{3}/mg TOC did not effect process performance significantly, but tended to increase residual coagulant concentrations and thus also coagulant demand.

DOC concentration was monitored at several water treatment steps. The results presented in Figure 5.3 show that the DOC levels in Daugava River vary significantly between seasons. The highest DOC concentration was observed in the autumn. Primary ozonation did not change DOC level significantly. During coagulation, sedimentation and filtration about 63% of DOC was removed on average. From statistical analyses the additional removal of DOC obtained in the subsequent treatment steps was not found to be significant.
Figure 5.3 Data from monitoring of DOC over a period of more than one year at Daugava WTP. Legend: RW-raw water, OZ-primary ozonated water, RF-after coagulation and rapid filtration, 2OZ-after main ozonation, DW-drinking water.

The UV absorbing fractions of NOM (Abs254), were effectively removed (80%) during coagulation and filtration (Fig. 5.4). Abs254 (UV-abs) was found to correlate well with Abs410 (colour) as shown in Figure 5.5.

Figure 5.4 Data from monitoring of UV-abs (ABS254) over a period of more than one year. Legend: RW-raw water, OZ-primary ozonated water, RF-after coagulation and rapid filtration, 2OZ-after main ozonation, DW-drinking water.
SUVA fluctuated significantly during the study period (data not shown), with an average value of 4.2 L mg⁻¹ m⁻¹, which indicate good treatability by coagulation (See Table 2.1 and Figure 2.2). From the results in Figure 2.2 and the average SUVA of 4.2 L mg⁻¹ m⁻¹, DOC removal efficiencies of 50-80 % should be achievable at Daugava WTP, thus indicating the presence of an optimisation potential.

The primary ozonation step did not change SUVA significantly (Fig. 5.6), whereas the main decrease in SUVA occurred in the coagulation/filtration and in the second (main) ozonation step.
NOM fractionation of water from the different treatment steps of Daugava WTP in October and December 2007 showed that the hydrophobic VHA and SHA fractions were removed from 4-6 mg/l in the raw water to about 1 mg/l and from 2-4 mg/l to about 1-2 mg/l, respectively during ozonation, coagulation and filtration. The hydrophilic CHA fraction was removed almost completely (< 0.5 mg/L) while the hydrophilic NEU fraction of DOC increased significantly during treatment to levels of 3-4 mg/l (Fig. 5.7). The hypothesis that the NEU fraction increase may be an indication of coagulant under-dosage will be tested in further experiments.

![Figure 5.7 Concentration changes of the different NOM fractions of DOC (mg/L) during full-scale treatment at Daugava WTP in October (upper) and December 2007. Legend: 1- raw water sample, 2- sample after ozonation (4 mg/l), 3- sample after coagulation, sedimentation and filtration, 4- sample after secondary ozonation, 5- drinking water sample., VHA - very hydrophobic acids, SHA - slightly hydrophobic acids, CHA - hydrophilic charged, NEU - hydrophilic neutrals.](image-url)
The relatively low VHA fraction removal obtained at Daugava WTP may be caused by two major factors: 1) Sub-optimum coagulant doses given the high pH during coagulation (no pH control), and 2) preozonation.

Coagulant dose requirements are discussed above. Regarding preozonation, Liu et al (2006) studied the effects of pre-ozonation on organic matter removal by coagulation. With AlCl₃, the coagulation efficiency was significantly deteriorated as a result of pre-ozonation (retardation of floc formation, decreased removal of turbidity, DOC, and UV₂₅₄. When PACl was used for coagulation, the adverse effects of pre-ozonation was mitigated, particularly when the specific ozone dosage was less than 0.69 mg O₃/mg TOC. From the differences between the UV₂₅₄ and DOC removals, the results indicated that pre-ozonation changed the molecular structure of the organic matter. However, the mineralization capacity of ozone was not remarkable. Only 5 % or so of DOC was removed as a result of mineralization at 0.6-0.8 mg/L of ozone alone. Fractionation results showed that the organic material was more low molecular weight and more hydrophilic after pre-ozonation, thus impairing the removal of DOC in the following coagulation.

Also Bose and Reckhow (2007) studied the effects of preozonation and enhanced coagulation studies on separate NOM fractions and concluded that preozonation of the humic and fulvic acid fractions resulted in a decline in the ability to adsorb to aluminium hydroxide surfaces. For the hydrophilic neutral fraction, however, preozonation increased the ability of this fraction to adsorb. Thus, preozonation of the tested raw water resulted in a progressive decline in DOC removal by alum coagulation with increasing ozone doses. Ozonation of pre-coagulated water demonstrated the beneficial effects of ozonation on the removal of non-humic NOM through alum coagulation. Therefore, a staged coagulation process was proposed with intermediate ozonation for waters containing both humic and non-humic NOM for maximum DOC and SUVA removal.

Since Daugava River contains both humic and non-humic NOM fractions, the application of ozonation prior to coagulation may therefore be questionable. Further testing will be performed to address this issue.

To confirm validity of the fractionation results presented in Figure 5.7, samples were also analysed with LCD-OCD chromatography for detection of the molecular size of DOC. The results (Fig. 5.8) showed a good correlation between humic substance concentration measurements based of surface properties (VHA and SHA detection with DOC-fractionation) and molecular size (LC-OCD methods).
Figure 5.8 Correlation of humic substance concentration analysis from XAD fractionation (i.e. surface properties/hydrophobicity) and from molecular size analysis (LC-OCD performed by TZW, Dresden)

Additional NOM-fractionation showed that the composition of NOM in raw and finished water varied significantly over the one year sampling period (Figure 5.9). Samples were taken during summer, autumn and winter conditions.

Figure 9 also shows that the VHA and SHA fraction concentration in raw water varied significantly over the year. These fractions are mainly represented by humic substances, implying that NOM changes in source water are mainly due to changes in the content of humic substances. Unlike the situation in raw water, the NEU and CHA fractions showed the greatest variability in the finished drinking water samples. Fractions of NEU were increasing while CHA were decreasing during late autumn and winter. We hypothesised that this phenomenon could be explained by a decrease in biological activity due to the decrease in temperature (see Figure 5.17). This in turn could result in less degradations of NEU and increased concentration of this fraction in drinking water. In summer, apparently the degradation was more effective and it appears that NEU is transferred to CHA.

To test this hypothesis samples from several sites water treatment steps were filtered through BDOC detection columns (detection time 2 hours) and humic fractions were analyses before and after filtration. Results clearly showed (Figure 5.10) that filtration through the biologically active column NEU fractions were transformed into CHA fractions. It is not clear from this study, what substances are degraded and what substances are produced in this process, but it appears that NEU and CHA could potentially be used for better understating of water treatment processes for NOM removal. Namely, NEU indicate easily available substrate but CHA represent more recalcitrant
substances and products of biological degradation. In further studies these hypothesis will be will examined.

Figure 5.9 Seasonal changes in NOM fraction concentrations of DOC (mg/L) in finished drinking water (C), and raw water samples (D) at Daugava WTP. VHA - very hydrophobic acids, SHA - slightly hydrophobic acids, CHA - hydrophilic charged, NEU - hydrophilic neutral.
Figure 5.10 Changes in XAD fraction during water filtration of water samples from different sites of Daugava WTP before (A) and after (B) filtration though biologically active column (matured BDOC detection column treatment with detection time of 2 hours). Legend: 1- raw water sample, 2- sample after ozonation (4 mg/l), 3- sample after coagulation, sedimentation and filtration, 4- sample after secondary ozonation, 5- drinking water sample. VHA - very hydrophobic acids, SHA - slightly hydrophobic acids, CHA - hydrophilic charged, NEU - hydrophilic neutral.
5.2 Enhanced coagulation optimisation studies at Daugava WTP

5.2.1 Aim of the experiments
To evaluate the effects of pre-ozonation and changes in coagulation-pH and coagulant dosage on TOC removal efficiency and process performance, a coagulation optimization procedure (i.e. identification of a “coagulation profile”) was performed in accordance with the approach described before.

As an initial step, a number of jar-tests were carried out at Daugava WTP in the winter-spring period. In total about 20 samples were taken from raw water and from pre-ozonated (4 mg O$_3$/l) water (i.e. after the primary ozonation step) and brought to the lab for analysis.

