

Stellingen

behorende bij het proefschrift

Algae and Particle Removal in Direct Filtration

of Biesbosch Water

Influence of Algal Characteristics,
Oxidation and Other Pre-Treatment Conditions

Branislav Petruševski
Delft, oktober 1996

1. The size of some successfully concentrated fragile algal cells, and the capability of the tangential flow membrane micro filtration system to process large volumes of water suggest that this technology can also be used for concentration of *Cryptosporidium* oocysts and *Giardia* cysts.
(This thesis, chapter 4)

2. During the round-table discussion at the IWSA-IAWPRC Joint Specialist Conference on Particle Removal in Jönköping in April 1990, it became apparent that the knowledge on elimination of plankton by treatment processes is still somewhat rudimentary.

(H. Bernhardt and J. Clasen, *J Water SRT-Aqua*)

It appears that water treatment research makes little use of the knowledge that emerges from phycological studies. Understanding of the algal properties is a pre-requisite to better understand the algal behaviour in water treatment, and consequently to achieve more efficient elimination.

(This thesis, chapter 2)

3. Phytoplankton contribute to our well-being, not only because they provide oxygen but also because they provide much of the food for higher organisms.

In the ensuing years we will probably see an increase in number of industries that exploit algae as food for economically important products. The renewed interest in the algae will no doubt reveal new uses for it.

(Raúl J. Cano and Jaime S. Colomé, Microbiology)

For the most water treatment engineers in the world it comes as a surprise that not everybody considers algae a nuisance or is primarily interested in their elimination.

4. The combination of coagulation and membrane micro- or ultra-filtration could be considered to be the "direct filtration" treatment of the future: the process combines the advantages of conventional treatment and membrane filtration. With the expected further reduction of membrane and operational costs, the process could become economically attractive.

5. If all earth's water fit in a gallon jug, available fresh water would equal just over a tablespoon - less than half of one percent of the total.
(National Geographic Special Edition Water, 1993)

But such global, static perception belies the opportunity for local economic trade-offs and re-use of water (e.g. use of recycled laundry and bath water for toilet flushing could reduce net consumption with at least 30% - with concomitant environmental and financial benefits).

6. Establishing an economically viable price for drinking water in developing countries is required, not only to establish a solid basis for reliable supply of high-quality drinking water, but also to change peoples' attitudes towards this commodity.
7. The boundary conditions of every Ph.D. research project could be learning everything about a minute problem, and learning a little about everything. A crucial problem is to find the right balance between these two extremes.
8. The chief tragedy of science is that small ugly facts can kill a nice hypothesis.

(Aldous Huxley)

However, this is more the tragedy of the scientist than the tragedy of science.

9. The maximum duration of a Ph.D. research project should be strictly limited. Prolongation of the project beyond a certain point neither contributes to research nor is of benefit to the candidate.

**ALGAE AND PARTICLE REMOVAL IN DIRECT FILTRATION OF
BIESBOSCH WATER**

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TR diss 2813

Algae and Particle Removal in Direct Filtration of Biesbosch Water

*Influence of Algal Characteristics, Oxidation
and other Pre-treatment Conditions*

DISSERTATION

Submitted in fulfilment of the requirements of
the Board of Deans of Delft University of Technology
and the Academic Board of the International Institute for Infrastructural,
Hydraulic and Environmental Engineering for the Degree of DOCTOR
to be defended in public
on Monday, 7 October 1996 at 13:30 h

by

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Published by

A.A. Balkema, P.O. Box 1675, 3000 BR Rotterdam, Netherlands (Fax: +31.10.4135947)

A.A. Balkema Publishers, Old Post Road, Brookfield, VT 05036-9704, USA (Fax: 802.276.3837)

ISBN 90 5410 407 4

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Printed in the Netherlands

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Acknowledgements

Most of all I wish to thank Professor G. J. Alaerts and ir. A.N. van Breemen for giving me the opportunity, trust and freedom to work on this project. Their supervision, criticism and encouragement throughout this five years is highly appreciated. My promoter Prof. G.J. Alaerts with his wide vision, broad knowledge, systematic approach and useful editorial remarks helped me to get this far. My mentor ir. A.N. van Breemen, with his enormous theoretical knowledge, research experience and feeling for practice helped me to direct my research.

I also wish to thank Prof. Dr. K.J. Ives (University College London), Prof. Dr. J.C. Schippers (IHE Delft) and Dr. J.C. Kruithof (Kiwa N.V. Research and Consultancy) for their involvement and constructive criticism of the draft version of the thesis.

This work would not have been possible without Water Storage Corporation Brabantse Biesbosch, that provided a fellowship and financially supported this research. I gratefully acknowledge their support. I would like to thank in particular Mr. G. Oskam for his support throughout the project.

Grateful acknowledgement is expressed to the Laboratory for Sanitary Engineering (Faculty of Civil Engineering, Delft University of Technology) for providing facilities for the experiments.

Printing of this thesis was financially supported by Kiwa N.V. Research and Consultancy, for which I am sincerely grateful.

Five M.Sc. participants: Mr. A. Vlaški, Ms. M. Nalubega, Mr. B.P. Twesigye, Mr. J.K. Sherchan and Mr. A. Ghosh and several students were involved in the study. They all provided valuable contribution, for which I am sincerely grateful.

Mr. C. Boeter of the Delft University of Technology provided invaluable help in setting up experimental work and helping in numerous ways throughout the project. I would also like to thank Ms. G. Bolier, Ms. L. Brandenburg, Mr. G. H. Corstjens, Mr. H. Monteny, Mr. T. Schuit and other staff members of the Sanitary Engineering Laboratory (TU Delft) for their participation and support.

VIII

I am grateful for the friendly working atmosphere that surrounded my experimental work at water treatment plant Kralingen (Waterworks Europoort, Rotterdam), where most of the experimental work was carried out. I would specially like to thank Mrs. M Koopman, Mr. H. Bansema, Mr. J. Balman and Mr. R. Westra for their kind cooperation.

I am grateful to Mr. A.C. van Aelst of Wageningen Agricultural University, for the SEM analysis. I also express my thanks to the IHE staff members for their support.

I would also like to thank Dr. H. Lubberding (IHE Delft) and Mr. H. Ketelaars (Water Storage Corporation Brabantse Biesbosch) for their help in proof-reading of the draft of this thesis and Mr. C. Ruiters (Stork Comprimo) for his help on the Dutch translation of the summary.

Finally, I would like to thank my wife Vesna and our children Sanja and Nikola for their continuous support, endless patience and understanding.

Abstract

Petruševski B. (1996) *Algae and particle removal in direct filtration of Biesbosch water*. Doctoral thesis, International Institute for Infrastructural, Hydraulic and Environmental Engineering (IHE)/Delft University of Technology (TUD), Delft, The Netherlands, 214 pages.

Direct filtration is an economically and environmentally attractive alternative to conventional treatment of impounded surface water, provided that the water source is of appropriate quality, namely low in turbidity, particulate matter, colour and dissolved organic matter. However, direct filtration has limited particle and algae removal capacity. Algae present in drinking water may introduce several problems, like formation of hazardous chlorinated by-products, adverse effect on drinking water taste and odour, aftergrowth in distribution network etc. Presence of algae in drinking water also indicates that other, possibly pathogenic microorganisms in algal size range (e.g. *Cryptosporidium* oocysts and *Giardia* cysts) may penetrate treatment as well. Problems related to algae and other particles passing treatment bring the feasibility of direct filtration into question.

Although algae related problems are ubiquitous and of high significance, current knowledge and understanding of behavioral response of phytoplankton to different treatment techniques, are poorly developed. Similarly, little experience has been gained with experimental facilities and methodologies.

The Biesbosch water storage reservoirs account for more than half of total amount of surface water used directly for drinking water production in the Netherlands. Water delivered from these reservoirs is of an exceptionally high quality, and is in principle suitable for direct filtration, with an exception of short algal blooms in spring. The possible penetration of algae and other particles, particularly during short algal blooms, together with the short filter runs during occasional intervals with very high concentration of zooplankton and filamentous algae, makes the application of direct filtration questionable. Currently all the water works that use Biesbosch water for drinking water purposes apply conventional treatment.

The aim of this study was to investigate the applicability of direct filtration as a single-stage process, or in combination with pre-treatment process(es), as an alternative to conventional treatment of Biesbosch water. The study attempts to increase the understanding of algal coagulation, flocculation and removal in direct filtration in order to allow significant improvement in the elimination efficiency of these micro-organisms.

A batch set-up, a modified jar test apparatus, and a pilot plant set-ups were developed and used for direct filtration modelling. In addition, a semi-batch and a continuous flow ozone reactors were developed and used for the pre-oxidation studies. Innovative procedure was introduced for preparation of model water, based on concentration of algae in natural water with the tangential flow, membrane micro-filtration system. In order to overcome the shortcomings of conventional water quality analysis, and to provide more insight into phytoplankton behavioral response to treatment, a video system (video camera attached to an inverted microscope) was employed for in situ observation. In addition, the effect of oxidants on the morphology of algae has been examined on fully hydrated samples with the high resolution scanning electron microscopy.

Algal removal efficiency in straightforward direct filtration strongly varied with different algal species (between 5 and 100%). An average overall algal biomass removal of 90% was achieved in this study. The main cause of inefficient algae removal was poor agglomeration. The motility of numerous algal species was of decisive importance for their poor agglomeration and removal.

Plankton related problems could only be reduced if an appropriate pre-treatment precedes direct filtration. Microstrainers applied as an initial treatment step extended short filter runs caused by zooplankton and large or filamentous algae. Pre-oxidation with ozone or potassium permanganate enhanced particle and algae removal in direct filtration.

Pre-ozonation improved particle and algae removal in direct filtration by more than 1-log removal unit (from 90% to 99.7%). An optimal ozone dosage exists that is correlated with algal concentration in raw water. Relatively low ozone dosages ($\leq 1.8 \text{ mgO}_3/\text{l}$) coupled with short contact time (2-3 minutes) were sufficient to achieve ozone-related beneficial coagulation effects with Biesbosch water.

Here, an alternative direct filtration process was developed that comprises pre-treatment with potassium permanganate, coagulation with ferric sulfate and cationic polymer, and filtration through anthracite-sand-garnet filter media. The treatment distinctly improved particle and algae removal in comparison to efficiencies commonly achieved in direct filtration. Algae and particle removal efficiency $> 99\%$ is consistently achieved. In addition the permanganate related drawbacks (MnO_2 passing the filter and pink colour of the water) were completely eliminated. This process is simple and does not require major investment costs.

The very efficient removal of algae is the consequence of several process mechanisms such as the immobilization of motile algae, the removal of organic coating on algae and particle surface, the release of algal biopolymers and simultaneous coagulation through sweep coagulation and adsorption and charge neutralisation.

Direct filtration that comprises pre-treatment with ozone or potassium permanganate, coagulation with ferric sulfate and the cationic polymer and filtration through anthracite-sand-garnet filter bed is a viable and economically attractive alternative to the conventional treatment of Biesbosch water.

Key words pretreatment, direct filtration, coagulation, flocculation, filtration, preoxidation, ozon, potassium permanganate, algae, algal removal, motility, particles, process mechanisms, concentration of algae, tangential flow membrane filtration.

Chapter 1

INTRODUCTION

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1.1. Impounded surface water as a raw water source

Ground water is generally the preferred raw water source for the production of potable water. However, the increasing demand for drinking and industrial water, together with the limited availability of ground water and the restrictions imposed on its abstraction increasingly favour the use of surface water.

At the same time, however, extensive use of fertilisers and the discharge of untreated, or insufficiently treated, industrial and domestic waste-water have resulted in eutrophication of surface water bodies. This has adversely affected surface water quality. Consequently, rivers - the most common source of fresh surface water, particularly in Western Europe - are generally characterised by poor and variable quality. In addition, rivers are regularly characterised by seasonal flow fluctuations. The common way of improving average river water quality and reducing the effect of flow and quality fluctuations is to store river water in impoundments or reservoirs. Retaining river water in these artificial lakes, combined with adequate water quality management, can greatly improve water quality, equalises quality and quantity variations and allows the selective intake of only good quality river water. Unfortunately, impoundment itself may favour mass growth of algae, particularly during the spring and late summer. Therefore, the production of drinking water from these water bodies cannot be dissociated from algal-related treatment and distribution problems.

1.2. Direct filtration, a promising alternative for treatment of impounded surface water?

A routine treatment of impounded surface water typically includes coagulation, flocculation, floc separation by either sedimentation or flotation, rapid sand filtration and disinfection. The treatment nowadays is almost compulsorily upgraded by a post-treatment such as softening, activated carbon adsorption, slow sand filtration, etc. Such traditional treatment flow schemes are expensive and require the use of relatively large amounts of chemicals. Direct filtration, on the other hand, is for many situations a simple and relatively inexpensive alternative, provided that the surface water is of appropriate quality, namely, low in turbidity, colour, particulate matter and dissolved organic carbon. Usually oligotrophic water meets best such quality criteria. Further, this treatment option is environmentally attractive because the required coagulant dosage and hence the sludge amount produced are considerably lower than those in conventional treatment.

Over the last decade, at least in most industrialised countries, the water quality in natural and artificial lakes has stopped deteriorating. There are even examples where eutrophic lakes have been turned into oligotrophic ones (Bernhardt, 1992). This significant improvement has been achieved through reduction of the input of nutrients in the surface water, and through implementation of limnological management such as light limitation by water mixing by air injection, or control of phytoplankton concentration through biomanipulation aiming at specifically designed food chains (Oskam and Van Breemen, 1992). Appropriately, the

number of surface water impoundments with water quality appropriate for direct filtration is steadily increasing. Unfortunately, though such significantly improved water quality may be on average within the limits acceptable for the application of direct filtration, seasonal algal blooms cannot be avoided, however.

Even though algae are not a component of special concern in the current drinking water regulations, there are several problems associated with their presence in drinking water. In treatment schemes employing chlorination, algae that end up in the filtrate react with and consume chlorine, thus necessitating the use of higher dosages of chlorine and forming by-products that may be hazardous to health (e.g. chloroform). Algae in drinking water have an adverse effect on its taste and odour, and increase the concentration of easily assimilable organic compounds, with their associated after-growth problems. In addition, the efficiency of algal removal is an indicator of the elimination of other, possibly pathogenic, microorganisms in the algal size range (such as *Cryptosporidium* oocysts and *Giardia* cysts). Direct filtration in principle can be designed and operated to efficiently confront these challenges and achieve very high particle and algae removal under operationally acceptable conditions. A very efficient removal of algae is, however, a difficult task for any treatment system, and in particular for direct filtration, as this represent the single particle removal barrier. Furthermore, current understanding of phytoplankton behavioural response to various treatment techniques, and the available experimental tools are still rather rudimentary, although algal-related problems are ubiquitous and of high significance.

1.3. The Biesbosch water storage reservoirs

The Biesbosch water storage reservoirs are three large artificial lakes located in the south-western part of the Netherlands, in the province North Brabant (Fig. 1.1). These reservoirs store polluted and highly eutrophic water from the River Meuse, yet keep the algal concentration at a relatively low level by applying limnological management approaches. In 1991 water from these reservoirs accounted for about one-eighth of the total drinking water supply in the Netherlands (Oskam and Van Breemen, 1992). This represents more than half of the total amount of surface water used for drinking water purposes. Water delivered from these reservoirs is of an exceptionally high quality, and is generally suitable for direct filtration. However, during the short spring algal blooms the algal concentration exceeds several times the yearly average levels, thus making direct filtration feasibility questionable. Currently, all the waterworks that use Biesbosch water for drinking water production apply conventional treatment. However, waterworks Deltan uses direct filtration from 1986 to produce industrial water supplied to General Electric Plastic in Bergen op Zoom.

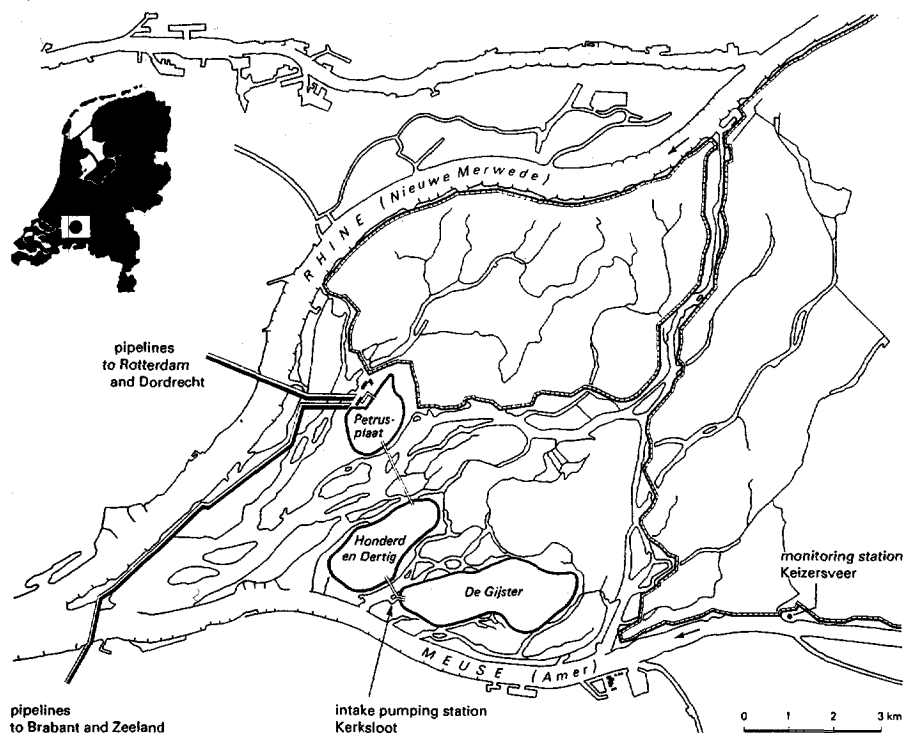


Fig. 1.1. Biesbosch water storage reservoirs (schematic)

1.4. Composition of the Ph.D. thesis

The aim of this study is to investigate the applicability of direct filtration to Biesbosch reservoir water. It focuses on particle and algal coagulation, flocculation, and removal in direct filtration (in this thesis the term "coagulation" means addition and mixing of coagulant in order to destabilize particles, and the term "flocculation" means agglomeration of destabilized particles). The study attempts to increase the understanding on the process mechanisms in order to improve significantly the elimination of algae and other particles in direct filtration. One preliminary, basic hypothesis is that floc formation is the critical step, and that this step strongly depends on pretreatment.

This Ph.D. thesis comprises a number of chapters which mostly are based on earlier published material, each of them discussing a particular aspect of algal coagulation and removal in direct filtration, under conditions pertinent to Biesbosch water treatment.

Literature on coagulation, flocculation, filtration and the direct filtration of algae laden water is reviewed in chapter 2. This chapter also includes a more general survey of literature on algae as considered relevant to water treatment practice. Finally, research hypotheses are formulated and a research approach defined as a starting point for the design of experiments.

The problems linked with the use of model water with cultured algae are discussed in chapter 3. The findings presented in this chapter question the extrapolation of results from studies that apply algal cultures to natural conditions. In addition, it expands on developing semi-batch and continuous flow experimental set-ups that are required to simulate direct filtration. The capability of straightforward direct filtration with ferric sulphate as a coagulant to remove turbidity and different algal species from Biesbosch water was also investigated. Similarly results from experiments designed to study the effect of dual- and three-layer filter media and to preliminary examine the effect of pre-treatment with different oxidants are included.

In chapter 4 a new method for the preparation of model water for algal-related water treatment study is developed. It is based on the concentration of freshwater algae with a tangential flow membrane micro-filtration system. This method allows the preparation of model water throughout the year with the natural algae from the water bodies which are intended to be used as a raw water source. This technique eliminates the problems associated with the use of model water with cultured algae, as well as those with natural waters that seasonally have too low algal concentration for experimental purposes.

The literature on different pre-treatment techniques is reviewed in chapter 5. Different pre-treatment techniques such as micro-straining, pre-flocculation and pre-oxidation are investigated, essentially to improve poor algal agglomeration and inadequate removal efficiency. Results from the batch experiments designed to study the role of micro-strainers and a separate flocculation unit in a direct filtration flow scheme are also presented. In addition, the chapter includes results from preliminary batch and continuous flow experiments designed to study the effect of pre-treatment with ozone and potassium permanganate oxidation on particle and algae removal in direct filtration. An innovative technique for *in-situ* observations of algal interaction with oxidants and iron precipitates is also introduced.

Chapter 6 presents results from batch and pilot plant experiments designed to optimise the coagulation conditions for in-line coagulation of Biesbosch water (direct filtration without separate flocculation). The optimal coagulation conditions established for in-line coagulation treatment schemes and achieved treatment efficiencies are compared with the coagulation conditions and treatment efficiency achieved in full scale conventional treatment. In addition, this chapter examines if the turbidity at very low levels can be used to assess direct filtration performance.

Preliminary experiments have demonstrated that pre-treatment with ozone or potassium permanganate has a markedly beneficial effect on the removal of particulate matter in direct

filtration. Results from further experiments designed to study the effects of Biesbosch reservoir water pre-ozonation on particle and algae removal in direct filtration are presented in chapter 7. The effect of ozone dosage, the significance of the time interval between ozonation and coagulation, the application of ozone in combination with hydrogen peroxide, and the use of cationic polymer as a secondary coagulant are discussed. Finally, an attempt is made to review the process mechanisms and a model that explains enhanced, ozone-induced particle and algae removal is proposed.

Chapter 8 introduces an innovative direct filtration treatment scheme that comprises pre-treatment with potassium permanganate, coagulation with dual coagulants and three-media filtration. The results presented demonstrate the effect of potassium permanganate on particle and algae removal. The problems caused by the use of potassium permanganate, namely residual manganese and filtrate turbidity, are investigated. Results of the treatment strategies to reduce these drawbacks are also presented.

Chapter 9 offers a general research overview and, in particular, discusses the mechanisms that allow particle and algae removal in direct filtration treatment schemes. In addition, a conceptual model is introduced that describes the fate of algae and other particles in the algal size range in the developed direct filtration treatment scheme.

As a supplement to this thesis, a video tape is included* that shows the representative algal species of the Biesbosch water storage reservoirs and, in particular, demonstrates high motility of some species. Throughout this study, algal motility has been confirmed to be critically important algal property which enables these organisms to escape treatment. In addition, the video tape shows that the introduced procedure for the concentration of algae with the tangential flow filtration system has no adverse effect on algal cell structure nor on their motility. The tape provides important qualitative information regarding the interaction of algae and coagulants (ferric sulfate and cationic polymer) and algae and oxidants (ozone and potassium permanganate).

1.5. References

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Oskam, G. and van Breemen, L. W.C.A. (1992). Management of Biesbosch reservoirs for quality control with special reference to eutrophication. In: *Eutrophication: Research and application to water supply*, D.W. Sutcliffe and G. J.Jones (eds.), Freshwater Biological Association, Cumbria pp 197-213.

*This tape can be ordered through Prof.Dr.ir. G.J.F.R. Alaerts, IHE Delft, P.O. Box 5048, 2600 GA Delft.

Chapter 2

DIRECT FILTRATION OF IMPOUNDED SURFACE WATER

State of the Art and Scope of the Study

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2.1. INTRODUCTION

In this chapter literature on direct filtration is reviewed with emphasis on the process selection and development for the treatment of impounded surface water, which is characterised by seasonally high algal concentrations. The importance of raw water quality for the application of direct filtration is analyzed. In addition, the literature is reviewed that examines the influence of pre-treatment that precedes filtration such as oxidation, microstraining and coagulation. The results are summarized from studies that investigate the effects of filter design and operational parameters (type and composition of filter media, filtration rate, backwashing, etc.) on direct filtration performance. Attention is paid to water treatment studies that deal with the coagulation, flocculation, oxidation and filtration of algae. Also, this chapter reviews fundamental literature on algae that is considered relevant to the direct filtration of impounded surface water. Finally, research hypotheses are established, the scope of the study defined and the research approach outlined.

2.2. BACKGROUND ON DIRECT FILTRATION

2.2.1. General

Direct filtration is a water treatment process which comprises the destabilization of particles present in the raw water by the addition of chemical(s), optional application of separate flocculation and, finally, filtration through a granular filter bed. In contrast to conventional methods of surface water treatment, the solid-liquid separation step (sedimentation or flotation) before the rapid sand filters is omitted; therefore, all the solids present in the raw water and those added during treatment must be removed and temporarily stored in the filter bed. "In-line coagulation" or "contact coagulation" (German: Flockungsfiltration) are frequently used terms for direct filtration processes without separate flocculation. Direct filtration supported by a flocculation unit is known as "floc filtration" (German: Flockenfiltration). A common treatment flow scheme for surface water treatment, incorporating direct filtration, is shown in Fig. 2.1.

The first direct filtration plant, based on a combination of coagulation and filtration without a separate sedimentation unit, was designed and patented by Hyatt in the United States in 1884 (Baumann 1988). From the very beginning, the rapid clogging of the filters limited the process feasibility. Technical developments in the early 40's, like the use of dual filter media and the application of polymers, proved to be prerequisites to increase direct filtration feasibility. In 1962, new drinking water standards that lowered the turbidity standard from 10 to 5 NTU, were adopted in the U.S. Consequently, several cities that previously could use untreated water, were forced to construct water treatment plants. These plants were based on conventional treatment technology. Sedimentation which preceded the filters, however, frequently failed to improve water quality. As a consequence, in practice the sedimentation step often was by-passed and coagulated suspension was brought directly to the filters. This

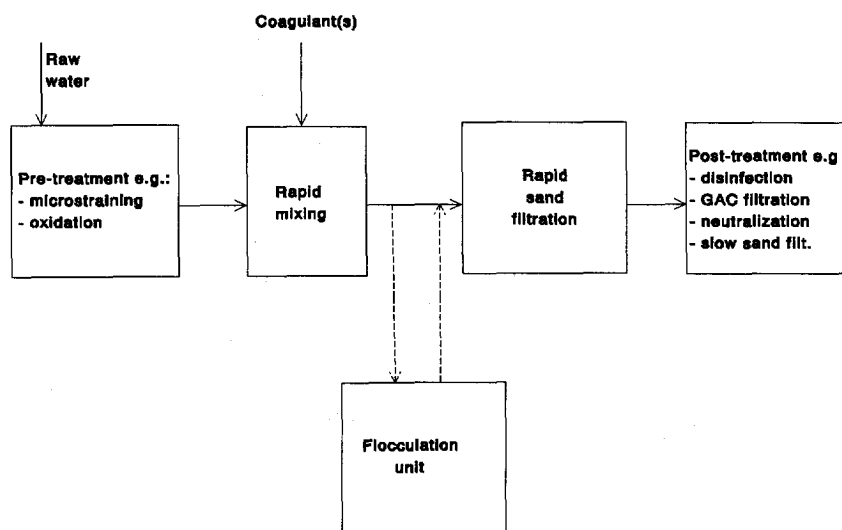


Fig.2.1. Surface water treatment scheme with direct filtration.

simplified treatment process was successful, thus confirming direct filtration credibility. In 1964, a direct filtration water treatment plant was constructed for the city of Toronto, followed by three additional direct filtration plants constructed in Ontario (McCormick and King 1982). From then on direct filtration has been widely applied worldwide and in particular in the U.S.

Direct filtration is in principle economically very attractive, because it may lead to lower capital, chemical and sludge treatment costs. The savings in capital costs, mainly because of the absence of sedimentation and flocculation units, can amount to up to 50% as compared to conventional treatment (Janssens *et al.* 1986). An additional benefit is the significantly reduced space requirement for plant construction. Direct filtration is also favourable environmentally as fewer chemicals are used, resulting in lower sludge production and reduced sludge disposal problems. Additionally, the treatment of produced waste water is simplified, since all the process waste streams are contained in a single stream as filter backwash water.

However, a number of limitations and drawbacks are associated with direct filtration. Firstly, direct filtration is economically attractive and viable only for raw water sources of appropriate quality; this means that there are limitations regarding raw water turbidity, colour and algal content. Because in the direct filtration mode filter runs are shorter, filters must be backwashed more frequently, and this requires a larger filter area, increased backwash water consumption and higher energy costs. Nevertheless, this increase in costs often is not particularly significant when compared with the savings in capital and chemical costs. Disadvantages also include the need for close monitoring of the raw water and filtrate

quality, and the need for skilled qualified personnel. As direct filtration is a much more sensitive process than conventional treatment, the need for pilot plant investigations prior to a full scale plant design, is more pronounced.

2.2.2. Raw water quality appropriate for direct filtration

The feasibility of direct filtration can be expressed as a function of the characteristics of the raw water, or the amount of chemicals required to achieve the targeted filtrate quality. The AWWA Filtration Committee report (1980) suggests checking either historical data on water quality, or monitoring water quality for two to three years before direct filtration is selected. In general, surface water with low turbidity, colour and algal count is adequate for direct filtration application. Depending on the source consulted, different upper limits of different raw water quality parameters have been proposed (Table 2.1.). These limits provide useful preliminary indication. However, final conclusion for a particular raw water source can be drawn only after detailed studies, preferably including pilot plant experiments.