5.2.2 Methodology used in the experiments
The following jar test procedure was used. The jar was filled with sample and pH was adjusted by addition of concentrated acid (HCl). Coagulant was added and the water was rapidly mixed in 1 minute, then slowly mixed (flocculated) for 30 minutes, and finally left for sedimentation in 60 minutes. Samples were taken from the top section of the jar and analysed with or without 0.45 µm membrane prefiltration to obtain results for dissolved and total fractions, respectively.

5.2.3 Results from enhanced coagulation experiments
Results of the experiments are summarised in Figures 5.11-5.16. As shown in Fig. 5.11 the best TOC removal was observed within a pH-range of 5.5-6.

With the low coagulant dose level of 10 mg/l of Al$_2$O$_3$ (i.e. 5.3 mg Al/L) pre-ozonation increased TOC removal efficiency from 40 to 50%. The difference was less pronounced at higher coagulant dose levels such as 15 mg Al$_2$O$_3$/l (8 mg Al/L), when removal efficiency at pH of 5.5 was 50-60% for both pre-ozonated and non-ozonated waters.

True colour removal was higher in pre-ozonated water, independent of coagulant dose and pH within the optimum range (5.5-6.0) (Fig. 5.12). It should be noted here that the coagulant doses applied may be sub-optimal, and that most of the colour was probably removed as a result of ozonation and correspondent splitting of aromatic rings of TOC. However, with the high alkalinity (1.5-3 meqv/L) and calcium content (1-2.5 mmol/L) of the Daugava water supplementary effects may be obtained from ozone-induced coagulation (micro-flocculation) mechanisms. Further experiments will be performed to study this matter, also with the use of elevated coagulant doses.

Removal of total turbidity (Fig. 5.14) increased with increasing pH in the range tested, however removal of dissolved turbidity (i.e. due to particles < 0.45 µm) was more effective in the pH range of 5.5-6 (Fig. 5.15).
Figure 5.11 Effects of coagulation pH and coagulant dose levels (as Al₂O₃) on TOC removal in coagulated raw water (A), and coagulated pre-ozonated water (B). Values are averages from about 20 measurements in the winter-spring (cold water) season.

Figure 5.12 Effects of pH and coagulant dose levels on true colour (dissolved) concentrations in treated raw water (A) and ozonated water (B). Values are average values from about 20 measurements in the winter-spring season.

Figure 5.13 Effects of coagulation pH and coagulant dose levels on turbidity after coagulation of raw water (A) and ozonated water (B). Values are average values from about 20 measurements in winter-spring season.
Removal of turbidity was slightly better in coagulated pre-ozonated water than in coagulated raw water.

Figure 5.14 Effects of pH and coagulant dose levels on dissolved turbidity after coagulation of raw water (A) and ozonated water (B). Values are average values from about 20 measurements in the winter-spring season.

Lowering of the coagulation pH to values of 5.5-6.0 significantly increased the total aluminium concentrations for both raw and pre-ozonated water (Fig. 5.15). Pre-ozonation did not significantly affect the residual total or dissolved aluminium concentrations (Fig. 5.16).

From an overall evaluation of the results, a pH around 6.0 seems optimal. However, residual aluminium coagulant concentrations remain high at all pH-values tested. This may be an indication of sub-optimal coagulant dose levels. Therefore, higher coagulant dose levels will be tested in the next experimental stages.

Figure 5.15 Effects of pH and coagulant dose levels on total aluminium concentrations in coagulated raw (A) and pre-ozonated waters (B). Values are averages from about 20 measurements in the winter-spring season.
Preliminary conclusions from Daugava enhanced coagulation experiments

With the coagulant dose levels used during the jar tests, the optimum pH is about 6.0 based on an evaluation of the overall results. This is significantly below the coagulation pH applied today at Daugava WTP (pH 6.7-7.7). However, there are indications that the applied coagulant doses are still below optimum levels. Higher doses will yield better results and normally also extend the optimum pH-window. This should be further tested at the full-scale Daugava WTP in accordance with the proposed enhanced coagulation optimization procedures.

Pre-ozonation did not seem to affect enhanced coagulation performance significantly within the range of process conditions tested here (i.e. coagulant dose and pH), although some beneficial effects were observed for some of the parameters. This is likely an effect of ozone-induced micro-flocculation obtained with the relatively hard and high alkalinity Daugava water. With higher coagulant doses, it is likely that the effects of pre-ozonation on the overall process performance will be reduced.

The effects of treatment on DOC removal was further investigated by studying changes of NOM composition (DOC fractions) during the treatment process at Daugava WTP. The results (Figure 5.17) showed that a limited removal of DOC was achieved after pre-ozonation, coagulation, sedimentation and filtration. The VHA and CHA fractions were both reduced, the SHA fraction remained relatively unchanged while the NEU fraction increased. The secondary (main) ozonation however, seemed to decrease significantly the DOC, VHA and CHA fraction concentrations. In finished drinking water however, the NEU fraction increased significantly, indicating the existence of a significant regrowth potential.
In summary, the results from the initial Daugava enhanced coagulation optimization efforts indicate that better coagulation performance can be achieved by the application of a strict pH control and elevated coagulant dose levels. From the jar-test results pre-ozonation did not seem to have any significant effect on DOC removal. The application of ozonation prior to coagulation at Daugava WTP will however be further investigated. Specific attention will be put on the possible detrimental effects of preozonation on VHA and SHA fraction removals which tend to be low during coagulation at Daugava WTP. The high NEU fraction concentration in finished drinking water is also a concern, because it may represent a problem with respect to regrowth in the distribution system.
5.3 Ozonation-biofiltration optimisation studies at Daugava WTP

5.3.1 Removal of DOC in pilot BAC experiments at Daugava WTP

The pilot plant consisted of 3 columns filled with the same depth (1.8 m) and type of media as in full scale plant (Fig. 5.18). A subflow of water was directed from the inflow of the full-scale BAC filters at Daugava WTP to the pilot columns. Filtration rate was similar for all the full scale and pilot scale columns. The pilot plant was operated for more than 6 months in order to reach the same condition as in the full scale BAC filters.

Both in the full-scale plant and in the pilot plant removal of DOC and BDOC was very low (see Fig. 5.19-5.21, and Fig.5.23). AOC and phosphorus (MAP) removal was close to 50% (Fig. 5.22).

During the first four months of experiments (December 2006-April 2007) water temperatures were below 5 °C. Then it started to increase constantly (Fig. 5.23). In July 2007 a temperature level of about 20 °C was reached. This facilitated bacteria development as indicated by the ATP increase (Fig. 5.24). The positive effect of temperature on biomass development was reflected in the correlation between ATP and temperature as shown in Fig. 5.25.

Figure 5.18 Scheme of the biofiltration pilot plant at Daugava WTP.
Figure 5.19  Biofilter inflow and effluent DOC concentrations in the Daugava pilot and full scale treatment plants.

Figure 5.20 Influent and effluent DOC concentrations in the full-scale BAC filters at Daugava WTP.
Figure 5.21 Average inlet and outlet DOC concentrations in the 3 biofilter pilot columns (A) (data from 6 months), and in the full scale Daugava WTP (B).

Figure 5.22 Changes in MAP (A) and AOC concentrations (B) during biofiltration in the Daugava pilot at different times. Error bars shows the standard deviation from average values for the 3 columns.
Figure 5.23 Changes in BDOC concentrations during the full-scale Daugava WTP treatment train in June and July, 2007. Legend: RW-raw water, OZ-primary ozonated water, RF-after coagulation, sedimentation and rapid filtration, 2OZ-after main ozonation, DW-drinking water.

Figure 5.24 Temperature, pH and red-ox potential of inflow water to the Daugava BAC pilot plant over a test period of about 6 months.
Figure 5.25 ATP concentration of inflow water to the Daugava BAC pilot plant over a test period of about 6 months.

Figure 5.26 Correlation between inflow water temperature and ATP concentration (average values from 3 columns) in the Daugava biofilter pilot plant.

Measurements of ATP levels at different depth in the biofilter columns indicate an exponential decrease of ATP level with depth (Figure 5.27)
Figure 5.27  ATP concentrations at different filter depths in the Daugava pilot biofilter columns.

5.3.2  Development of an operational BAC model

Based on the results an operational biofiltration model was developed (SIMBIO - Simple Operational Model for BIOfilters).

The model is based on the following assumptions:

- Substrate consumption is not limited by biofilm diffusion
- Degradation takes place only in the biofilm
- Biomass is equally distributed in the media
- No adsorption of DOC takes place

The SOMBIOS model predicts BDOC removal efficiency in the filter depending on biomass, temperature and loading rate.