Table 2.1. Average raw water quality acceptable for direct filtration

| PARAMETER | Edzwald <i>et al.</i> (1987) | AWWA (1980) | Culp (1977) | | |
|-----------------------|---------------------------------|----------------|----------------|------------|--------------|
| Turbidity (FTU) | < 20-30 and < 30-40 | < 5 | < 25 | < 200 | low |
| Colour (mgPt-Co/l) | | < 40 | and < 25 | and low | and < 100 |
| Algal count (ASU*/ml) | low | < 2000 | < 1000 | | |
| Iron (mg/l) | - | < 0.30 | - | | |
| Manganese (mg/l) | - | < 0.05 | - | | |

A tentative diagram for selection of the appropriate solid-liquid separation option was recently proposed by Janssens and Buekens (1993). In this diagram turbidity and the algal concentration expressed as chlorophyll- α are recommended as decisive raw water quality parameters that define the appropriate solid-liquid separation step (Fig.2.2). Direct filtration would be in any case, an appropriate treatment option for the raw water sources with turbidity < 10 FTU and chlorophyll- α < 10 $\mu\text{g/l}$. Based on a nonlinear optimization program Wiesner *et al.* (1984) and Wiesner (1985) proposed direct filtration as a cost-optimal treatment configuration for raw water with the suspended solids concentration < 15-20 mg/l. Even though the diagram and the model may be useful tools for preliminary selection of a suitable floc separation process it should be noted that the effect of other important water

* ASU/ml - area standard unit (1 ASU=400 μm^2) represents the horizontally projected area of algal cell settled in the counting slide

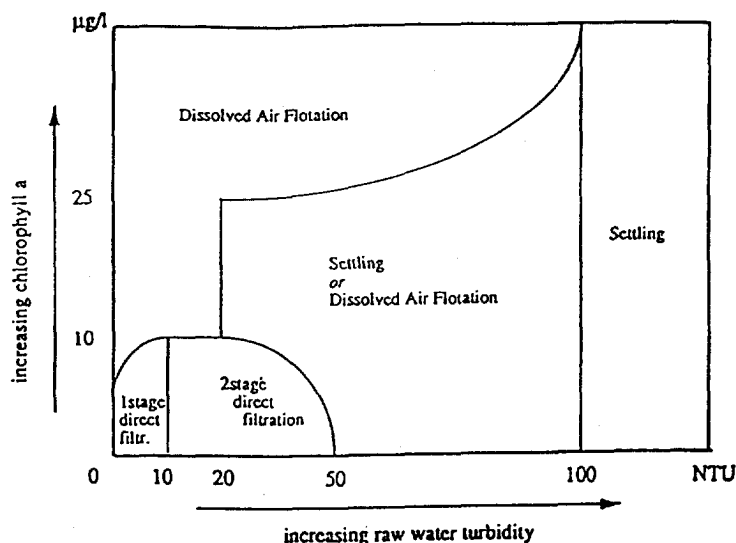


Fig.2.2. Floc separation processes: selection diagram (Janssens and Buekens 1993).

quality parameters like raw water colour and the concentration of dissolved organic matter is neglected. It is well known that surface waters with high concentration of dissolved natural organic matter require high coagulant dosages that consequently can exclude direct filtration as viable treatment option.

Wagner and Hudson (1982) proposed that preliminary assessment of suitability of a raw water source for application of direct filtration can be performed on the basis of the required amount of metal coagulant needed to obtain low-turbidity effluent in jar test experiments followed by filtration through laboratory filter (Whatman No. 40, Whatman Ltd., England). They concluded that economical direct filtration performance is doubtful if the required coagulant dosage, stated as alum (which I beleive to be $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$) is higher than 20 mg/l; raw water that requires a coagulant dosage < 6-7 mg/l is suitable for direct filtration; and raw water that requires coagulant dosages between 6 and 20 mg/l are in the marginal area, and the potential for direct filtration must be evaluated case by case. The last approach seems logical, bearing in mind that metal coagulants frequently contribute more significantly to filter clogging than natural impurities removed from raw water. However, this limitation may be overcome in certain circumstances by replacing the conventional metal coagulants with synthetic or natural organic polyelectrolytes. This is particularly the case when the colour of raw water is high and the required dosages of coagulant are proportional to the colour level. Consequently, direct filtration can be applied for treatment of raw water with colour > 25-30 mgPt-Co/l only if polymers are used as the main coagulants (Hutchison 1976, McCormick and King 1982).

Water from Petrusplaat, the last in the series of Biesbosch water storage reservoirs, meets most of these quality requirements suggesting that Biesbosch water is likely suitable for application of direct filtration. However, a high concentration of algae during short spring blooms causes doubt regarding process reliability.

2.2.3. Direct filtration process mechanisms

The removal of colloidal and suspended matter in direct filtration involves three subsequent steps: coagulation, flocculation (agglomeration) and capture of formed agglomerates and impurities in the filter bed.

2.2.3.1. Coagulation

The function of the coagulation step is to alter the surface properties of colloidal and fine particulate matter in the raw water, and consequently to provide favourable conditions for the formation of agglomerates that can be efficiently brought into contact and attached to the filter grain or existing deposits in the filter bed. This is basically achieved through destabilization of colloidal and suspended particles by coagulant addition. The stability of inert colloidal particles is described by the classical DLVO theory proposed by Deryagin and Landau (1941) and Verwey and Overbeek (1948). In addition to the colloid interaction described by DLVO theory incorporating the Van der Waals attraction and the electrical attraction or repulsion forces, other effects like hydration and hydrophobicity, steric interaction and polymer bridging are known to be important in certain cases (Gregory 1993). Also, the mineralogy of the inert particulates influences the mechanisms of coagulation and flocculation (Alaerts and van Houten 1982). Particle destabilization decisively influences removal efficiency in rapid gravity filters (Boyd and Ghosh 1974, Adin *et al.* 1979, O'Melia 1985, Amirtharajah 1988).

Therefore, appropriate conditions for particle destabilization should be carefully determined. Coagulants used in direct filtration are identical to those used in conventional coagulation treatment. Mostly iron and aluminium salts are used. Coagulation diagrams that define conditions for effective chemical destabilization with aluminium sulfate [$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$] and iron coagulants (Johnson and Amirtharajah 1983, Amirtharajah *et al.* 1993, Ahsan 1995), may be very useful as a supplement or preparation to jar tests. In addition to metal coagulants, natural and synthetic organic polyelectrolytes are increasingly applied. Organic polyelectrolytes are often used as filter aids in addition to metal coagulants, in order to improve the floc characteristics, since mineral flocs are known to be weak, with a low compressibility. These polyelectrolytes are also known to enhance the rate of orthokinetic flocculation of the system, when already initiated by metal coagulant. Application of cationic polyelectrolytes as the main coagulant is also frequently reported (AWWA Committee Report 1980, Wagner and Hudson 1982, Edzwald *et al.* 1987).

The main difference between the coagulation in conventional treatment and direct filtration

relate to the limited storage capacity of the filter bed available for the deposition of flocs. Excessive coagulant dosages are, therefore, expected to rapidly clog filters with associated fast headloss development and unacceptably short filter runs. This is particularly the case when metal coagulants, producing voluminous flocs, are used. Dosages of metal coagulant should in principle be very low; the destabilization of hydrophobic particles is attempted as much as possible by an adsorption and charge neutralization mechanism, as higher dosages would result in sweep coagulation with corresponding voluminous metal precipitates. Destabilization of hydrophillic colloids cannot be very efficiently achieved through adsorption and charge neutralization due to water layer bounded to the surface of the particle. Destabilization of hydrophillic colloids is consequently mainly achieved through sweep coagulation associated with higher coagulant dosages. Amirtharajah (1988) demonstrated that most full-scale direct filtration plants in US operate within a domain that corresponds to charge neutralization, i.e. with dosages of 2-20 mg aluminium sulfate/l and pH from 6.5 to 7.5.

In conventional treatment, coagulation by charge neutralization is, in general, not very effective when the concentration of colloids is very low. This is mainly due to the lack of contact opportunities between destabilized particles (low particle concentration), and subsequent slow agglomeration. In the case of direct filtration, raw water is a very dilute suspension. Nevertheless, after the addition of a coagulant, destabilized water solution flows through the filter bed, and high velocity gradients are generated (e.g. $G \geq 100 \text{ s}^{-1}$ at a filtration rate of 10 m/h and a filter media with an effective size $< 1.0 \text{ mm}$). Consequently, flocculation may takes place at much higher rates than in the conventional coagulation-flocculation processes due to higher G values and much higher particle contact opportunities (particle-particle, particle-grain). On the other side higher G and small pore sizes may limit particle diameter, and therefore reduce flocculation rate.

A more detailed review of literature on coagulation with metal coagulants in direct filtration of impounded surface waters is given in chapter 6.

2.2.3.2. Flocculation

The flocculation (agglomeration) of destabilized colloidal and fine particulate matter takes place in the flocculation unit (if present), in the pipes that connect rapid mixing and filtration units, in the supernatant water above the filter media, and in the pores of the granular filter bed.

The need for a separate flocculation unit preceding direct filtration is still the subject of some controversy. Numerous full-scale direct filtration plants are operating efficiently without a flocculation basin. However, there is evidence that the performance of certain plants was significantly improved after a flocculation unit had been installed (Monsevizt *et al.* 1978). If applied, a flocculation unit will alter the particle size distribution (PSD). It is known that PSD has a pronounced influence on filter removal efficiency and head loss development in the filter bed. Fundamental studies (Yao *et al.* 1971) found a minimum particle removal

efficiency for a particle diameter of app. 1 μm . Habibian and O'Melia (1975) have shown that head loss per unit mass of deposited particles in the filter bed is inversely related to particle size. Submicron particles caused considerably higher head loss for similar mass removal than large particles. With respect to minimizing treatment costs Wiesner (1985) and O'Melia (1985) proposed contact filtration as optimal treatment configuration for raw water with very low particle concentration (mass concentration of particles < 8 mg/l), dominated by very small particles (volume average diameter < 1.5 μm). Direct filtration supported by a separate flocculation unit is an economically viable treatment configuration for raw water with somewhat higher particle concentration (mass concentration of particles < 15 mg/l) dominated by particles > 2 μm . Edzwald *et al.* (1987) came to similar conclusions and suggested that in the case of reservoir water with low turbidity and a low to moderate total organic carbon (TOC) level, separate flocculation does not have a strong effect on filter performance due to slow flocculation kinetics.

Consequently, the need for a separate flocculation unit is closely correlated to raw water quality and in particular to PSD and particle concentration. A shift in the PSD towards the larger particles will reduce head loss development in the filter bed. However, if the applied flocculation time is too long, very large flocs may be formed thus inducing cake filtration. On the other hand an appropriate separate flocculation unit may induce a shift in the PSD from submicronic size to particle diameters of 1 to 3 μm , and consequently reduce filter removal efficiency.

Literature on the existence of flocculation in filter pores and its influence on filtration efficiency was reviewed by Graham (1986). This issue is also the subject of some controversy. While some authors proposed that flocculation in the filter bed is an important mechanism, other more fundamental studies have demonstrated the absence of this effect. Such contradictory conclusions are mainly the consequence of the experimental difficulties of direct measurement of filter pore particle flocculation. Graham (1986) made an attempt to quantify filter pore orthokinetic flocculation by using laboratory-scale model filters, hydrophobic silica particles and nonionic polyacrylamide polymer. He found that the particle collision efficiency factor increased with the shear rate. In addition, Graham compared the collision efficiency factor in a jar test, capillary-tube apparatus and filter pores under equivalent conditions. This comparison has shown that in rapid filtration practice, using cationic polymers and at high shear rates ($G > 150 \text{ s}^{-1}$), filter pore collision efficiency is between those in tube flow (lower boundary), and in jar test (upper boundary). Filter pore collision efficiency factor may be as high as 0.5 for suspensions destabilized by cationic polymer (Graham 1986). More recently it appears that it is possible to differentiate between the flocculation and filtration effects by making experiments with model waters with different concentration of impurities (C), because filtration is first, and flocculation is second order process with respect to C (Ives 1996, personal communication).

Further agglomeration of a destabilized suspension, in addition to agglomeration in a separate flocculation unit and in filter pores, may theoretically also occur in pipes that transport

coagulated suspension and in the supernatant above the filter media. However, the effect of these transportation units on particle agglomeration can be neglected given the low velocity gradients in the supernatant above the filter media, and the short residence time in pipes that connect the rapid mixing and filtration unit. The exception may be the case where pipes are intentionally designed to provide flocculation.

2.2.3.3. Particle capture in filters

Destabilized and agglomerated particles should be removed in the filter bed. Particle capture in filters may be divided into two interconnected processes: particle transport, a physical-hydraulic process, and particle attachment to filter grain, largely a physical-chemical process. Particle transport mechanisms notably straining, interception, inertia, gravity settling, diffusion due to Brownian motion, and hydrodynamic action act simultaneously and contribute to particle-grain contact with varying degrees of relative importance, depending on the nature of the suspension and filter medium. Ives (1975) represented the efficiency of filter transport mechanisms in a simplified form by equation (1):

$$\Lambda = \text{const} \left[\frac{d}{D} \right]^{\alpha} \left[\frac{KT}{3\pi\mu dVD} \right]^{\beta} \left[\frac{g(\rho_s - \rho)d^2}{18\mu V} \right]^{\gamma} \left[\frac{\mu}{VD\rho} \right]^{\delta} \quad (1)$$

where:

- Λ - filter efficiency (-)
- d - particle diameter (m),
- D - grain diameter (m),
- K - Boltzmann's constant (J/°K),
- T - thermodynamic temperature (°K),
- V - approach velocity of filtration (m/s),
- g - gravitational acceleration (m/s²),
- ρ - density of liquid (kg/m³),
- ρ_s - density of particles (kg/m³),
- α - exponent of interception group,
- β - exponent of diffusion group,
- γ - exponent of gravity group,
- δ - exponent of hydrodynamic group.
- μ - dynamic viscosity of liquid (kg/m s),

The first dimensionless factor in equation accounts for interception, the second for diffusion, the third for gravity and the fourth for hydrodynamic action. Straining, being not strictly a transport mechanism, and inertia, known to be insignificant, were not considered. After rearranging, equation (2.1) gives equation (2.2)

$$\Lambda = \text{const} \frac{d^{\alpha-\beta+2\gamma}}{\mu^{\beta+\gamma-\delta} D^{\alpha+\beta+\delta} V^{\beta+\gamma+\delta}} (KT)^{\beta} \frac{(\rho_s - \rho)^{\gamma}}{\rho^{\delta}} \quad (2)$$

By analysing equation (2) Ives (1975) concluded:

- (a) smaller filter grain sizes D and smaller filtration velocity V improve transport efficiency;
- (b) increase of water temperature with associated decrease in the viscosity will improve transport efficiency, provided that $(\beta + \gamma) > \delta$; consequently, the viscosity effect is most marked for small and dense particles;
- (c) an increase in particle size d will improve filtration, with an exception for very small particles affected by diffusion forces (β large compared to $\alpha + 2\gamma$); a particular particle size is consequently associated with minimum filtration efficiency.

Yao *et al.* (1971) numerically determined and experimentally confirmed that critical particle size is about $1 \mu\text{m}$; for particles $> 1 \mu\text{m}$ transport efficiency increases because of enhanced interception and gravity; for particles $< 1 \mu\text{m}$ more efficient transport will be achieved by diffusion. In addition, their model predicts that the density of the suspended particles larger than $1 \mu\text{m}$ exerts significant effect on filtration attributable to settling, while other filtration parameters like filtration velocity, temperature and media size have considerably less influence on filtration efficiency. Boyd and Ghosh (1974) experimentally demonstrated that variation in particle size distribution in the range $3.9\text{--}7.0 \mu\text{m}$ has very little effect on the filter coefficient measured as particle size-frequency distribution with filter depth.

Boyd and Ghosh (1974) and Adin *et al.* (1979) concluded that the transportation mechanism is not critical in the conventional rapid sand filtration, because the transport mechanisms involved provide a sufficient particle-grain contact rate even for particles that have minimum transport ability. Consequently, attention should be focused on the attachment step as the major factor that determines filtration efficiency.