The effluent BDOC concentration and thus the removal efficiency is dependent on the BDOC consumption rate and the BDOC inflow concentration (load):

\[ BDOC_{out} = S_{in} \left(1 - \frac{q_s}{L} \right) = S_{in} - \frac{q_s w}{Q_w} \]

where:
- \( S_{in} \) - BDOC inflow concentration
- \( q_s \) - BDOC consumption rate
- \( w \) - weight of the sorbent
- \( Q_w \) - flow
- \( L \) - BDOC loading rate

The weight of the sorbent is needed in order to calculate the accumulated biomass per volume.
The BDOC consumption rate is dependent upon the biomass growth rate, thus on temperature:

\[
\mu = \frac{S \mu}{S + K_S} FT
\]

\[
FT = e^{\frac{\left( T_{opt} - T \right)^2}{\left( T_{opt} - T_i \right)^2}} \left( \frac{20 - T}{20 + T - 2T_{opt}} \right) e^{\left( T_{opt} - T_i \right)^2}
\]

\[
\mu \text{ - maximal growth rate of bacteria } 0.2 \text{ h}^{-1},
\]

\[
K_S \text{ - Monod half saturation constant}
\]

\[
T \text{ - temperature}
\]

\[
FT \text{ - correction factor for temperature}
\]

The biomass distribution in the column is assumed exponential:

\[
B = \int X(h) dm = \frac{AX_0 \rho}{k} (1 - \exp(-kh))
\]

The model was developed for Windows Excel environment with (macros) iteration options (see Figure 5.28).

To use the model for prediction of BDOC removal some data input is needed:

(a) ATP measurements in the filter (upper 10-30 cm)
(b) BDOC concentration in the column inflow.

Before use the models should be verified against BDOC columns in which BDOC measurements are done.
Model for BDOC removal in BAC (steady state)

<table>
<thead>
<tr>
<th>Parameter/Input value</th>
<th>Symbol</th>
<th>Unit</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter Diameter of column</td>
<td>d</td>
<td>m</td>
<td>0.03</td>
</tr>
<tr>
<td>Height of the column</td>
<td>h</td>
<td>m</td>
<td>1.80</td>
</tr>
<tr>
<td>Porosity</td>
<td>ε</td>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td>Flow yield</td>
<td>Qw</td>
<td>m³/h</td>
<td>0.00024</td>
</tr>
<tr>
<td>Retention time</td>
<td>t</td>
<td>h</td>
<td>12.0637</td>
</tr>
<tr>
<td>Density of sorbent</td>
<td>p</td>
<td>g/m³</td>
<td>500000</td>
</tr>
<tr>
<td>Weight of sorbent</td>
<td>w</td>
<td>kg</td>
<td>362</td>
</tr>
<tr>
<td>Volume of the column</td>
<td>V</td>
<td>m³</td>
<td>0.00145</td>
</tr>
<tr>
<td>Biomass Maximum growth rate</td>
<td>µmax</td>
<td>h⁻¹</td>
<td>0.20</td>
</tr>
<tr>
<td>Monod half saturation constant</td>
<td>Ks</td>
<td>mg/l</td>
<td>0.4</td>
</tr>
<tr>
<td>Number of bacteria that are contained in each mg of organic carbon in cell biomass</td>
<td>b</td>
<td>cell/g</td>
<td>1.00E+06</td>
</tr>
<tr>
<td>Concentration of bacteria per gram of sorbent</td>
<td>X0</td>
<td>cell/GAC</td>
<td>6.50E+06</td>
</tr>
<tr>
<td>First order constant</td>
<td>k</td>
<td>m⁻¹</td>
<td>1.21E+00</td>
</tr>
<tr>
<td>Fraction of dead biomass converted to BDOC</td>
<td>κ</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Growth rate</td>
<td>µ</td>
<td>h⁻¹</td>
<td>0.17</td>
</tr>
<tr>
<td>Accumulative bacteria mass in filter</td>
<td>B</td>
<td>cell</td>
<td>9.53E+08</td>
</tr>
<tr>
<td>Accumulative bacteria mass in filter</td>
<td>B</td>
<td>cell</td>
<td>2.39E+09</td>
</tr>
<tr>
<td>Temperature</td>
<td>T</td>
<td>°C</td>
<td>20</td>
</tr>
<tr>
<td>Temperature shape parameter</td>
<td>Ti</td>
<td>°C</td>
<td>40</td>
</tr>
<tr>
<td>Temperature correction function</td>
<td>FT</td>
<td></td>
<td>1.00</td>
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<tr>
<td>Substrate BDOC input concentration</td>
<td>Sm</td>
<td>mg/l</td>
<td>2.00</td>
</tr>
<tr>
<td>Capacity of degradation</td>
<td>C</td>
<td>mg Chol/l</td>
<td>4.73</td>
</tr>
<tr>
<td>BDOC consumption rate (substrate uptake)</td>
<td>qB</td>
<td>mg C/h</td>
<td>1.08E-03</td>
</tr>
<tr>
<td>BDOC load</td>
<td>L</td>
<td>mg C/h</td>
<td>0.46</td>
</tr>
<tr>
<td>BDOC out</td>
<td>S</td>
<td>mg/l</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Figure 5.28 Algorithm (a) and EXCEL interface (b) used in the model.
5.4 Optimization studies at VIVA pilot, Trondheim WTP

A flow sheet of the pilot at VIVA WTP in Trondheim, Norway is shown in Figure 5.29 below. The pilot contains three parallel process trains: 1) alkaline filtration, 2) ozonation-biofiltration, and 3) enhanced coagulation-contact filtration. In the first experimental stages, an iron-based coagulant (PIX) is applied in the enhanced coagulation studies. This is due to the fact that this coagulant works well at low pH conditions (i.e. pH 4-5), which is ideal for a rapid dissolution (i.e. low contact time requirements) of the calcium carbonate filter material (for the purpose of corrosion control). Later, chitosan and/or alum coagulants may be candidates for further testing.

Figure 5.29 VIVA WTP pilot process sheet, showing the three different water treatment trains: 1) alkaline filtration (reference), 2) ozonation-biofiltration, and 3) enhanced coagulation-contact filtration.

5.4.1 Rapid NOM fractionation at VIVA WTP

Rapid NOM fractionation was performed on raw water from Trondheim (VIVA WTP) according to the procedures described before. The results (Lake Jonsvatnet) are presented in Figure 5.30. For comparison, the results from two pristine lakes (Storvatnet and Stolsvatnet) located in Southern Norway are included as well.

The fractionation results indicate that NOM from VIVA WTP is dominated by the hydrophobic humic fractions (VHA and SHA). Thus, good treatability by coagulation should be expected. The hydrophilic NEU fraction, that is not amendable to removal by coagulation, is relatively low, thus indicating a limited regrowth potential in this raw water.
The high percentage of the VHA and SHA fractions (75-80 %) also indicates that ozonation is required in order to provide a good overall biodegradability if biofiltration processes is used for treatment of this water.

Figure 5.30 Absolute concentrations (upper) and distribution (%) among the various NOM fractions obtained from simplified DOC fractionation analysis of three Norwegian raw water sources: Lake Jonsvatnet (i.e. VIVA WTP raw water), Lake Stølsvatnet and Lake Storvatnet.

5.4.2 Enhanced coagulation optimization studies at VIVA WTP

Initial optimization experiments were performed according to the enhanced coagulation optimization procedures described before. Results from the initial optimization trials (i.e. identification of enhanced coagulation profiles) are presented in the Figures 5.31-5.34 below. Raw water quality during the test period was in the range of 0.1-0.4 NTU; 13-15 mg Pt/L; 9.3-10.2 m⁻¹; 2.6-3.0 mg/L; and 3.1-3.8 Lm⁻¹mg⁻¹ for turbidity, colour, UV-abs, DOC and SUVA, respectively. The optimization tests were performed with a constant filtration rate of 10.2 m/h. Hydrochloric acid and CO₂ was used for pH and corrosion control purposes.
Figure 5.31 On-line (red) and lab-analysed (blue) filter effluent turbidity data obtained with different coagulation pH (4.2.5.2) and coagulant dosage levels (1.5-3 mg Fe/L as PIX113) during pilot-scale optimization trials at VIVA WTP, Trondheim Norway.

Figure 5.32 True colour (upper) and UV-abs removal efficiencies obtained with different coagulation pH and coagulant (Fe) dosage levels during pilot-scale optimization trials at VIVA WTP, Trondheim Norway.
Figure 5.33  DOC (upper) and SUVA removal efficiencies obtained at different coagulation pH and coagulant (Fe) dosage levels during pilot-scale optimization trials at VIVA WTP, Trondheim Norway.

Figure 5.34 Residual Fe concentrations obtained at different coagulation pH and coagulant (Fe) dosage levels during pilot-scale optimization trials at VIVA WTP, Trondheim, Norway.

Figure 5.35 shows the effects of coagulation pH and coagulant dose levels on coagulated water zeta potentials. By comparing the results in Figure 5.35 with the results in Figures 5.32 and 5.33, best performance (i.e. best colour, UV-abs and DOC removal) seems to be achieved with low zeta potentials in the range of -8 to +8 mV. This agrees well with the findings of Parsons et al (2007), who concluded from pilot and full-scale studies that good alum and ferric coagulation performance and minimized DOC residuals was obtained at low zeta potentials in coagulated water. Although the exact range of optimal zeta potentials...
potentials appears site specific, they reported that best results were normally obtained within the range of -10 to +3 mV (Figure 5.36).

Figure 5.35 Effects of coagulation pH and coagulant dose (1.5-3 mg Fe/L as PIX) on coagulated water zeta potential. Results obtained during pilot-scale optimization trials at VIVA WTP, Trondheim, Norway.

Figure 5.36 Effects of zeta potential on DOC removal performance (i.e. DOC residuals) obtained with ferric sulphate coagulation at pH 3-7 at two WTPs: 1) Albert WTP: 6.6-9.7 mg DOC/L; 16.5-24.3 mg Fe/L., and 2) Bamford WTP: 4.5-10.2 mg DOC/L; 11.3-25.5 mg Fe/L (Parsons et al 2007).

The studies of Parsons et al (2007) further revealed significant differences in zeta potential between the hydrophobic and hydrophilic fractions when pH was varied within the range of 1-9 (Figure 5.37). The two hydrophobic fractions showed great variability (from +5 to – 25 mV) and profiles similar to the tested raw water at Albert WTP. The hydrophilic fractions however, had more stable zeta potentials within the range of ±5 mV for all the tested pH values.
Figure 5.37 Zeta potentials for a range of pH values for different NOM fractions. Albert WTP, April 2002 samples (Parsons et al 2007).

A strong relationship between the residual DOC and the initial hydrophilic non-acid fraction (HPHNA) of NOM were also identified (Figure 5.38). Even if coagulation is able to remove some hydrophilic NOM, the concentration of the hydrophilic NOM fraction may be a good indicator of the amount of DOC recalcitrant to removal by coagulation. On the other hand the hydrophobic fraction may be used as a good indicator of the amount of DOC that can be removed by coagulation.

Figure 5.38 Effects of initial hydrophilic non-acid NOM fraction concentration on residual DOC at three sites (Parsons et al 2007).

It is however evident from the above results, that although helpful in studying coagulation mechanisms, zeta potential measurements do not seem very applicable for NOM removal predictions or for the purpose of coagulation process control. For low turbidity raw waters with low to moderate NOM content and thus limited coagulant dose requirements, solids concentration in coagulated water may also be too low for zeta potential measurements to apply.
For the purpose of operation optimisation, NOM fractionation techniques seem very interesting. Thus predictions of NOM fractions amendable to removal by coagulation can be made from measurements of the HAF/VHA, FAF/SHA, HPIA/CHA fractions of DOC, while predictions of DOC recalcitrant to removal by coagulation can be made from the HPINA/NEU fractions of DOC.

5.4.3 Seasonal variability

The seasonal variation in NOM fraction concentration in raw waters may be significant (Figure 5.39). Thus, treatability and coagulant demand among the different NOM fractions may also show significant variability (Figure 5.40).

Figure 5.39 Seasonal variations in raw water NOM fraction make-up at Albert WTP expressed as DOC concentrations (upper) and as a percentage of the total DOC concentration (Parsons et al 2007).
Figure 5.40 Percentage removal of DOC fractions by alum coagulation at pH 6 from Australian raw waters: a) Mt.Zero, and b) Moorabool (van Leeuwen et al 2002).

The figures presented above illustrate well the need for improvements in the current process control and optimisation practices. In addition to the seasonal variability in DOC concentration, NOM fraction concentrations, coagulant demand and DOC removal efficiency may vary significantly over the year as illustrated in Table 5.1. Therefore it may not be sufficient to control the coagulation process from on-line measurements of DOC (or colour or UV-abs). NOM fractionation and/or zeta potential measurements may also be implemented in future operation strategies.

Table 6.1 Seasonal variations in raw water NOM concentrations, coagulant dose demand and DOC removal obtained from coagulation investigations of raw waters from Albert WTP, UK (Parsons et al 2007).

<table>
<thead>
<tr>
<th>Seasonal water</th>
<th>DOC (mg.L⁻¹ as C)</th>
<th>UV₂₅₄ (m⁻¹)</th>
<th>SUVA (L·mg⁻¹·m)</th>
<th>Coagulant dose (mg.L⁻¹ Fe)</th>
<th>DOC removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>11.4</td>
<td>52.6</td>
<td>4.6</td>
<td>14.4</td>
<td>81</td>
</tr>
<tr>
<td>Summer</td>
<td>8.9</td>
<td>50.8</td>
<td>5.7</td>
<td>8.0</td>
<td>88</td>
</tr>
<tr>
<td>Autumn</td>
<td>10.2</td>
<td>60.2</td>
<td>5.9</td>
<td>12.2</td>
<td>75</td>
</tr>
<tr>
<td>Winter</td>
<td>9.2</td>
<td>40.1</td>
<td>4.4</td>
<td>10.0</td>
<td>63</td>
</tr>
</tbody>
</table>

Based upon an evaluation of the overall results obtained with a ferric coagulant (PIX-113) at the VIVA pilot, a coagulant dosage of 2.0 mg Fe/L and a pH of 4.5 were taken as the optimal coagulation conditions for this coagulant and this raw water. The identified optimal coagulation conditions will be employed in future filtration optimization experiments (i.e. identification of the optimal “filtration profile”). Extended NOM fractionation investigations are also included in the future activities, using raw and treated waters from Trondheim and other end-users (the cities of Riga, Bergen, etc.)
5.5 Full-scale optimization trials at Skullerud WTP, Norway

Skullerud WTP (Fig. 5.41) is a direct filtration plant with a treatment capacity of 1800 m$^3$/hr in two parallel lines. The treatment includes alum coagulation at pH about 6, flocculation (2 units), and filtration in 3M filters (3 units per line). A non-ionic polyacryl amid is used as a filter aid in small quantities (0.1 mg/L). This polymer is also used in the spent backwash water/sludge treatment process. The 3-M filter bed has an upper layer of 3-3.5 mm low density PE granules, a second layer of 2-2.5 mm high density PE granules, and a bottom layer of 0.8-1.2 mm sand. Each layer is 60 cm deep.

Corrosion and pH control is provided by the addition of Ca(OH)$_2$ and CO$_2$. Sodium hypochlorite is used for disinfection, but UV-disinfection units are under installation. The sludge from filter backwash thickening is sent through the sewer system to a near-by wastewater treatment plant, while decanted water is equalised and returned to the raw water inlet.

The design filtration rate is 9 m/hr., and the actual rate is 6-8 m/hr. Filter run times are typically 14-15 hours for filtration rates of 8 m/h, and raw water colour and TOC levels of 20-30 mg Pt/L and 3.5-5 mg TOC/L, respectively, and alum dose levels of about 2.1 mg Al/L. Typical treated water quality levels are: colour 2-6 mg Pt/L; turbidity <0.1 NTU; residual Al < 0.15 mg/L.

Backwashing is performed with air followed by water for fluidisation (45 m/h in 6-10 minutes). During filter ripening a filtrate-to-waste procedure is used for a time period of 10 minutes.