The attachment of particles to the filter grains is determined primarily by the surface characteristics of the particles and filter grains. To achieve efficient adherence colloidal suspensions to be filtered should be unstable (Gregory 1975). Consequently, the coagulation step controls the actual attachment of the particles to the grain. The same forces that control inter-particle stability, notably the attractive van der Waals forces, and the electrical attraction or repulsion forces, control the particle attachment to the filter grains. In addition, coagulants may induce a bridging effect that promote the attachment of particles to the filter grain surface. The strength of adhesion of particles to filter grains is, however, difficult to determine, since colloidal interactions at very close distance are not well understood (Gregory 1993).

In addition to particle transport and attachment, the third step, deposit detachment, may also influence overall particle capture efficiency in direct filtration. The detachment step was first suggested by Mints (1966). Shear strength of the deposit affects its detachment. Adin *et al.* (1979) reported that coagulation with alum results in a very effective attachment, however,

these deposits are relatively poor in resisting shear forces in high-rate filtration. Cationic polymers, however, cause strong attachment forces between the removed matter and the filter grains (Adin and Rebhun 1974, Adin *et al.* 1979), and thus increase the shear strength of the deposit and, consequently, reduce detachment. Detached particles or aggregates of particles are entrained in the flow and behave like other particles in suspension and may be re-deposited or may leave the filter with the filtrate (Ives 1975).

2.3. ALGAE AND DIRECT FILTRATION

2.3.1. Algae-related problems

Raw water of high and constant quality, as required for the application of direct filtration, may be most frequently found in surface water impoundments and lakes. The production of drinking water from these sources is inevitably associated with numerous algae-related problems. As far as direct filtration is concerned, these problems may be grouped into three categories: (a) problems related to algae or algal products passing through filters, (b) the rapid clogging of the filters caused by a high concentration of large or filamentous algae (b) and (c) the hindrance of the coagulation and flocculation of other impurities present in raw water caused by algae-derived extra-cellular organic matter (EOM) resulting in a higher coagulant dosage required.

Proper eutrophication control strategies coupled with adequate reservoir management may considerably diminish the last two categories of inconvenience. To lessen the problems of the first category, treatment systems should remove algae very efficiently. However, the acceptable algal concentration in drinking water is not explicitly specified in water quality standards. Indirectly, algae are included through unspecific parameters such as turbidity, colour, or TOC. However, drinking water fulfilling acceptable levels for these parameters may still contain a relatively high algal load. The German Association of Drinking Water Reservoirs established an interim standard of 0.1 $\mu\text{g/l}$ as the maximum allowable concentration of chlorophyll- α in the produced water. Even though algae are not specifically mentioned, there are numerous reasons to prefer efficient algal removal and the production of drinking water with very low concentration of algae:

- (a) algae that penetrate treatment, in schemes that use chlorine for disinfection, increase chlorine demand and serve as precursors for the formation of trihalomethanes and other halogenated, by-products that may be hazardous to health (e.g. chloroform);
- (b) when present in the drinking water, algae may introduce toxins and deteriorate the drinking water's taste and odour;
- (c) algae that pass treatment also indicate that the removal of other particles in the algal size range, such as cysts and oocysts of pathogenic microorganisms like *Giardia* and

Cryptosporidium, may be inefficient as well; and

(d) algae that pass filters contribute to biological aftergrowth in the distribution network.

The biological stability of drinking water and the aftergrowth problems are of particular importance in the Netherlands, where chlorination is no longer systematically used to preserve the quality of drinking water in the distribution system. Therefore, the impact of algae on the assimilable organic carbon (AOC) is discussed here in more detail.

Some recent evidence has shown that organic debris, including that from algae, is important for the growth of bacteria (van der Kooij and Hijnen 1985, Watson 1990). This also can be observed in Fig.2.3, which shows a fresh, non-fixed colony of *Pandorina* sp. cells in Biesbosch water (a), and the same colony after 24 hours with a large number of bacteria that intensively grow on a mucilage capsule attached to peripheral cells (b). Watson (1990) reported that approximately 35% of particulate organic carbon (POC) in filtered water, and 21% of POC in the distribution system, is assimilable by bacteria. It is, however, difficult to distinguish the specific algal contribution from that of other particulate and dissolved organic carbon sources in the total AOC. However, there is no doubt that algae and their products offer a favourable environment for bacterial growth. Algae are also the regular diet for some species of protozoa and higher organisms that can grow in the distribution system. Consequently, algae that pass through rapid sand filters promote biological aftergrowth in the carbon filters, treatment plant mains, and distribution systems may cause hygienic, technical and aesthetic problems.

The effects of different treatment steps used for conventional treatment of Biesbosch reservoir water (water treatment plant Kralingen, Rotterdam) on AOC and dissolved organic carbon (DOC) concentrations are given in Fig.2.4 (van der Kooij 1990). In addition to high AOC reduction following filtration, it can be observed that pre-ozonation considerably increases AOC. The AOC increase is most likely partly correlated with the forced lysis of algal cells and secretion of algal biopolymers under strong oxidative conditions. Efficient algal removal associated with intensive cell lysis cannot be accepted in view of problems created with biological aftergrowth.

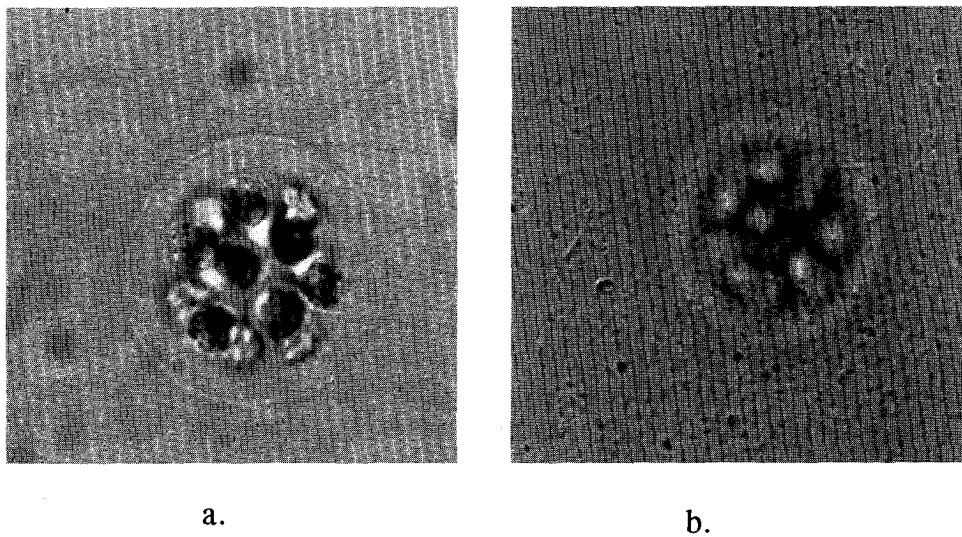


Fig.2.3. Fresh colony of *Pandorina* sp. from Biesbosch reservoir (a), and the same colony after 24 hours with bacteria growing on its mucilage (b).

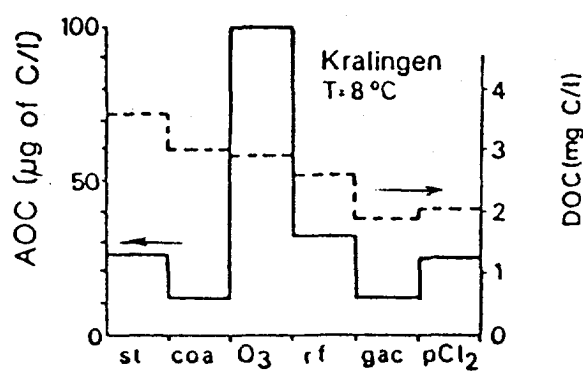


Fig.2.4. Effect of a standard water treatment on AOC and DOC; st-straining, coa-coagulation, O₃-ozonation, rf-sand filtration, gac-carbon filtr., pCl₂-chlorination (van der Kooij 1990).

2.3.2. Algal properties important for water treatment

The term algae encompasses a large assemblage of photosynthetic organisms. There are two basic types of algal cells: *eukaryotes*, that possess a nuclear membrane and high degree of internal differentiation, and *procaryotes*, that lack a membrane and have a lower level of internal differentiation. Algal removal efficiency in both conventional treatment and direct filtration is generally significantly lower and less reliable than removal of other impurities present in water. Several factors are responsible for this. The main one is that algae are living organisms with very specific properties. Algae include many thousands of species (Palmer 1980), of different sizes, shapes and other properties. Many of these properties determine the removal efficiency, which implies different treatment strategies for different species. Also, the algal population in surface water impoundments passes through seasonal cycles of dominant algal genera and species. In addition, gradual changes in predominance are evident over the years. Even the same species of algae may show a significantly different behaviour as a function of growth stage or difference in the composition of its suspending aqueous medium (Petrusevski *et al.* 1993). The capability of standard treatment processes to remove algae, and some of the related problems, are listed in Table 2.2. Characteristics and drawbacks of the standard treatment process strongly suggest that very efficient and operationally and economically attractive algae removal can be only achieved by the combined process that includes several unit treatment processes. The combined process that comprises microstraining, oxidation and direct filtration seems to be particularly suitable for impounded surface water.

The dominant algal properties that are commonly believed to influence algal behaviour in water treatment are: size, shape (form), mobility, cell surface characteristics, ability to produce extra-cellular organic matter (EOM), and low cell density that in some species may be affected by vacuole formation. Some of the frequently occurring freshwater algae are shown in Fig. 2.5, and their characteristics indicated in Table 2.3.

2.3.2.1. Algal size

Algae are frequently divided according to their size (Lee 1989) to:

- picoplankton - algae smaller than 2.0 μm ,
- nanoplankton - algae smaller than 75 μm , but larger than 2.0 μm ,
- macroplankton - algae larger than 75 μm .

As a consequence of their small size, two types of problems may be expected: firstly, algae pass through treatment, particularly when very small species abound, and, secondly, certain macroplankton and nanoplankton species when present in high concentrations rapidly clog filters and microstrainers.

Table 2.2. Algal removal as function of treatment technique

| Unit Operation | Removal efficiency | Associated problems |
|--------------------------------|--|---|
| 1. Microstraining | * only high for species larger than mesh size (usually 35 μm) | * fast clogging during blooms * some filamentous species become matted and are difficult to remove |
| 2. Coagulation + Sedimentation | * varies over a wide range as a function of dominant species, growth phase and process parameters; * some species pass treatment easily (e.g. very small algae) | * process optimisation difficult |
| 3. Coagulation + Flotation | * higher than with coag./sedimentation; * certain species difficult to remove (e.g. large diatoms) | * process optimisation and operation difficult |
| 4. Rapid Sand Filtration | * generally low, and depends on dominant algal species | * fast filter clogging if algal concentration high |
| 5. Slow Sand Filtration | * very high for most algal species * some very small species may pass filters | * fast clogging if algae present in moderate concentration * possible proliferation of algae on filter surface and in the supernatant |
| 6. Oxidation | * kills algae or alters their properties and consequently enhances their removal during later treatment stages | * release of dissolved organics in water if higher dosages applied * possible production of oxidation by-products that may be health-hazardous |
| 7. Direct Filtration | * considerably higher than with rapid sand filtration * small, unicellular species may pass filter | * fast clogging possible if algal concentration very high |

Table 2.3. Nominal mean maximum dimension (NMMD), volume, shape and specific properties of some common freshwater algae

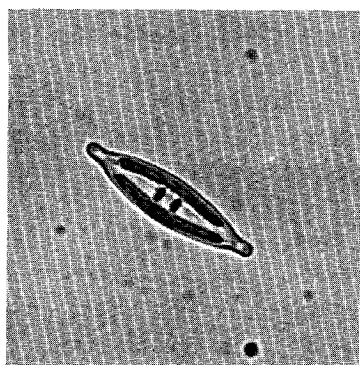
| ALGAL GENUS | NMMD (μm) | VOLUME (μm^3) | SHAPE | SPECIFIC PROPERTIES |
|--------------------------|---------------------------|-------------------------------------|----------------|------------------------|
| Chlorophyta | | | | |
| <i>Chlamydomonas</i> | 10 | 4445 ^{#2} | ellipsoid/oval | flagellar motility |
| <i>Chlorella</i> | 4 | 33 ^{#1} | sphere | |
| μ -algae | 2 | 4 | sphere | |
| Bacillariophyta | | | | |
| <i>Navicula</i> | 15 | — | cigar shaped | gliding motility |
| <i>Asterionella</i> | 80 | 685 ^{#2} | star-shaped | forming circ. colonies |
| <i>St. hantzschii</i> | 11 | 600 ^{#1} | cylindrical | long bristles |
| <i>St. astraea</i> | 26 | 5930 ^{#2} | cylindrical | - |
| <i>Melosira</i> | 300 | 2277 ^{#2} | cylindrical | long filaments |
| Cryptophyta | | | | |
| <i>Rhodomonas</i> | 8 | 129 ^{#2} | ellipsoid | highly motile |
| <i>Cryptomonas</i> | 25 | 2526 ^{#2} | ellipsoid | motile |
| Cyanophyta ^{#3} | | | | |
| <i>Microcystis</i> | 200 (colony) | 4.2*10 ⁶ . ^{#1} | sphere | mucilaginous colonies |

Notes:

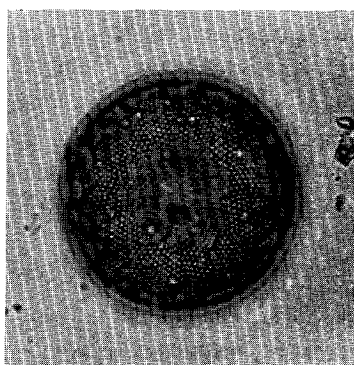
^{#1} Reynolds (1984),^{#2} Michielsen and Ketelaars (1994),^{#3} Cyanophyte (cyanobacteria) are bacteria; nevertheless due to similarity in size, occurrence in surface water and problems created in drinking water treatment these organisms will be treated here as algae.

Pico- and nanoplankton dominate surface water impoundments commonly used for water supply purposes. Furthermore, a significant number of algae species falls within the size range 1 to 10 μm . Due to the relatively inefficient transportation step, particles of such a size class are the most difficult to remove by filtration (see paragraph 2.2.3.3.). Very small algae ($\leq 10 \mu\text{m}$) can pass through the filtration unit. Therefore, algal removal efficiency can be substantially improved if the algae of such a small size are agglomerated. However, algal flocculation is generally difficult to achieve, since algal properties tend to hinder their agglomeration (see 2.3.3.2, 2.3.3.3, 2.3.3.4 and 2.3.3.5).

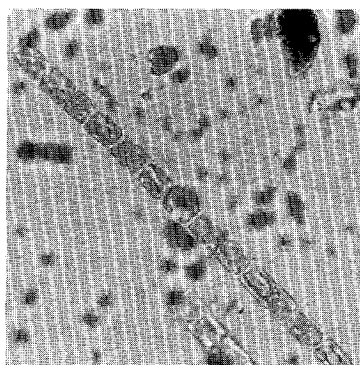
Very large algae, and particularly such a species that have very long filaments, may also be troublesome. Some of them, e.g. the diatom *Melosira islandica*, are efficiently removed in the filters, but their removal, particularly during blooms, causes rapid filter surface clogging. Further, algae which are very long but narrow (2-4 μm), like the cyanobacteria alga *Oscillatoria rubescens*, are difficult to agglomerate and to efficiently retain in filters by using metal coagulants. In addition, this alga is very sensitive to shear and, consequently, broken algal fragments pass filters even more easily (Bernhardt and Clasen 1991).