![Treatment process flow-sheet of the Skullerud WTP in Oslo, Norway](image)

Figure 5.41 Treatment process flow-sheet of the Skullerud WTP in Oslo, Norway

5.5.1 Optimization trials and results

Full-scale optimization trials at Skullerud WTP were performed in accordance with the optimization procedures described before. The process performance and coagulation conditions used before start-up of the optimization trials
were used as reference values, i.e. 22 mg/L of alum and a coagulation pH of 6.2. It should be noted here that Sku llerud WTP is a well-operated plant with produced water quality levels well in compliance with the national drinking water quality standard, i.e. turbidity < 0.2 NTU; Colour < 5 mg Pt/L; TOC < 3 mg/L; residual Al < 0.15 mg/L; TTHM < 50 µg/L.

Thus, the major objective of the trials was to identify optimization potentials in terms of chemicals and energy used, sludge production, costs, etc.

Prior to the optimization tests, the applied (existing) coagulant dose level was compared to the coagulant dose prediction model developed by Eikebrokk (1999) and described in the state-of-the-art Techneau report (Eikebrokk et al, 2006). Based on model predictions, the existing applied dose was considered too high, thus indicating a significant potential for reductions in coagulant dose level, sludge production, energy (e.g. less frequent backwash due to extended filter run length), operation costs, etc. Model predictions and the applied coagulation conditions (existing) are illustrated in Figure 5.42.

![Figure 5.42 Comparison of existing coagulant dose level to operation model predictions/recommendations for minimum practical and minimum absolute dose levels (to comply with the water quality standard).](image)

The results from the full-scale tests for optimum coagulation profile identification are presented in the Figures 5.43-5.45 below.

During the test period, raw water colour and TOC was in the range of 23-28 mg Pt/L, and 4.0-5.4 mg/L, respectively. Turbidity was < 0.5 NTU.

Starting with the existing (reference) dosage of 22 mg/L of alum (2.0 mg Al/L), the dosage level was systematically decreased in steps of 2 mg/L down to a minimum level of 12 mg/L (1.1 mg Al/L). For every coagulant dose level, at least 4-5 different pH-values were tested within the range of pH 5.8-7.0. In order to maintain compliance with the water quality standards,
small pH-steps (0.1 units) were taken. Water samples (raw water, coagulated water and filtered water) were taken when the on-line filter effluent turbidity readings were stable, normally after 3-5 hours of filtration. Prior to the next test the filter was backwashed before the coagulation conditions were altered in accordance with the pre-defined test protocol.

Figure 5.43 Residual Al concentrations obtained with different coagulation pH and coagulant dosage (alum) levels during full-scale optimization trials at Skullerud WTP.

Figure 5.44 Filter effluent turbidities obtained with different coagulation pH and coagulant dosage levels during full-scale optimization trials at Skullerud WTP.
Figure 5.45 Colour and TOC removal efficiencies obtained with different coagulation pH and coagulant dosage levels during full-scale optimization trials at Skullerud WTP.

### 5.5.2 Cost savings

Cost savings associated with utilisation of increasing parts of the total optimisation potential are illustrated in Figure 5.46. The maximum obtainable cost savings are close to 40 k€ per year when the alum dose is reduced from an existing level of 23 down to the detected minimum value of 14 mg/L. This corresponds to a unit cost savings of about 0.36 cents/m³ for the actual production capacity of 30 000 m³/day. Coagulants, lime and energy (for pumping) are the dominating cost items. Minor savings are also obtained from reductions in the dosage of CO₂, polymer, and chlorine.

![Graph showing cost savings](image)

Figure 5.46 Identification of possible operation cost savings as a result of full-scale optimisation trials at Skullerud WTP, Norway (Treatment capacity is 30 000 m³/year). Values are relative to a reference alum dose of 23 mg alum/L, i.e. the coagulant dose employed prior to the optimisation experiments.
Based on the optimization results (Figures 5.43-5.46), the following conclusions were drawn:

- A knowledge-based enhanced coagulation optimization procedure can easily be implemented at existing WTPs without compromising treated water quality
- The optimization potentials appears to be quite significant (i.e. reduced coagulant dose, sludge production, energy use, operation costs, etc)
- By utilizing the full optimization potential, close to 40 % less coagulant usage and 40 % less sludge production could be obtained at Skullerud WTP. In addition, less lime and CO₂ is needed for corrosion control and 5-10 % less energy is needed for water backwash and sludge processing due to less solids loads and prolonged filter runs.
- However, lowering of the coagulant dosage level leads to a narrowing of the pH-window for optimal process performance. A strict process and pH control is therefore required in order to be able to utilize the entire optimization potential. Thus, a good balance should be found between the extent of optimization potential utilization and the increased operation control challenges.
- When approaching the absolute minimum coagulant dose level, filter effluent turbidity and residual coagulant concentrations are the most sensitive parameters. Colour, UV-abs and TOC appear less sensitive to changes in pH and coagulant dosage.
- By utilizing the full optimization potential, maximum operational cost savings of close to 0.03 NOK (0.36 cents) pr. m³ could be achieved at this WTP. With an annual water production of 11 mill. m³, this amounts to about 311 000 NOK (39 000 €) per year.

5.5.3 Rapid NOM fractionation
Simplified NOM fractionation of treated water and untreated raw water from Skullerud WTP was performed in cooperation with the Australian Water Quality Centre (AWQC). Water samples was taken during the optimization period when low coagulant doses were applied (0.31 mg Al/mg TOC).

The results from Skullerud WTP were compared to optimization results obtained with a similar raw water quality in a contact filtration pilot plant located at SINTEF. Here three different coagulant dosage levels were tested at optimum pH conditions identified according to the optimization procedure described before:

1) Coagulant under-dosing, i.e. 0.3 mg Al/mg DOC,
2) Optimal dosage, i.e. 0.42 mg Al/mg DOC, and
3) Coagulant over-dosing, i.e. 0.54 mg Al/mg DOC.

DOC fractionation (Figure 5.47) showed VHA, SHA and CHA fractions removal in the range of 35-70 %. The CHA fraction appears to be the most
sensitive to the coagulant dose level. The NEU fraction was removed by less than 10 % for the optimum and over-dose situation. In the case of under-dosing however, a negative removal (i.e. increased fraction concentration) of close to 30 % was obtained. Thus, non-removable neutral hydrophilic NOM was produced during under-dosing conditions.

The full-scale results from Skullerud WTP seem to confirm this picture. With the low specific dosage of 0.31 mg Al/mg DOC applied in this test period, the NEU fraction increased in this case as well, indication that an increase in the NEU fraction may be taken as an indication of coagulant under-dosing. More tests will be performed in order to further test the validity of this hypothesis. The regrowth potential seems well correlated to the NEU fraction. Thus an increase in this fraction concentration needs attention.

![Graph showing NOM (DOC) fractions removal](image)

Figure 5.47 Obtained NOM (DOC) fractions removal in pilot studies during coagulation conditions characterized as under-dosage, optimal dosage and over-dosage compared to results from full-scale tests at Skullerud WTP (right).

5.6 Full-scale optimization trials at Vansjo WTP, Norway

Vansjo WTP is a direct filtration plant with design similar to Skullerud WTP. The raw water is more NOM-laden with typical colour and TOC levels of 50-70 mg Pt/L and 6-10 mg/L, respectively. The ALG-dosage was normally within the range of 2.5-3.0 mg Al/L.

This plant did not perform as well as the Skullerud WTP, and periodic in-compliance with the water quality standards was detected. In specific, turbidity, residual aluminium and TOC exceeded the maximum levels of 0.3 NTU, 0.1 mg Al/L and 3 mg TOC/L, respectively (Figure 5.48). Thus, improved water quality and process performance was the main motivation for implementing an optimization process here.
Comparison of the applied coagulant dosage with model predicted dose recommendations (Figure 5.49) revealed that the applied coagulant dosage was too low in this case. The normal response to this is excessive residual aluminium concentrations, in line with the results presented in Figure 5.48.

Based on the operation optimization efforts the coagulant dose level was increased, thereby solving the long-term water residual aluminium problems. However, the corresponding increased sludge production exceeded the plant’s capacity, and the plant has now been up-graded with increased sludge processing capacity, and new pre-treatment and separation process steps.