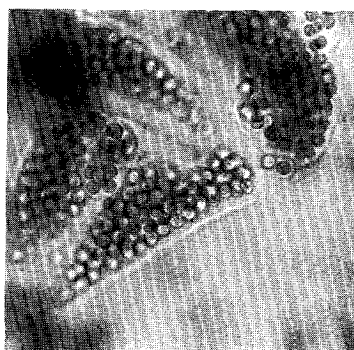
a.



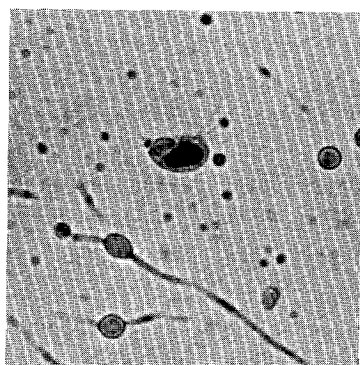
b.



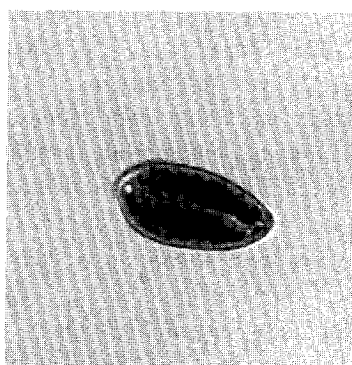
c.



d.



e.



f.

Fig.2.5. Some freshwater algae typical for the Biesbosch water storage reservoirs: (a) *Navicula* sp., (b) *Stephanodiscus astrae*, (c) *Melosira* sp., (d) *Microcystis aeruginosa*, (e) *Rhodomonas* sp. and (f) *Cryptomonas* sp.

2.3.2.2. Algal shape (form)

Algal shape factors that affect their behaviour in water treatment are the presence of bristles, large length to width ratio, form of cell unification, etc. For instance, the diatom *Stephanodiscus hantzschii* has very long bristles (40 μm) that prevent contact between cells and hence prevent their agglomeration (Bernhardt and Clasen 1991). However, it can be observed that *S. hantzschii* in Biesbosch water does not have these long delicate needles all the year round, but only during certain periods.

The form of cell unification may significantly contribute to filter clogging problems. The diatom *Tabellaria*, for example, with cells generally united in a zigzag arrangement by flexible gelatinous cushions is known to produce a clogging membrane on the top of the filter (Palmer 1980). Similarly, large colonies of diatoms *Asterionella formosa* and *Fragillaria crotonensis* can be efficiently filtered even without coagulant, however surface filtration was found to predominate (Bernhardt and Clasen 1991).

2.3.2.3. Motility

The subject of algal motility attracted considerable interest from phycologists, however, this algal property attracted very little attention in water treatment research. Motility is the algal response to external stimuli like light, and gravitational, chemical or thermal gradients, that allows these organisms to search for a suitable environment (Häder and Hoiczky 1992). Algae exhibit a variety of active cell motility phenomena. Flagellar motility is the most widely known and studied type of active algal cell locomotion. It is present in different algal genera. Even the cells of centric diatoms that are not flagellate form motile flagellated gametes. Some algal species that form colonies like *Pandorina* sp. and *Synura* sp. exhibit high flagellar motility because each cell of the colony bears two flagella. Flagellates exhibit several types of swimming behaviour and are able to change the type and speed of their locomotion. Flagellar swimming velocities between 5 and 500 $\mu\text{m s}^{-1}$ were reported (Goldstein 1992). Racey *et al.* (1981) found that *Chlamydomonas reinhardtii* has an average forward speed of 379 $\mu\text{m s}^{-1}$ and an average backward speed of 218 $\mu\text{m s}^{-1}$. We observed that *Rhodomonas minuta* (Cryptophyta) moves much faster than *Chlamydomonas* sp. and is probably the fastest swimming alga among the species present in Biesbosch water (see video tape, Appendix 3). No quantitative data on *R. minuta* motility were found in the literature. However, comparison with the values reported for *Chlamydomonas* sp. suggests that the swimming velocity of *R. minuta* is likely considerably higher than 1000 $\mu\text{m s}^{-1}$.

It is probably less known that non-flagellated algae can also be highly motile. Gliding motility is another variety of algal cell motility that is widespread throughout different algal classes and genera. Gliding can be defined as an active translocation of an organism in contact with a solid or semisolid substrate, or even through a highly viscous matrix, without a microscopically detectable organelle for locomotion or a visible change in shape (Jarosch 1962, Halfen and Castenholz 1971, Häder and Hoiczky 1992). Gliding is always accompanied by slime secretion. It has been observed with numerous cyanobacteria,

especially in benthic species. Flexing, bending, jerking, and twitching are typical for rod-shaped unicellular forms, while filamentous forms display continuous movements (Häder and Hoiczky 1992). It has been reported that the trichomes of *Oscillatoria* sp. can glide with high velocities of up to $11 \mu\text{m s}^{-1}$. Other cyanobacteria that can glide are *Anabaena* sp., *Nostoc* sp., *Phormidium* sp. etc. The representatives of the eucaryotic organisms which can glide are pennate diatoms (like *Navicula* sp., *Synedra* sp., *Nitzschia* sp., etc.) and desmides (like *Closterium* sp., *Cosmarium* sp.). In addition, several species of Euglenophyceae and *Chlamydomonas* sp., which are flagellates, also use gliding motility besides flagellar movement. The gliding motility in the pennate diatoms shows an irregular pattern that includes frequent stops and reversals, with a velocity range from 0.2 to $25 \mu\text{m s}^{-1}$. *Navicula* sp. are able to glide over surfaces with observed rates of up to $14 \mu\text{m s}^{-1}$ (Lee 1989). The movement is associated with extrusion of a slime trail that is left behind a diatom (Häder and Hoiczky 1992). Gliding motility is also present with several protozoa. Rotational movement has been observed with the centric diatom *Actinocyclus* sp.

Ives (1955) noted that several aspects of algal motility may interfere with water treatment processes. He encountered difficulty while measuring the electrophoretic mobility of motile algae, particularly *Chlamydomonas* sp. and concluded that motility is completely unaffected by the applied potential. He also quoted the work of Palin who observed under the microscope that the motile organisms have the ability to free themselves and move through the coagulated suspension. Bernhardt and Clasen (1991) came to a similar conclusion, surmising that flagellates might be able to liberate themselves from flocs.

2.3.2.4. Algal cell surface characteristics

Little research has been devoted in this area. Ives (1955, 1956, 1959) studied the electrophoretic mobility of algae, and found that over the investigated pH range (2.5-11.0) the algae remain electronegative. Northcote *et al.* (1958) tried to obtain additional information on the surface characteristics by examining the composition of the cell wall of *Chlorella*. An analysis of the cell wall showed a high concentration of proteins (27%) and cellulose (46%), suggesting that these materials may control the surface properties of this alga. The colloidal proteins carry a negative charge at higher pH and a positive one at low pH values. The isoelectric point occurs around $\text{pH}=4$, although it may be shifted to lower values if certain anions are present. The study of the surface characteristics of cellulose by microelectrophoresis indicates an isoelectric point at $\text{pH}=2.5$, with a negative charge at higher pH values. Consequently, algae have an isoelectric point in the acid region with an increasing negative charge at higher pH values. In surface water algae always carry negative charge. Ives (1959) reported that zeta potential and charge density at a constant pH varied from genus to genus and even varied between different species of the same genus.

Since inorganic colloids in natural water also have negative surface charges (Fig.2.7) but agglomerate more easily, the poor agglomeration of algae cannot be attributed to their surface charge only. In addition to cell motility and architecture, the other surface characteristics, and in particular the composition of their cell walls, presumably play an important role.

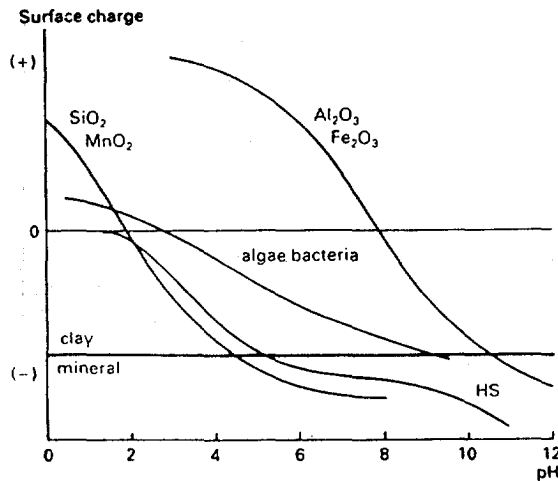


Fig.2.6. Semi-quantitative plots of surface charge against pH for typical natural aquatic colloids. HS=humic substances (from Tipping 1988).

Using electron microscopy, Kreger (1962) found that the cell wall of many algal species has a structure of microfibrils embedded in a pectic or mucilaginous substance, which looks smooth or slightly grainy, and usually appears as an amorphous or continuous matrix. Microfibrils form the skeleton of the algal cell wall. The composition of the microfibrils and continuous matrix is different among the algal divisions and sometimes even among algal species. The main constituents are cellulose, but glucose and smaller amounts of xylose, galactose, uronic acid, etc are also present. In addition, the other components of the cell walls are polyuronic acid, alginic acid and fuconic acid. X-ray diffraction patterns reveal the existence of different kinds of cellulose among different species. However, the Bacillariophyta (i.e. diatoms), which are important in water treatment, do not contain cellulose in the inner cell layer, while there is still some doubt about the presence of cellulose in the division of Cryptophyta (Morris 1971).

The cell wall of cyanobacteria differs considerably from all other algal divisions and is basically the same as that of Gram-negative bacteria. Smarda *et al.* (1979) found that the cell walls of these cyanobacteria are composed of a number of layers (Fig.2.7). The inner two layers are the same in all species, while the structure of the wall outside of the second inner layer depends on environmental conditions and the amount of the mucilage secreted. The mucilage layer, frequently called capsule, protects the cells from drying and is involved in gliding. The major constituent of the cyanobacterian cell wall is mucopeptide, constituting up to 50 % of the cell's dry weight (Lee 1989).

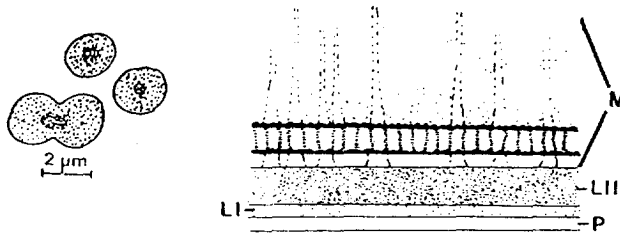


Fig.2.7. Cell wall of the blue-green alga *Synechocystis aquatilis*; (P) plasmalemma, (LI, LII) two wall layers, (M) mucilage; (Smarda *et al.* 1979).

The division of Bacillariophyta is characterized by silicified walls. The algal cells are surrounded by a rigid two-part, box-like cell wall composed of silica (frustule), enveloped by an organic component composed of amino acids and sugars (Lee 1989).

It may be speculated that these very complex and specific algal cell wall composition and properties contribute to poor algal agglomeration, probably through insignificant collision efficiency during the flocculation stage, as well as additional detachment once flocculated.

2.3.2.5. Extracellular organic matter (EOM)

Part of the organic matter produced by algae during photosynthesis, is not converted into new cell matter, but released from the cell as EOM (Haarhoff and Cleasby 1989).

EOM causes three types of inconveniences: a threat to public health (as THM precursor), unaesthetic appearance (taste and odour problems), and inhibition of coagulation and filtration treatment processes. Volatile EOM components of particular algal species affect the taste and odour of water, or may even be toxic. Table 2.4 presents the critical concentration of algae producing odorous compounds, and the classification of odour produced (Langlais *et al.* 1991).

Bernhardt *et al.* (1985a) found that EOM may strongly influence the aggregation of particles during the flocculation process. The highmolecular portion of the EOM predominantly influences flocculation process (Hoyer *et al.* 1985). There is also evidence that the filtration process is seriously hindered when water with a high concentration of species, known to produce large quantities of EOM, is filtered. The length of the filter runs is considerably shortened.

Information on the chemical nature of EOM is still incomplete. Composition and properties of the EOM are dependant on algal species and growth phase. (Hoyer *et al.* 1985). EOM may consist of a variety of chemical components, mainly carbohydrates, organic acids and peptides, frequently present in trace amounts. A large part of EOM compounds is present in a dissolved form, although some macro-molecular substances may be present as colloids. A fraction of the algal EOM has a polymeric nature, exhibiting characteristics similar to other anionic polymers (Haarhoff and Cleasby 1989). EOM serves as a substrate for bacteria present in the water. Part of the EOM is eventually completely mineralised, and part transformed into high molecular weight organic compounds which are difficult to degrade biologically (Bernhardt *et al.* 1985a).

Lüsse *et al.* (1985) reported that the amount of the EOM produced by phytoplankton may vary widely from 5% of photosynthetically fixed carbon, when the phytoplankton is healthy and vigorously growing, to 95% under stress conditions. The main sources of EOM are active transport-excretion, diffusion of organic molecules through the cell wall, solubilization and dispersion of the cell wall components.

Table 2.4. Odours associated with some freshwater algae (Langlais *et al.* 1991)

| ALGAL GENUS | ODOUR PRODUCED | | CRITICAL CONCENTRATION LIMITS | |
|---------------------------|-------------------------|----------------|-------------------------------|----------------|
| | when algal are moderate | abundant | (cells/100 ml) | (colon./100ml) |
| Cyanobacteria | | | | |
| <i>Microcystis</i> sp. | Musty | Pharmaceutical | 3,500000 | - |
| <i>Anabaena</i> sp. | Herbal | Rotten | 530000 | 20000 |
| <i>Aphanizomenon</i> sp. | Earthy | Sewer | 660000 | 20000 |
| <i>Oscillatoria</i> sp. | Herbal | Earthy/Spicy | 5,300000 | 300000 |
| Chlorophyta | | | | |
| <i>Chlamydomonas</i> sp. | | | 360000 | - |
| <i>Pandorina</i> sp. | Herbal | Fishy | 20000 | - |
| <i>Scenedesmus</i> sp. | | | - | 150000 |
| Bacillariophyta | | | | |
| <i>Asterionella</i> sp. | Herbal | Fishy | 300000 | - |
| <i>Melosira</i> sp. | Geranium | Musty | 250000 | - |
| <i>Stephanodiscus</i> sp. | Herbal/Spicy | Fishy | - | - |
| <i>Tabellaria</i> sp. | Herbal/Spicy | Fishy | 75000 | - |
| Cryptophyta | | | | |
| <i>Cryptomonas</i> sp. | - | - | 120000 | - |

2.3.3. Coagulation of algae-laden waters

The destabilization of colloidal and suspended particles and their initial agglomeration are essential for efficient removal in the filtration stage. Two types of obstacles occur. Firstly, algal agglomeration is difficult, and secondly, EOM hinders agglomeration, also of other particulates that normally flocculate easily. It is not possible to define universal optimum conditions for the chemical treatment of algae-laden water. Following parameters influence the process: the dominant algal species, the amount and the type of EOM, the algal growth stage and concentration, type and concentration of other organic and inorganic compounds present in the water, the type and dosage of coagulant and coagulant aid, the solution pH and temperature, mixing conditions, etc.