5.7 Ozonation-biofiltration studies at VIVA pilot, Trondheim WTP

5.7.1 Pilot test results

The ozonation-biofiltration pilot plant at VIVA (Figure 5.29) consists of a up-flow bubble contactor where ozone is dissolved into water and a reaction tank where dissolved ozone has time to react with water and where ozone
degradation kinetics (and CT-values) can be studied. At the water flow used in these tests (0.2 L s\(^{-1}\)), the HRTs in the tanks are 2 and 22 min, respectively. In the biofilter, CaCO\(_3\) is used as a filter media to study whether biofiltration and corrosion control can be achieved in the same filter. This would make upgrading of many Norwegian treatment plants with ozonation easier. The biofilter has been operated at filter velocity of 11 m h\(^{-1}\) and EBCT of 19 min based on original bed height. Due to gradual dissolution of CaCO\(_3\), the bed height has decreased during the study and therefore EBCT has become slightly reduced.

The experiments started fall 2007 to provide baseline results for further process optimisation. The average ozone dose has been 2.6 mg L\(^{-1}\) which equals a carbon based specific dose of 0.93 mg O\(_3\)/mg DOC and a colour specific dose of 0.2 mg O\(_3\)/mg Pt. For comparison, occasional samples were taken also from the alkaline filter without prior ozonation.

Figure 5.50 shows DOC concentrations (a) and UV absorbance (b) in the raw water and filter effluents. The values have varied between 2.7 and 3.0 mg L\(^{-1}\) for DOC and between 9.5 and 10.1 m\(^{-1}\) for UV absorbance. The content of organic matter in VIVA raw water is therefore much less than in Daugava WTP and do not vary very much.

Figure 5.50 DOC concentrations (a) and UV absorbance (b) in raw water and filter effluents.

Figure 51 shows the average TOC and DOC values at different process stages. Great majority of the organic matter is dissolved (on average, raw water DOC is 99\% of the TOC. This is natural since the average turbidity is low (0.14 NTNU). There is no removal of DOC or TOC during the ozonation stage. The average DOC removal in ozonation-biofiltration process has been 13\%. This is less than has been observed in other studies in Norway. For example, in a study carried out in Leirsjøen (Trondheim) the average removal efficiency was 23\% (Melin et al., 2002). Low DOC removal in VIVA may be due to low raw water DOC, different raw water characteristics, or that process will require further optimization. This shall be studied next in the project. In the alkaline filter without ozonation, there was no removal of DOC (average 1\%) indicating that the raw water do not contain significant amount of BDOC. This is probable since the source water (Lake Jonsvatnet) do not receive
industrial effluents and has very long theoretical HRT (about 10 years). This will be checked with further BDOC tests.

Figure 5.51 Average TOC and DOC concentrations in the pilot plant.

Figure 5.52 shows DOC samples taken along the biofilter column. It shows initial rapid DOC removal in the top part of the biofilter and then gradual removal throughout the column. This is contrary to some other studies where the majority of the removal occurred on the top of the biofilter (Melin et al., 2006). It may be that ozonated water in VIVA is very slowly biodegradable. On the other hand, the filters are backwashed daily, which may be too often thus not allowing the typical layering of biofilm with majority of the biofilm on the top of the biofilter. Optimizing backwash procedures is one of the next steps in the project. It is also a challenge to analyze such small changes in DOC as observed in the pilot plant, so more measurements are required to obtain reliable results.

Figure 5.52 DOC profile through the biofilter.
Figure 5.53 shows average colour and UV absorbance in the pilot plant. The removal occurs during ozonation stage and there is no removal in the biofilter or reference CaCO₃ filter. The average removal in ozonation-biofiltration process has been 68% for colour and 60% for UV absorbance. Higher colour removal (as well as better biodegradability) may be achieved with higher ozone doses and this will be tested later.

![Figure 5.53 Average colour (a) and UV absorbance (b) in the pilot plant.](image)

Turbidity in VIVA raw water is very low with average of 0.14 NTU (Figure 5.54). Therefore, no significant removal in the filters can be expected. Although on average, turbidity in the effluent of the biologically active filter is lower, the differences are too low to make any conclusions.

![Figure 5.54 Average turbidities in the pilot plant.](image)

5.7.2 Column based biodegradability testing

After procedure for BDOC measurements in laboratory biofilter columns was developed in Riga (method 2 in Chapter 4.2.2), similar set-up was build in Trondheim in September 2007. Initially, the biofilter was operated with recirculation of water consisting 1/3 of VIVA raw water and 2/3 of biofilter effluent from the NTNU pilot plant. After one month, the feed was changed to ozonated water from the VIVA pilot. The circulated water was changed weekly. After 11 weeks, experimentation with columns was started.

So far, there are results from only one test where the effect of different retention times in the columns were studied (Figure 5.55). The feed was
ozonated water from the VIVA pilot plant. Scatter in the DOC results makes it
difficult to draw conclusions from this test alone, but the optimal EBCT (total
two columns) seems to be between 2.5 and 10 hrs. Further tests are being
carried out.

Figure 5.55 Effect of EBCT on outlet DOC concentrations. Results are from two
parallel BDOC columns.

If the last point is taken as final BDOC, the ozonated water in VIVA contains
0.55 mg BDOC L\(^{-1}\). At the time of sampling, the biofilter removed 0.30 mg
DOC L\(^{-1}\). Removal of 55% BDOC is quite good result for biofilter (Melin et al.,
2002), so low amount of DOC removal in the biofilter may be the result of
relatively low BDOC after ozonation.
6 Process operation models to be tested

In future pilot and full-scale optimization experiments, selected operation models will be tested and verified. Some of the actual model candidates for testing are presented below.

6.1 Modelling of DOC removal

The removal of natural organic matter (NOM) by coagulation is impacted by a number of factors, e.g. NOM character and concentration, turbidity and alkalinity, other organic as well as inorganic constituents of the raw water. High levels of variation can occur in a range of water quality parameters such as turbidity, alkalinity, colour, NOM, algae and micro-organisms.

Mathematical models that relate the character and concentration of dissolved organic matter in the raw water to inorganic coagulant dosing that maximize the removal of DOC have been developed. The models can also be used to predict the required coagulant dosage when treating raw waters of different quality. Van Leeuwen et al (2005) used models to predict alum coagulant dosage that were subsequently applied to treat two Australian raw waters in jar tests and in pilot plant trials. DOC removals of 50-60% were obtained with application of the model predicted alum doses for maximizing DOC removal when coagulation was performed at pH 6. Much higher coagulant doses at similar pH resulted in comparatively minor additional DOC removal. THMFP was found to be proportional to the residual DOC and appeared to be linearly related. Formation of individual THMs was consistent in each water source but different between the two sources.

Harrington et al (1991) developed an interactive, user-friendly computer program to simulate inorganic water quality changes, THM formation, disinfectant decay and removal of NOM in water treatment processes. Furthermore, they discussed the selection, development and verification of empirical models to include in the program.

Tseng and Edwards (1999) presented a Langmuir model for prediction of full-scale removal of TOC during enhanced coagulation. Case studies of 27 full-scale utilities showed accurate prediction of TOC removal by coagulation at a range of utilities using alum, ferric, or poly aluminium chloride coagulants.

Edwards (1997) predicted the concentration of DOC remaining after enhanced coagulation with a standard error of about 10% or 0.4 mg/L. Model inputs were coagulant dosage, coagulation pH, raw water UV_{254}-abs, and raw water DOC. When calibrated to a specific site, the standard predictive error could be improved to 4% or 0.27 mg DOC/L. Performance differences between equimolar dosages of alum and ferric coagulants were attributed to: equal or better removal of DOC using ferric at very high coagulant dosages; equal or better removal of DOC using alum at lower coagulant doses; or...
differing acidity of coagulants, producing a performance advantage for the more acidic coagulant.

6.2 Predicting DOC removal

A model for predicting the DOC concentration remaining after enhanced coagulation was developed by Edwards (1997). This model takes into account only adsorption mechanisms, described by a Langmuir isotherm. The model uses only parameters that are routinely measured, and it can readily be applied at water treatment plants.

The fraction of non-sorbable DOC that is not removed by coagulation is calculated by:

\[
\text{Fraction non-sorbable DOC} = K_1 (\text{SUVA})_{\text{raw water}} + K_2
\]  

where \( K_1 \) and \( K_2 \) are empirical fitting constants.