2.3.3.1. Flocculation of algae

Referring to earlier fundamental studies (Ives 1956, Tenney and Stumm 1965, Tenney *et al.* 1969), Bernhardt and Clasen (1991) contend that flocculation of micro-organisms usually follows the same principles as the coagulation of mineral colloids. However, they recognized that the huge variety of algal species, their cell structures and properties induce numerous deviations from general principles. Typical examples are:

- (a) algae with long needles like the diatom *Stephanodiscus hantzschii* that prevent a direct contact between neutralized cell surfaces,
- (b) long filamentous algae like *Oscillatoria rubescens* that can be considerably larger than metal-hydroxo-complexes and consequently do not conform to any stoichiometric law,
- (c) large colony-forming algae like *Fragilaria crotonensis* that can be filtered without coagulant conditioning,
- (d) gel forming algae like *Dictyosphaerium* that have macromolecular compounds attached to their cell wall; the gelatinous cell coating has a substantial influence on the process of coagulation and flocculation,
- (e) small motile flagellates like *Cryptomonas* and *Rhodomonas* that are able to liberate themselves from the floc.

Therefore, the addition of a coagulant to raw water containing algae may not necessarily lead to the formation of larger aggregates. In addition previous considerations may offer an explanation why once formed algal aggregates are not always stable (Eppler *et al.* 1982).

Frequently, dosages of metal coagulant or cationic polymer, required for efficient algal agglomeration, may be too high for the application of direct filtration. For instance, Tenney and Stumm (1965) reported that the required dosage of cationic polyelectrolyte needed for rapid micro-organisms flocculation may be as high as 100 mg/l. Analysis of particle size distribution of algal suspension coagulated with low dosages of ferric chloride (≤ 2.0 mg Fe(III)/l), indicated that discrete algal cells (*Chlorella* sp., *M. aeruginosa*) do not agglomerate easily, and a large number of free algal cells remained in the water after treatment (Jodlowski 1990). These cells may easily pass through a subsequent filtration step.

In addition to metal coagulants, natural and synthetic cationic polyelectrolytes, may be efficient in the destabilization of particular algal species (Tilton *et al.* 1972). However, a cationic polymer of a certain type may be effective in agglomeration of one species of algae and completely ineffective for other species. Jodlowski (1990) reported that cationic polyelectrolyte Praestol 666 BC and Wisprofloc P efficiently agglomerate *Scenedesmus* sp. cells, while they were ineffective for *Chlorella* sp.

2.3.3.2. Impairment of flocculation and filtration by EOM

Haarhoff and Cleasby (1989), Bernhardt *et al.* (1985a, 1985b) and Hoyer *et al.* (1985) found that the algal EOM strongly influences the particle agglomeration and floc filtration. Bernhardt *et al.* (1985a) reported that flocculation disturbances were encountered each autumn at the Wahnbach Reservoir, in Germany. They correlated interference with the appearance of algal EOM in the reservoir water, following extensive algal growth. The disturbance was already effective at very low EOM concentration (0.1 mg C/l). As a consequence, filtrate turbidity and residual aluminium increased.

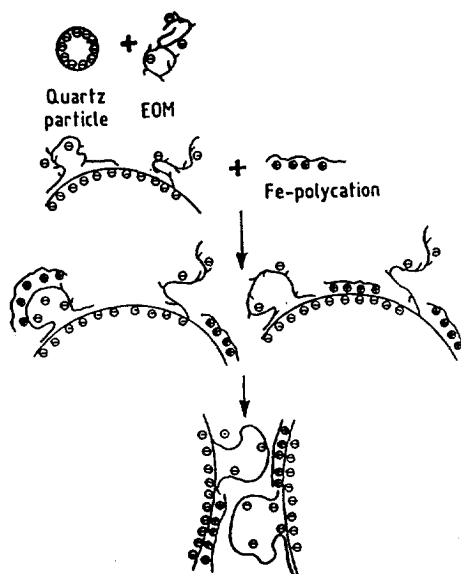


Fig.2.8. Effect of EOM as a coagulant aid at low EOM concentration as compared to the particle surface concentration (Bernhardt *et al.* 1985b).

It was shown that the EOM often carries a negative surface charge (Lüsse 1988, Bernhardt and Clasen 1991). Most sources agree that EOM up to a certain concentration behaves as a flocculation aid and above it inhibits the coagulation process. Haarhoff and Cleasby (1989) reported that EOM for concentrations up to 1 mg/l behaves as a flocculation aid. Bernhardt *et al.* (1985b) proposed, as mechanism, that when the ratio of EOM concentration to the particle surface concentration is low, EOM may bind to other negatively charged particles

(e.g. quartz particles) by hydrogen and covalent bonds, and form so-called loops and tails. After addition of metal coagulant, agglomeration can occur through the electrostatic patch model (Fig.2.8). Bernhardt *et al.* (1985b) concluded that EOM behaves like an anionic flocculant aid if $\text{Fe(III)}/\text{EOM} < 3$ and $\text{EOM}/(\text{particle surface concentration}) < 75 \text{ mg/m}^2$. At higher ratios, hindrance of the agglomeration process is evident; efficient agglomeration can only be carried out as long as a sufficient amount of iron hydroxo-complexes is available.

EOM concentrations above 1 mg/l are reported to inhibit the agglomeration and filtration processes. When present in higher concentrations, a part of EOM remains in solution and reacts with added metal coagulant producing inactive complexes. These colloidal complexes easily pass treatment and increase the turbidity and residual iron. In addition, iron bound in complexes is no longer available for coagulation of the particulate matter that is present in raw water (Bernhardt *et al.* 1985b). The treatment efficiency may be improved by increased coagulant dosages. This however, adversely affects the filter run length.

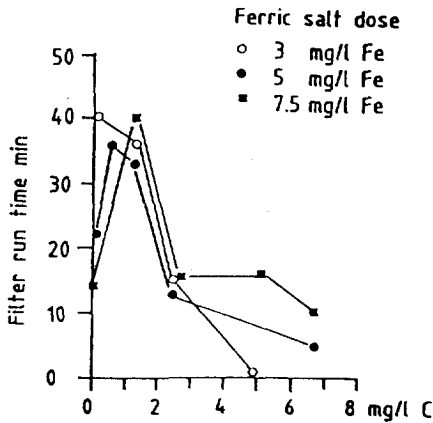


Fig.2.9. Effect of the EOM concentration from *Scenedesmus* sp. on filter run time, defined by particle breakthrough (Bernhardt *et al.* 1985a).

Bernhardt *et al.* (1985a) demonstrated that very low concentrations of EOM from *Scenedesmus* sp. cultures cause early breakthrough of particles (Fig.2.9). This effect is even more pronounced at low coagulant dosages. They also reported that different algal species and different algal growth phases hinder agglomeration and filtration processes at different EOM levels. EOM released from cyanobacteria is more effective in hindering flocculation-

filtration than that from green algae, and the greatest disturbances are caused by EOM from *Melosira* sp. Generally, the algal EOM produced during the logarithmic growth phase

appears the more effective as a process inhibitor, than EOM produced during the late stationary phase.

In most investigations on the influence of EOM on algal flocculation, model water with pure algal cultures was used (Eppler *et al.* 1982, Haarhoff and Cleasby 1989, Tilton *et al.* 1972, Bernhardt *et al.* 1985a, 1985b, 1985c, Lüsse *et al.* 1985, Hoyer *et al.* 1985, Kunikane *et al.* 1986, Sukenik *et al.* 1987, etc.). The most frequently used alga was *Chlorella* sp., partly because it is a good representative of the green algae, but also because it is easily available and not difficult to cultivate. An important methodological improvement was made by Lüsse (1988), using a specific algal culture method adapted to the natural environment. The results obtained from these studies using algal cultures may be useful in understanding fundamental principles and mechanisms. However, the extrapolation of to natural waters is highly questionable especially in view of the huge variety of algal species present in natural waters, and the general algal tendency to vary surface and other properties with a change of environmental conditions (Petruševski *et al.* 1993).

2.4. ROLE OF PRE-TREATMENT

Poor algae removal, short filter runs and impairment of coagulation and filtration by EOM may be experienced when direct filtration is applied to algae-laden waters. Raw water pre-treatment may enhance agglomeration and filtration efficiency and prevent rapid filter clogging. It may involve application of microstrainers, pre-oxidation, the use of different coagulants and filter aids, and separate flocculation. The use of different coagulants and filter aids was already discussed (see 2.2.3). Other pre-treatment techniques associated with direct filtration will be reviewed in this paragraph.

2.4.1. Microstrainers

Microstrainers are to reduce algal and zooplankton load during blooms. The most frequently used microstrainer fabric has a nominal mesh size of 35 μm . Finer mesh sizes, although resulting in higher removal efficiency are not commonly used due to fast clogging. Particles (and algae) exceeding microstrainers' pore size are efficiently removed. The build-up of deposits on the microstrainer fabric will also allow the partial removal of particles finer than the nominal pore size. Microstrainers generally efficiently remove zooplankton and filamentous algae. It is obvious that the microstrainers' removal efficiency is correlated to particular algal species in the raw water, and, depending on algal size, may vary over a wide range. A more detailed review of literature on algal and zooplankton removal with microstrainers is included in chapter 5.

2.4.2. Pre-oxidation

2.4.2.1. General

The efficiency of the coagulation, flocculation and subsequent floc removal (sedimentation, flotation or filtration) may be improved by an oxidative conditioning prior to coagulant addition. The effect of oxidants such as chlorine, chlorine dioxide, ozone, potassium permanganate and hydrogen peroxide, has been extensively investigated. In the past, pre-chlorination was most frequently applied. However, variety of chlorinated compounds might be formed as a consequence of chlorination: trihalomethanes - THM (e.g. chloroform, bromoform), haloacetic acids - HAA, haloacetonitrils - HAN etc. After the discovery of possible toxic or carcinogenic characteristics of some chlorination by-products, the use of pre-chlorination was restricted. Oxidation with chlorine dioxide will not produce chlorinated hydrocarbons, but large amounts of chlorite will be formed (at a dosage of 0.5 mg/l of chlorine dioxide up to 0.1 mg/l of chlorite was found in drinking water, Schalekamp 1986). Chlorite, similar to nitrite, causes methaemoglobinaemia in the human body. The simultaneous addition of small dosages of chlorine dioxide and chlorine, as used by the Zurich Water Supply Company, minimizes chloroform and chlorite formation (Schalekamp 1986). The same pre-oxidation effect but without formation of halogenated compounds and chlorite, assuming that water contains no bromide, may in many cases be obtained by pre-ozonation. Consequently, ozone is increasingly used as a pre-oxidant. However, recently the use of ozone came under question, since it was recognised that bromate formed by ozonation of waters containing bromide is likely cancerogenic. The other oxidants like potassium permanganate and hydrogen peroxide, although found to have certain positive effects on treatment efficiency, are rarely used as pre-oxidants.

2.4.2.2. Pre-ozonation

Beneficial effects of pre-ozonation have been observed by numerous researchers (Jekel 1983, Janssens *et al.* 1986, Singer 1990). Janssens *et al.* (1986) conducted a comparative investigation of pre-ozonation and pre-chlorination prior to direct filtration. They found that both oxidants positively influence coagulation. In most cases pre-ozonation resulted in better overall direct filtration performance in terms of head loss development, filter run time and filtrate turbidity. In addition to these coagulating effects, ozone contributed to other beneficial effects like the inactivation of viruses, decoloration, taste and odour improvement, reduction of phenol and UV absorbance at 254 nm, etc. Pre-ozonation significantly alters the THM formation curve. The process parameters that likely control ozone's effect on THM formation potential are the ozone dose, pH, alkalinity and nature of the organic matter (Langlais *et al.* 1991). However, at the low ozone dosages that are commonly associated with pre-ozonation ($< 0.5 \text{ mgO}_3/\text{mg TOC}$) little reduction of THM precursor can be obtained (Janssens *et al.* 1987, Langlais *et al.* 1991), or even an increase in THM precursors may be found.

The combination of pre-ozonation with direct filtration generated much more interest in the United States than in Europe, partly due to the success of the Los Angeles Aqueduct Filtration Plant (Langlais *et al.* 1991).

The mechanisms in which ozone acts as a coagulant aid are not yet known precisely. However, it is known that the pre-ozonation affects particles' behaviour and shifts the particle size distribution toward larger particles, thus initiating a certain degree of flocculation. Pre-ozonation, in addition, induces the formation of colloidal particles from dissolved organic matter, thus enhancing organics removal during the subsequent flocculation (Langlais *et al.* 1991).

When pre-ozonation is applied to algae laden water the beneficial effects may be attributed to a combination of several mechanisms:

- splitting of the EOM molecules (Sukenik *et al.* 1987);
- alteration and removal of EOM and other organic matter adsorbed on inorganic particles; small amounts of the adsorbed organic matter can stabilize particles in water (Jekel 1983);
- reaction with the adsorbed organic coating on the algal surface, which enhances their colloidal stability (Singer 1990);
- oxidation and modification of the algal cell wall structure thus reducing the stability of algae (Sukenik *et al.* 1987);
- release of algal biopolymers in response to ozone treatment, that can act as coagulation aid for particulate matter (Sukenik *et al.* 1987, Singer 1990, Bernhardt and Clasen 1991, Langlais *et al.* 1991).

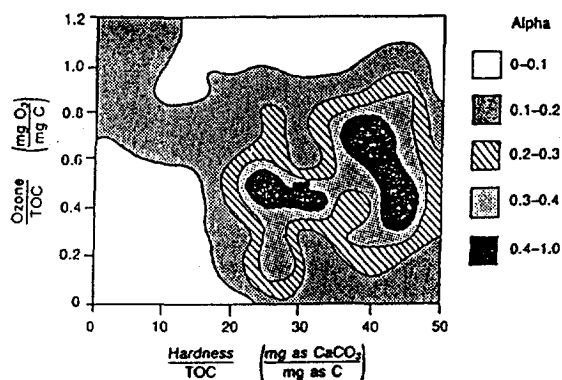


Fig.2.10. Effect of hardness, TOC and ozone dosage on the collision efficiency coefficient α (Chang and Singer 1988).

Generally, very little is known about the relationship between raw water quality and the coagulation effect of ozone (Langlais *et al.* 1991). Singer (1990) reported that it is necessary that a critical concentration of organic material is present in the water to benefit from pre-ozonation. Singer and Chang (1988) established the relationships between raw water quality (hardness and TOC) and the coagulating effects of ozone, as expressed by α , the collision

efficiency coefficient (Fig. 2.10). Dowbiggin and Singer (1989) reported that ozone-induced colloid destabilization was not observed in the absence of Ca^{2+} . They attributed the destabilizing effect of Ca^{2+} to several mechanisms:

- (a) adsorption and charge neutralization through Ca^{2+} complexation with both metal-oxide surface functional groups and the natural organic material that coats particles,
- (b) double-layer compression by Ca^{2+} , and
- (c) Ca^{2+} cation bridging between negatively charged humic matter or negatively charged solid surfaces.