The sorbable DOC can then be calculated by:

\[
\text{Sorbable DOC} = \{1 - \text{fraction non-sorbable DOC}\} \text{DOC}_{\text{initial}}
\]  

The model is based on the Langmuir equation:

\[
\frac{x}{M} = \frac{a b [C]_{eq}}{1 + b [C]_{eq}}
\]  

where \( x \) is DOC removed (mg/L DOC), \( M \) is coagulant added and metal hydroxide formed (mmole/L), \( C_{eq} \) is sorbable DOC in solution at equilibrium, and \( a \) and \( b \) are sorption constants. The constant \( a \) can be determined by:

\[
a = x_3 \text{pH}^3 + x_2 \text{pH}^2 + x_1 \text{pH}
\]  

where \( x_1, x_2 \) and \( x_3 \) are fitting constants. Combining these equations gives:

\[
\frac{\{(1 - \text{SUVA} K_1 - K_2) \text{DOC}_{\text{initial}} - [C]_{eq}\}}{M} = \frac{\{(x_3 \text{pH}^3 + x_2 \text{pH}^2 + x_1 \text{pH}) b [C]_{eq}\}}{[1 + b [C]_{eq}]}
\]  

This equation can be solved in an Excel sheet if the six empirical constants \( (K_1, K_2, x_1, x_2, x_3, b) \) are known. The DOC concentration remaining after coagulation is then:

\[
\text{DOC (mg/L)} = C_{eq} \text{(mg/L)} + \text{non-sorbable DOC (mg/L)}
\]  

Edwards (1997) also determined the values for the empirical constants, still keeping the standard error below 10%. These general values for the empirical constants are listed in Table 6.1 below.
Table 6.1 Parameter values used for the model for predicting DOC removal (Edwards, 1997).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fe coagulant</th>
<th>Al coagulant</th>
<th>General</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard error, %</td>
<td>9.3</td>
<td>9.5</td>
<td>10</td>
</tr>
<tr>
<td>x₃</td>
<td>4.96</td>
<td>4.91</td>
<td>6.44</td>
</tr>
<tr>
<td>x₂</td>
<td>-73.9</td>
<td>-74.2</td>
<td>-99.2</td>
</tr>
<tr>
<td>x₁</td>
<td>280</td>
<td>284</td>
<td>387</td>
</tr>
<tr>
<td>K₁</td>
<td>-0.028</td>
<td>-0.075</td>
<td>-0.053</td>
</tr>
<tr>
<td>K₂</td>
<td>0.23</td>
<td>0.56</td>
<td>0.54</td>
</tr>
<tr>
<td>b</td>
<td>0.068</td>
<td>0.147</td>
<td>0.107</td>
</tr>
</tbody>
</table>

Several other empirical models predicting DOC or TOC removal by coagulation can be found in the literature. Some of these are summarized in Table 6.2. However, according to Tseng and Edwards (1999) the accuracy of these models is lower than the Langmuir adsorption model described above.

Table 6.2 Models developed to predict DOC or TOC removal during coagulation.

<table>
<thead>
<tr>
<th>Coag</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al a)</td>
<td>TOC&lt;sub&gt;final&lt;/sub&gt; = 0.405TOC&lt;sub&gt;raw&lt;/sub&gt; - 0.55dose + 0.688pH&lt;sub&gt;coag&lt;/sub&gt; - 3.32</td>
<td>Moomaw et al (1992)</td>
</tr>
<tr>
<td>Fe a)</td>
<td>TOC&lt;sub&gt;final&lt;/sub&gt; = 0.52TOC&lt;sub&gt;raw&lt;/sub&gt; - 1.49dose + 0.740pH&lt;sub&gt;coag&lt;/sub&gt; - 3.50</td>
<td>Moomaw et al (1992)</td>
</tr>
<tr>
<td>Al b)</td>
<td>TOC&lt;sub&gt;final&lt;/sub&gt; = 1.076[TOC&lt;sub&gt;raw&lt;/sub&gt;]&lt;sup&gt;0.923&lt;/sup&gt;[dose]&lt;sup&gt;0.298&lt;/sup&gt;[Alk&lt;sub&gt;raw&lt;/sub&gt;]&lt;sup&gt;0.173&lt;/sup&gt;</td>
<td>Zhu (1995)</td>
</tr>
<tr>
<td>Fe b)</td>
<td>TOC&lt;sub&gt;final&lt;/sub&gt; = 0.839[TOC&lt;sub&gt;raw&lt;/sub&gt;]&lt;sup&gt;1.094&lt;/sup&gt;[dose]&lt;sup&gt;0.355&lt;/sup&gt;[Alk&lt;sub&gt;raw&lt;/sub&gt;]&lt;sup&gt;0.150&lt;/sup&gt;</td>
<td>Zhu (1995)</td>
</tr>
<tr>
<td>Al c)</td>
<td>ln(TOC&lt;sub&gt;final&lt;/sub&gt;) = - 0.33 + 1.31 ln(TOC&lt;sub&gt;raw&lt;/sub&gt;) - 0.54 ln(dose) - 0.08 ln(TOC&lt;sub&gt;raw&lt;/sub&gt;)ln(dose) + 0.077 pH&lt;sub&gt;coag&lt;/sub&gt; ln(dose)</td>
<td>Harrington et al (1992)</td>
</tr>
<tr>
<td>Fe c)</td>
<td>ln(TOC&lt;sub&gt;final&lt;/sub&gt;) = - 0.16 + 1.25 ln(TOC&lt;sub&gt;raw&lt;/sub&gt;) - 0.71 ln(dose) - 0.05 ln(TOC&lt;sub&gt;raw&lt;/sub&gt;)ln(dose) + 0.092 pH&lt;sub&gt;coag&lt;/sub&gt; ln(dose)</td>
<td>Harrington et al (1992)</td>
</tr>
<tr>
<td>Al or Fe d)</td>
<td>TOC = a + b (2.717)&lt;sup&gt;-c(dose)&lt;/sup&gt;</td>
<td>Chowdhury and Owen (1996)</td>
</tr>
</tbody>
</table>

a) dose in meq/L Al or Fe;
b) alk. in mg/L CaCO₃ and dose in mg/L as Al₂(SO₄)₃·18H₂O or FeCl₃·6H₂O
c) dose in mg/L as Al₂(SO₄)₃·18H₂O or FeCl₃·6H₂O
d) a, b and c are different empirical constants depending on the TOC, alkalinity and the coagulant used.
6.3 Empirical models and guidelines for optimum operation

Several empirical model equations have been published to predict the required coagulant dose for removal of TOC. Some of these are summarized in Table 6.3. Empiric models have also been developed to predict sludge production, filter run times, etc.

Table 6.3 Model equations for coagulant dosage requirements

<table>
<thead>
<tr>
<th>Models</th>
<th>Equations</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enhanced coagulation alum dose</td>
<td>$A_l = 10.9 + 2.63 \times (TOC_0) + 0.17 (Alk) + 0.74 \times (pH)$</td>
<td>in Rodriguez at al (2000)</td>
</tr>
<tr>
<td>Enhanced coagulation alum dose</td>
<td>$A_l_{min} = 0.043 \times \text{Color} + 0.30$</td>
<td>Eikebrokk (2004b)</td>
</tr>
<tr>
<td>1)</td>
<td>$A_l_{pract} = 0.054 \times \text{Color} + 0.37$</td>
<td></td>
</tr>
<tr>
<td>Enhanced coagulation ferric</td>
<td>$F_e_{min} = 0.107 \times \text{Color} + 0.58$</td>
<td>Eikebrokk (2004b)</td>
</tr>
<tr>
<td>dose 1)</td>
<td>$F_e_{pract} = 0.134 \times \text{Color} + 0.72$</td>
<td></td>
</tr>
<tr>
<td>Alum dose depending on</td>
<td>$A_l = 4 \times \text{Color}^{-1/2}$</td>
<td>Soviet Building</td>
</tr>
<tr>
<td>water color of water</td>
<td></td>
<td>Norms (1984)</td>
</tr>
</tbody>
</table>

$TOC_0$: concentration of TOC before treatment (mg/l),
$A_l$: coagulation dose (mg/l),
Alk: water alkalinity (mg/l CaCO3),

1) Absolute and practical minimum dosages determined by the residual coagulant concentration standard (< 0.15 mg Me/L).

Based on numerous pilot plant experiments using 3 model waters with low turbidity and increasing NOM and SUVA levels, Eikebrokk (2004b) developed several simple operational models for the enhanced coagulation – contact filtration process. The models presented below were developed for water with color 15 – 50 mg Pt/L, TOC 2 - 6 mg/L, turbidity < 0.5 NTU and SUVA 3.8 – 4.8 using 2M anthracite-sand filters. The models describe required coagulant dose, sludge production and filter run time to break through, which in turn can be used to determine net water production and backwash water production for various operational conditions.