Low ozone dosages, between 0.5 and 1.5 $\text{mg O}_3/\text{l}$, are often the most effective. Excessive dosages can lead to deterioration of subsequent coagulation (Reckhow *et al.* 1986). However, as organic matter present in the raw water has a strong influence on the pre-ozonation efficiency, it is more appropriate to express the ozone to carbon ratio instead of expressing an absolute ozone dosage. Results from several treatment plants in the United States, successfully applying ozone as a pre-oxidant, suggest the median of the specific ozone dosages to be 0.3-0.4 mgO_3/mgC . Even lower dosage of approximately 0.2 mgO_3/mgC may be sufficient for raw waters characterised by very low algal concentration. Pilot studies demonstrated that somewhat higher specific ozone dosages may be needed during algal blooms when direct filtration is applied (Langlais *et al.* 1991).

However, the applied oxidant dosages should not be too high to avoid the cell lysis and subsequent release of the algal intra-cellular compounds into the medium. Breaking of the cell wall and accumulation of the macromolecules such as polysaccharides, proteins and nucleic acids in the water may also inhibit flocculation (Sukenic *et al.* 1987). In addition, as already mentioned under paragraph 2.3.1.2., intensive cell lysis will increase the AOC thus causing biological aftergrowth. Jodlowski (1990) reported that cultured *Scenedesmus* cell disruption was observed at dosages higher than 4.5 mgO_3/l . Ginocchio (1981) found that at about 2 mgO_3/l (0.6 $\text{mgO}_3/\text{mg TOC}$) the algal species *Asterionella*, *Synedra*, *Tabellaria* and *Cyclotella* were not affected. The diatom *F. crotensis*, on the other hand, lost colour and *O. rubescens* appeared to be more strongly entwined. In our experiments with Biesbosch reservoir water it was found that at an ozone dosage of 2.4 $\text{mg O}_3/\text{consumed/l}$ (0.75 $\text{mgO}_3/\text{mgTOC}$) *Navicula* sp., *Melosira* sp., and *Chlamydomonas* sp. completely lost their colour (see chapter 7). The observed discrepancies may be partly attributed to differences in the algal species, and partly to differences in the concentration and composition of natural organic matter in the raw water.

In addition to the improvement of general coagulation efficiency, Ginocchio (1981) found that the efficiency of direct filtration in terms of algal removal improved after preliminary ozonation (2 mgO_3/l). In experiments conducted with *Chlorella* sp. and *Scenedesmus* sp. cultures, Jodlowski (1990) found that the application of low ozone dosages (0.8-2.9 mgO_3/l) before coagulant addition, enhanced algal agglomeration, diminishing the number of discrete algal cells. However, particle size analysis with an optical image analysis system indicated that ozone did not increase the average floc size.

Unfortunately the use of ozone as an alternative oxidant is also associated with disadvantages. Ozone forms oxidation by-products (carboxylic acids, aldehydes, ketones, organic peroxides, etc.), a few of them suspected to be hazardous to health, though presumably less harmful than chlorination by-products. Janssens *et al.* (1987) reported that pre-ozonation, especially at low ozone dosages (1 mgO₃/l), produced mutagenic activity (test with strain *Salmonella typhimurium* TA 98). However, this mutagenic activity was removed by double layer direct filtration. In addition, ozonation by-products are often biodegradable (Kruithof *et al.* 1994). Janssens *et al.* (1987) reported that the concentration of ozonation by-products such as aldehydes and carboxylic acids, increased with increase of ozone dosage. Their removal by flocculation was poor. Filtration (anthracite-sand media) achieved by-products removal but only above 10C°. Activated carbon filtration, that follows dual media filters, reduced their concentration below the detection limits. No correlation was observed between the amounts of by-products formed after ozonation, and algal concentration in the raw water.

In addition, recent investigations (Kruithof *et al.* 1993, Kruithof and Meijers 1993, Von Gunten and Hoigné 1993, Siddiqui and Amy 1993) revealed that the ozonation of waters containing bromide may lead to the formation of brominated organohalogens or bromate at a level suspected of being hazardous to health. There is currently no economically feasible treatment technology to eliminate once formed bromate (Meijers and Kruithof 1993). Kruithof *et al.* (1993), Kruithof and Meijers (1993) and Orlandini *et al.* (1994) found that the concentration of formed bromate positively correlates with the applied ozone dosage. In batch experiments with Biesbosch water Kruithof *et al.* (1993) and Kruithof and Meijers (1994) found that the concentrations of bromate formed at low ozone dosages (< 1 mg/l) did not exceed the detection limit of app. 2 µg/l. These results suggest that the use of low ozone dosages and a short contact time to improve particle and algae removal in direct filtration should not necessarily be associated with bromate-related problems.

Finally, pre-ozonation or application of other oxidants does not necessarily have favourable effects on treatment efficiency. For example, when filamentous algae are dominant, oxidants break up large colonies or filaments thereby reducing filterability (Watson 1990). In addition, Reckhow *et al.* (1986) and Langlais *et al.* (1991) reported that pre-ozonation failed to show beneficial effects with certain raw waters.

2.5. FILTER DESIGN CONSIDERATIONS

2.5.1. Filter media

In general, the finest media giving long filter runs associated with good filtrate quality should be selected. Coarser media will give prolonged runs, but careful filter operation and application of polymers is required to prevent early breakthrough. Filter depth also has a pronounced effect on filter performance. The greater the depth, the more storage capacity is in principle available, which could result in longer filter runs (AWWA Filtration Committee 1980). However, greater bed depth will increase the price of the filter box, which must be balanced with savings arising from less frequent backwashing.

Although there are some conflicting experimental results, one may deduce that dual media give better results than single media, and multi media are showing benefits in comparison with dual media. This is to be expected considering the benefits of coarse-to-fine-filtration. Most full-scale municipal direct filtration plants in the US presently are using dual media beds (AWWA Filtration Committee 1980). The upper coarse anthracite layer acts as a flocculation basin and flocs storage tank, where the greater portion of solids are retained (more than 90 % in a case with 1.3 mm effective coal size - Hutchison and Foley 1974). The tendency towards the use of coarser coal with an effective size from 1.3 to 1.7 mm is noticeable. The application of coarser filtering material, commonly anthracite, may be particularly beneficial for direct filtration of impounded surface waters with high algal concentration. The fine sand layer below the anthracite polishes the filtrate quality from the coarse layer and ensure low effluent turbidity. The depth of this layer usually varies from 0.2 to 0.5 meters, with an effective grain size around 0.4-0.5 mm, commonly applied in the United States (AWWA Filtration Committee 1980, McCormick and King 1982), and somewhat coarser (0.4-0.8 mm) commonly applied in Europe (Janssens *et al* 1986).

Some recent pilot plant investigations demonstrated the advantages of multi layer beds as compared with dual media, especially regarding the removal of phytoplankton. Three layer filters enhanced phytoplankton removal efficiency and prolonged filter runs (Janssens *et al.* 1986, Watson 1990). In addition to anthracite and sand, garnet is most frequently used as the third, low layer. Alternatively, a very specific multi-media filter that consists of a very coarse upper layer of carbon (size 3-5 mm), a middle hydroanthracite layer (size 1.5-2.5 mm) and a bottom sand layer (size 0.7-1.2 mm) is used in the direct filtration plant developed primarily for phosphorus elimination at the Wahnbach Reservoir Association (Bernhardt 1981). These multi-media filters allow application of high coagulant dosages (4-10 mg Fe(III)/l and 0.1-1.0 mg/l cationic polyelectrolyte as a flocculation aid) with long filter runs (10-80 h). In addition to very efficient phosphorus removal (96.3%) this plant very efficiently eliminated algae (94.9% removal of chlorophyll- α).

Naghavi and Malone (1986) reported that use of very fine sand/silt filtering material (median grain size diameter from 0.064 to 0.200 mm, bed depth from 3.17 to 12.7 mm and filtration

rate 9.4 m/h) resulted in very high average removal (98.7 %) of *Scenedesmus quadricauda* from model water even without coagulant. However, filter run times are short due to rapid clogging of the filter surface.

2.5.2. Filtration rate

Reported filtration rates at direct filtration plants in the US vary from 2.5 to 14.5 m/h, with some more recent plants operating at filtration rates as high as 24 m/h. Filtration rates have been raising over the last twenty years (AWWA Filtration Committee 1980).

If higher filtration rates are applied, flocs penetrate deeper in the filter bed, which will increase the filter storage capacity. On the other hand, an increased filtration rate introduces greater shear forces, with increased likelihood of dislodgment of particles that had been deposited earlier. A possible measure against this is to use polyelectrolytes as filter aids. As already discussed in paragraph 2.2.3 the application of particularly cationic polymer increases the shear strength of the deposits in the filter bed thus allowing higher filtration rates. In general, filtration rates > 10 m/h require the use of polyelectrolytes. Higher filtration rates reduce the filter ripening period, but lower ones generally produce a better filtrate quality for the rest of the run.

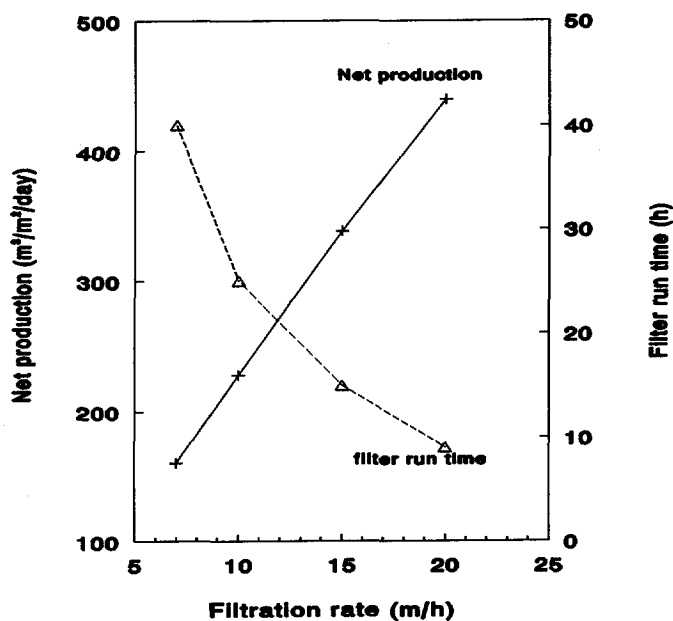


Fig.2.11. Effect of filtration rate on net water production and filter run time.

In addition to the effect of filtration rate on the filtrate quality and the requirement to apply chemical conditioning, the filtration rate strongly influences the filtration plant investment costs. The filtration rate governs the net water production per unit filter area. Assuming that at increased filtration rate a filtrate of acceptable quality is still being produced, net water production per unit filter area and per unit time may be higher even if the filter run length has become shorter. Therefore, establishing firm boundaries of acceptable filter run length does not seem reasonable, considering that the final goal of the water treatment plant is to produce high quality water in an economic way irrespective of the filter run time (Logsdon 1978). Figure 2.11 describes a typical relation between net water production per unit filter area and unit time ($\{\text{total volume produced}\} - \{\text{volume used for filter backwashing}\}$), and filter run time, for different filtration rates. The filter run time for different filtration rates was determined in direct filtration pilot plant experiments with Biesbosch water (coagulant: 2 mg Fe (III)/l, anthracite / sand filter media, maximum acceptable head loss in filter media 2.5 m). The diagram shows that the filtration rate has a more pronounced effect on the water production than the filter run time. From the graph it follows that one of the most important objectives when designing a direct filtration plant, is to maximise the filtration rate. In industrial applications, operational runs as short as two hours may be found acceptable on economic grounds; in municipal plants common practice is to have filter runs of at least 8-10 hours. The main reasons for short filter runs, according to AWWA Filtration Committee (1980), were high raw water turbidity and phytoplankton concentration and improper coagulant dosage.

2.5.3. Filter backwashing

The filters operating in direct filtration mode require more backwash water and higher backwash rates than the filters in a conventional scheme due to better adherence of the impurities to the grains, and the large amount of stored flocs. Usually, backwash rates fall within the range of 30 to 50 m/h (AWWA Filtration Committee 1980). The need for air scour is much more pronounced than in conventional filter plants. Filter backwashing must be carefully considered, particularly when polyelectrolytes are used as the main coagulants. If backwashing in that case is not successful, mud balls may be formed in the filter bed. Backwash water requirements may be high compared with conventional filters. This is particularly evident during algal blooms. Use of air-scour before backwash can reduce the total backwash water consumption.

2.6. CONCLUSIONS

Direct filtration is an attractive process for low-turbidity surface water treatment compared to conventional treatment given the comparatively lower investment and operational costs and favourable environmental related aspects. However, this treatment can be applied only if the source water quality is appropriate, meaning that in general, turbidity, colour and algal count should be low. Guidelines that can be found in the literature (e.g. guidelines given in Tab. 1.1. and Fig. 2.2) may be useful for a preliminary assessment. However, the final conclusion regarding the feasibility of direct filtration for treatment of particular raw water can be drawn only after detailed study that preferably includes pilot plant experiments.

Removal of colloidal and suspended matter in direct filtration involves coagulation, flocculation (agglomeration) and filtration. Coagulation based on charge neutralization achieved with low dosage of metal coagulant (2-20 mg aluminium sulfate/l) is typical for direct filtration. Subsequent agglomeration in a flocculation unit (if present) and in the pores of the granular filter bed is essential for efficient removal in the filter bed. The need for a separate flocculation unit should be related to raw water quality and specifically the mass concentration of particles and particles size distribution. The flocculation unit may be economically attractive for raw water with mass concentration of particles between 8 and 15 mg/l, dominated by particles $> 2 \mu\text{m}$. The removal of destabilized and agglomerated particles in the filter bed includes two interconnected processes: particle transport and particle attachment to filter grains. Smaller filter grains, smaller filtration velocity, increase of water temperature and increase of particle size (only for particles $> 1 \mu\text{m}$) improve particle transport and consequently filtration efficiency. Minimum transport and filtration efficiency can be expected for particles of app. $1 \mu\text{m}$. Efficient attachment of agglomerates to the filter grain can be achieved only when the colloidal suspension is unstable. Use of (cationic) polymer in addition to metal coagulant can increase the shear strength of deposit and can consequently reduce deposit detachment.

In addition to previous considerations, algae-related inconveniences may be experienced when direct filtration is applied to impounded surface water. These include: problems related to algae, algal products and other particles in the algal size range (like cysts and oocysts of the pathogenic microorganisms) passing through filters, the rapid clogging of the filters caused by a high concentration of large or filamentous algae during occasional algal blooms and the hindrance of the coagulation and flocculation of other impurities present in raw water caused by algae-derived extra-cellular organic matter (EOM).

Proper water quality management strategies combined with adequate pre-treatment that precedes direct filtration (microstraining, type and dosage of coagulant and filter aids, and other coagulation conditions) and appropriate filter design (dual or multi filter media, appropriate filtration rate, sufficient head available for headloss in filter media) can reduce rapid filter clogging and coagulation impairment caused by EOM in particular situations.