6.3.1 Required coagulant dosage

Minimum required coagulant dose (Eikebrokk, 1999):

$$\text{Dose (mg Me/L)} = A \cdot \text{Raw water Color (mg Pt/L)} + B \quad (7.7)$$

where A and B are constants depending on the coagulant and operational conditions.

It is also defined a practical minimum coagulant dose which is 25 % higher than the absolute minimum dose determined from the above equation. For granulated aluminium sulphate as a coagulant the absolute minimum and the practical minimum coagulant doses at optimum coagulation pH are given by:
\[ A_{\text{min}} = 0.043 \cdot \text{Color} + 0.30 \]  
\[ A_{\text{pract}} = 0.054 \cdot \text{Color} + 0.37 \]  

(7.8)  
(7.9)

For ferric chloride as a coagulant these doses are given by:

\[ F_{\text{min}} = 0.107 \cdot \text{Color} + 0.58 \]  
\[ F_{\text{pract}} = 0.134 \cdot \text{Color} + 0.72 \]  

(7.10)  
(7.11)

### 6.3.2 Sludge production

Sludge production at optimum coagulation (Eikebrokk, 1999):

\[ \text{SS}(\text{mg/L}) = \text{SS}_{\text{RW}} + k \cdot \text{Dose} \]  

(7.12)

where \( \text{SS}_{\text{RW}} \) is the suspended solid concentration in the raw water, \( k \) is a constant depending on the type of coagulant and \( \text{Dose} \) is the coagulant dose (mg Me/L).

For granulated aluminium sulphate and ferric chloride as coagulant, respectively, the sludge production (mg SS/L) is then given by:

\[ \text{SS}_{\text{Al}} = \text{SS}_{\text{RW}} + 4.2 \cdot \text{Dose} \]  
\[ \text{SS}_{\text{Fe}} = \text{SS}_{\text{RW}} + 2.5 \cdot \text{Dose} \]  

(7.13)  
(7.14)

### 6.3.3 Filter run time to break through

Filter run time to breakthrough at optimum coagulation (Eikebrokk, 1999):

\[ t_{\text{BT}} = a \left( v_f \cdot \text{SS} \right)^b \]  

(7.18)

where \( t_{\text{BT}} \) is time of filtration until breakthrough (hrs), \( v_f \) is rate of filtration (m/hr), \( \text{SS} \) is the suspended solids concentration in coagulated water, i.e. sludge production (mg SS/L), and \( a \) and \( b \) are constants specific to the filter and coagulant.

For alum without any polymer as filter aid and \( \text{SS}_{\text{RW}} = 0 \), the time of filtration is:

\[ t_{\text{TB}} = 298 \left( v_f \cdot \text{Dose}_{\text{Al}} \right)^{-1.29} \]  

(7.19)

### 6.3.4 Net water production

The net water production would depend on the operational mode of the process. If ripening water is used as clean water, and the filter is backwashed with raw water, the net water production is (Eikebrokk, 1999):

\[ Q_{\text{Net}} = \left[ 24 / t_p \right] \left[ v_f \cdot t \right] \]  

(7.20)

If ripening water is used as clean water, and the filter is backwashed with clean water, the net water production is:
\[ Q_{\text{Net}} = \frac{24}{t_p} \left[ v_f \cdot (t_f - t_r) - v_s \cdot t_s \right] \quad (7.23) \]

Where \( Q_{\text{Net}} \) is the daily water production (m\(^3\)/m\(^2\) day), \( v_f \) and \( v_s \) are the rates of filtration and backwash (m/hr), respectively, \( t_f, t_s \), and \( t_r \) is the time of filtration, backwash and ripening (hrs), respectively, and \( t_p \) is the total time between each backwash (\( t_f + t_s + \text{time for valve operation, etc} \)) in hrs.

### 6.3.5 Backwash water production

As for net water production, the production of backwash water is given by:

\[ Q_{\text{BW}} = \frac{24}{t_p} \left[ v_s \cdot t_s \right] \quad (7.24) \]

where \( Q_{\text{BW}} \) is the daily production of backwash water.

By combining these and similar simple empirical operational models it should be possible to develop powerful tools and software for operation control, optimization and automation. However, the models have to be further developed by i.e.:

- Verify and make the models applicable for other raw water qualities, operational conditions, process configurations, etc.
- Extend the models to include other coagulants, polymer addition, etc.
- Investigate the effect of polymer addition and why the polymer is very efficient in some cases and far less effective in other cases.
7 Future activities

Future WP5.3 activities include a number of characterization efforts and optimization experiments. Some major activities are shortly described below.

7.1 NOM characteristics and treatability evaluations
SINTEF and RTU will continue NOM characteristics and treatability trials and evaluations, in pilot as well as full-scale. Activities include a first tier of NOM protocols including SUVA, BDOC, and rapid fractionation. IHE-Delft will augment this with measurements of fluorescence excitation-emission matrix (EEM) and size-exclusion chromatography with dissolved organic carbon detection (SEC-DOC). EEM allows one to track humic-like NOM, effectively removed during coagulation, and protein-like NOM, amenable to removal by biofiltration. SEC-DOC allows one to track biopolymers, potentially removable by biofiltration, low molecular weight acids, significantly removable by biofiltration, and humic substances, effectively removed by coagulations. Both EEM and SEC-DOC can provide quantitative as well as qualitative information. The samples requirements are minimal, some hundred mL. Sample preparation includes in-field 0.45 um filtration and air shipment in prewashed nalgene bottles on ice.

The Delta UV probe from S::can will be further tested for on-line water quality monitoring and for the purpose of enhanced coagulation control. The latter will be tested in cooperation with Techneau end-users (e.g. Bergen, Norway).

7.2 Biodegradability characteristics
A simple method for measurements of BDOC degradation will be developed.

7.3 Ozonation and biofiltration optimization efforts
The SOMBIO model developed in this study will be further verified in pilot-scale. The model shows that one of the factors negatively affecting removal of BDOC in biofilters at Daugava WTP is low ATP level in media. One of the problems which is overcome at the pilot scale is reduction of residual ozone concentration at the inflow to the biofilters. This was done by purging of ozonated water with air. Now, continuous ATP measurements will be carried out to check if ozone was responsible for low ATP level in the column.

In the VIVA pilot, the effects of ozone dose on BDOC formation and removal kinetics will be studied and optimized. The effects of backwash procedures on biofilter performance will be also be studied and optimized.
7.4 Enhanced coagulation optimisation efforts

The on-going operation optimisation studies will be continued, primarily in Riga and in Trondheim.

A 5-step operation optimisation procedure (Chapter 4??) will be further tested, further developed and verified in pilot and full-scale experiments. The optimisation procedure will also be implemented at full-scale plants in cooperation with Techneau end-users (e.g. Bergen, Norway).

The optimisation procedure includes the following 5 steps:

1. Raw water characterisation efforts (Ch. 2)
   a. Standard water quality parameter analyses (Turbidity, pH, alkalinity, colour, UV-abs, TOC, DOC, hardness, metals, etc.)
   b. Analysis of SUVA, BDOC and NOM fractionation
   c. Advanced NOM analysis (IHE-Delft): Fluorescence excitation-emission matrix (EEM) and size-exclusion chromatography with dissolved organic carbon detection (SEC-DOC)

   In order to identify seasonal variations, water sampling and analysis should be distributed over the year (e.g. every second month).

2. Mapping of pre-optimisation (i.e. existing) operation conditions and process performance, incl. treated water quality, chemicals/energy used, sludge production and operation costs

3. Treatablity evaluations based on Step 1 and 2 results, and comparison of pre-optimisation results with model predictions regarding coagulation conditions and performance (Ch. 7)

4. Implementation of the suggested optimisation experiments, including water sampling and analysis programs (Ch. 4)

5. Reporting of water characterisation and optimisation results, including identification of optimisation benefits with respect to operation performance, process safety and stability, resources use, waste production and overall cost-benefit

7.5 Process operation model testing and adaptation

The SOMBIO model developed in this study will be further verified in pilot-scale. BDOC degradation kinetic constant will be introduced to the SOMBIO model used for prediction of BDOC removal in biofilters.

7.6 Input to the Treatment Process Simulator

The operation model candidates for inclusion in the TPS should be identified with the proper formats, including the SOMBIO model.
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