The problem of algae and other particles in the algal size range passing treatment is becoming increasingly important given the more stringent drinking water quality standards, the problem of biological water stability, and the recently recognized widespread occurrence of the oocysts and cysts of the pathogenic microorganisms *Cryptosporidium parvum* and *Giardia lamblia* in surface water. Results from several studies suggest that the problem of inefficient particle and algae removal in filtration may under certain conditions be diminished by oxidative pre-conditioning, nowadays commonly by ozone. However, applied ozonation conditions should be very carefully optimized, given the growing public concern regarding the hazardous properties of oxidation by-products (THMs, bromate). Currently available information suggest that the applied ozone dosage and the contact time should be minimized to reduce these problems. In addition, the capability of alternative oxidants or innovative technical solutions to further improve particle and algae removal, at same time minimize the side effects, should be investigated.

As noted by Bernhardt and Clasen (1991) our knowledge of algae removal in treatment processes and, in particular, of algal coagulation and algal response to oxidative pre-treatment is still rudimentary. It appears that water treatment research makes little use of the knowledge that emerges from phycological studies. Understanding of the algal properties seems to be pre-requisite to better understand algal behaviour in water treatment, and consequently to develop a solution for their more efficient elimination.

2.7. RESEARCH OBJECTIVES, METHODOLOGY AND HYPOTHESIS

The objectives of this research are:

- * to identify the algal properties responsible for poor algal agglomeration and removal,
- * to develop methodologies (optimisation of coagulation conditions, oxidative pre-conditioning, filter design) to significantly improve particle and algae removal in direct filtration,
- * to develop conceptual models to describe the mechanisms that allow particle and algae removal in direct filtration, and
- * to optimize the direct filtration treatment process.

The study will specifically address the question: is direct filtration a viable alternative for treatment of Biesbosch water characterised by a fluctuating and seasonally high algae load.

Following hypotheses were used for experimental design:

- a. Model waters, prepared from pure algal cultures, that are commonly used in water treatment studies, do not reflect adequately the behaviour of algae from natural environment. Consequently, an alternative technique for model water preparation should be established that more adequately represents algae in their natural environment.

Concentration of fresh water algae in the reservoir water with the tangential flow membrane filtration system can provide adequate model water with high algal concentration for the algae related treatment studies.

- b. Most of earlier research on algae filtration suffers from simplifications: the studies are conceived as black box experiments, usually considering algae as inert particles, upon which classical colloid-chemical coagulation theory is applied.

To understand algal behaviour in water treatment and to improve algal removal efficiency it is necessary to consider phycological and ecological algal properties and also to study the behaviour of individual algal species. The classical coagulation theory should be augmented with considerations that take into account these very specific algal characteristics that affect their behaviour during coagulation-filtration processes.

Active motility of particular algal species is one of the properties that enable these organisms to resist treatment and penetrate effluent much easier than other inert particles present in the natural water. Their immobilisation by oxidative pre-treatment is essential to enhance their coagulation and removal.

c. Optimised direct filtration treatment system may currently achieve an average algae removal efficiency of typically 90-95%. Accordingly, direct filtration is producing filtrate with a considerable algae concentration with a variety of associated problems.

Direct filtration is capable of systematically achieving higher removal of algae and other particles in the algal size range. However, this can only be achieved in multi-media filter beds, using appropriate oxidative pre-treatment and very efficient coagulation. The critical step in the direct filtration process scheme is pre-treatment with coagulants and oxidants, rather than filtration.

The research approach also includes following considerations:

- a. Because of the duration and complexity of pilot scale filter tests, simpler and smaller scale set-ups are to be developed, whose results correlate well with real-life situations. Also, larger-scale direct filtration pilot plants are to be used as well to assess process performance on a larger scale. Consequently, an array of laboratory and pilot direct filtration plant are to be used, each yielding part of the information.
- b. Using these experimental set-ups, and guided by the theories on coagulation, flocculation, filtration and oxidation, the system parameters and mechanisms are to be identified, and optimized.
- c. New analytical approaches must be applied to provide the required detailed information.
- d. All operational conditions must be selected to reflect adequately Biesbosch water treatment.

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Chapter 3

INFLUENCE OF ALGAL SPECIES AND CULTIVATION CONDITIONS ON ALGAL REMOVAL IN DIRECT FILTRATION

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ABSTRACT - The influence of growth media on the behaviour of cultured algae in direct filtration was examined. *Chlorella vulgaris* and *Selenastrum capricornutum* cultured on Jaworski and Z-8 media were used for model water preparation. Different removal patterns were found under identical treatment conditions for the same algal species in the same growth phase cultured on different growth media. In addition, different removal efficiencies under identical treatment conditions were found for cultured and natural *Microcystis aeruginosa*. Therefore, extrapolation of the results from model studies, applying algal cultures to natural conditions is highly questionable. The efficiency of direct filtration for the removal of dominant algal species present in Biesbosch Water Storage Reservoirs was investigated. Different removal efficiencies were found for different algal species. The most difficult to remove were *Rhodomonas minuta* and μ -algae. High removal efficiency was found for *Stepha nodiscus hantzschii* and other centric diatoms. An average overall algal biomass removal of 90% was achieved. Algal penetration through filters is a consequence of algal size and inefficient coagulation and flocculation (agglomeration). In comparison with anthracite-sand filter media, the three layer anthracite-sand-garnet filter media consistently produced filtrate of superior quality as measured by turbidity, residual iron and particle count. Straightforward direct filtration of Biesbosch water cannot be accepted as a viable treatment alternative for production of drinking water.

3.1. INTRODUCTION

Numerous problems are associated with the production of drinking water from eutrophic waters with a high algae count. As far as direct filtration is concerned, problems caused by algae may be grouped into three categories: (a) problems related to algae or algal products passing through filters, (b) the rapid clogging of the filters caused by a high concentration of large or filamentous algae with associated short filter runs and increased use of backwash water; and (c) the hindrance of the coagulation and flocculation of other impurities present in raw water caused by algae-derived extra-cellular organic matter (EOM). Direct filtration is in principle capable of removing most algal species relatively efficiently. However, this requires careful optimisation of the direct filtration procedure. Because of the algal penetration through filters, and rapid filter clogging, it is not advisable to apply direct filtration to raw water with high algal concentration. According to the AWWA filtration committee report (1980), water with algae counts of up to 2000 ASU*/ml are suitable for direct filtration, corresponding to approximately 8000 *Stephanodiscus hantzschii* cells/ml, or 60000 *Chlorella vulgaris* cells/ml. Oligotrophic and mesotrophic waters are generally considered to be relatively problem-free for the application of direct filtration. Water from very eutrophic reservoirs and lakes with higher concentrations may be more efficiently treated by conventional methods (coagulation, flocculation, sedimentation or flotation and rapid sand filtration). Algal concentration in mesotrophic water according to the definition of the OECD Cooperative Programme on Monitoring and Control of Eutrophication may be as high as 11 μg chlorophyll- α /l. Although no standards are set specifically for algal concentration in drinking water, the algal count should be kept as low as possible for numerous reasons such as increased chlorine demand, presence of haloform precursors,

* ASU - area standard unit represents the horizontally projected area of algal cells settled in the counting slide (1 ASU = 400 μm^2).

biological aftergrowth of bacteria and zooplankton in activated carbon filters and distribution mains, and introduction of natural toxins. The German Association of Drinking Water Reservoirs established an interim standard of 0.1 $\mu\text{g/l}$ as the maximum allowable concentration of chlorophyll- α in the produced water. Assuming this level in drinking water as a target, the algae removal efficiency in direct filtration applied to mesotrophic water should be higher than 99%.

Generally, two approaches exist to study algal response to different treatment conditions and to establish optimal operational conditions for full scale plants. In the first, and most frequently used one, small scale laboratory experiments use reproducible, controlled model water with a mono-algal culture. The second entails more representative simulation experiments on a larger scale, with natural water incorporating particle and algae heterogeneity. When the algae from natural water are used, their concentration fluctuates over the year and, in the case of water sources suitable for direct filtration, it is often too low for experimental purposes, with the exception of short bloom periods.

This chapter discusses algal removal efficiency in direct filtration. The preliminary study objective was to assess routine approaches in laboratory investigations dealing with algae-related water treatment studies which use model water with algae from pure cultures. In addition, the influence of algal species, their growth phase and the composition of filter media on direct filtration performance was investigated. Finally, the capability of straightforward direct filtration, with ferric sulfate as a coagulant, to remove turbidity and particles from Biesbosch water was evaluated.

The findings reported are part of a comprehensive research programme that was aimed at assessing the applicability of direct filtration to Biesbosch reservoir water, characterised by a seasonally high algae load. Water from these reservoirs is used as a raw water source for the city of Rotterdam. In addition, it partly covers the requirements of the city of Dordrecht and waterworks in the provinces of Brabant and Zeeland.

3.2. EXPERIMENTAL PROCEDURES

3.2.1. Experimental set-ups

A modified jar test apparatus (MJTA), and continuous flow experimental set-ups: a bench-scale direct filtration pilot plant (BSDFPF) and a mobile automated direct filtration pilot plant (MDFPP) were developed and used for direct filtration studies.

Modified jar test apparatus

Because of the duration and complexity of pilot scale filter tests, simpler and smaller scale set-ups are required to preliminarily examine a variety of process conditions and to identify key process parameters. A standard jar test apparatus that is used for settling or flotation

studies cannot simulate filtration process. Therefore, a standard jar test apparatus (three 1.8 l double-glass jars equipped with stainless steel stirring paddles with dimensions 7.5 x 2.0 cm coupled to a variable speed gear [Engel-GMBH, Wiesbaden]) was connected to small scale filters, diameter 60 mm, height 400 mm, with sand as the filtration medium, commercial fraction 0.80-1.25 mm, bed thickness 200 mm (Fig.3.1). The modified jar test procedure consisted of the addition of a coagulant, 30 seconds rapid mixing at $G=1000\text{ s}^{-1}$, slow reduction of the mixing intensity to $G=10\text{ s}^{-1}$ in a period of 30 s, seven minutes of slow mixing at $G=10\text{ s}^{-1}$ to simulate the retention period of coagulated water in the filter supernatant and filtration at the constant filtration rate of $1.8 \cdot 10^{-3}\text{ m/s}$. Prior to the filtration the filters were filled with tap water to the top and the jar outlet valves were opened afterwards to avoid disruption of the filter layer by coagulated water. Initial portion of filtrate from each filter (0.4 l, approx. twofold the volume of backwash water present in the filter at the beginning of the experiment) was discharged, and the following 1.0 l of filtrate from each filter was collected in beaker for further analysis. The filter run length with MJTA was limited to approx. 5 minutes. The filters were backwashed after each filter run with tap water under standardised conditions (a backwash period of 10 min at a backwash rate sufficient to provide 20% filter bed expansion).

It is obvious that due to the limited jar volume the MJTA can only simulate filter performance during the initial filter ripening period.

In a part of the study reported in this chapter, MJTA was used to assess the influence of algal growth media on algae removal in direct filtration. In addition, MJTA was used to compare removal of natural and cultured *Microcystis aeruginosa*. Model water with algal cultures and natural Biesbosch water were used in these experiments.

Bench scale direct filtration pilot plant

BSDFPP (Fig. 3.2) was developed in order to overcome some of the MJTA limitations (e.g. the short filter run and consequent inability to simulate the effect of the filter bed ripening, the effect of dual and three media, etc.). The plant consists of four parallel filter columns, 100 mm in diameter with associated flow-measuring and regulating devices, and chemical dosing and mixing equipment (in-line static mixer with $G=1400\text{ s}^{-1}$ and mixing time $< 1\text{ s}$ at filtration rate of $2.7 \cdot 10^{-3}\text{ m/s}$). The BSDFPP allows simultaneous filter runs with four filters that may operate under different direct filtration conditions (e.g. filtration rate, composition of filter media, coagulation conditions). The filter columns were constructed of segments (100 and 200 mm) allowing a variation of bed thickness and composition. The filters were operated at constant filtration rate of $2.7 \cdot 10^{-3}\text{ m/s}$, a value selected after preliminary optimization experiments. A constant filtration rate was maintained with the help of the flow-regulating hand-operated needle valves and rotameter installed on filtrate lines. Filtrate flows were checked and if required adjusted every 30 min. The lack of an automated filter rate control system and filtrate quality monitoring equipment limited the maximum filter run length with this set-up to approximately 5 to 8 hour, given the safety precautions in the laboratory prevented overnight runs.

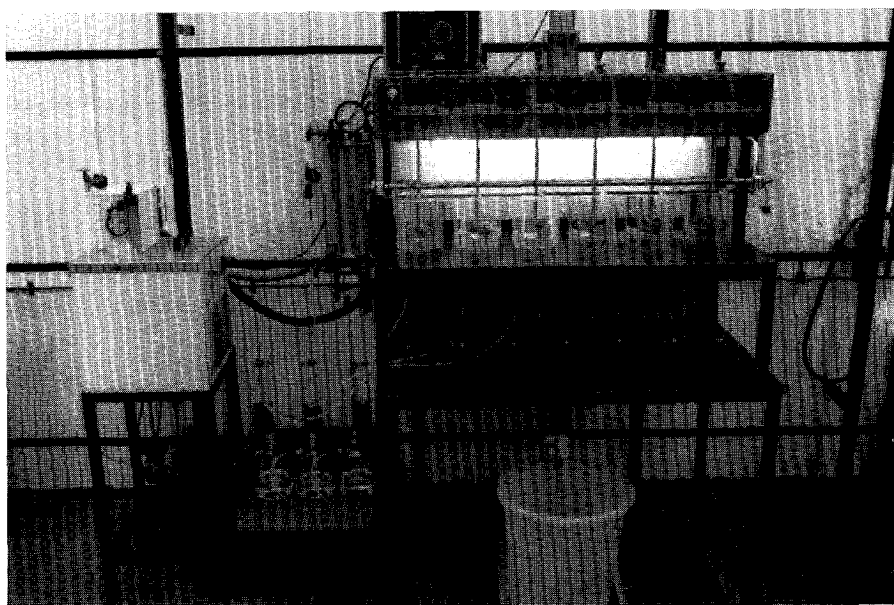


Fig.3.1. The modified jar test apparatus used for direct filtration studies.

Natural Biesbosch water was used in filter runs with BSDFPP. Due to the large volumes of water required for filter runs with BSDFPP, it was impossible to use this set-up to assess the influence of growth media on algae removal. In the part of the study reported specifically in this chapter, BSDFPP was used to establish an optimum coagulant dosage and in addition, to make a preliminary assesment of the effect of filter media on direct filtration performance.

Mobile automated direct filtration pilot plant

The MDFPP developed at the Sanitary Engineering Laboratory (Delft University of Technology), was also used in experiments with natural water (Fig.3.3). This installation allows continuous automatic operation and assessment of direct filtration on a larger scale. The plant consists of two filter columns (190 mm in diameter), a chemical dosing unit and process control, measuring and regulating equipment (Fig.3.4.). Application of up to three different chemicals was possible, with automatic plant operation and continuous measurements of filtrate turbidity and head loss development. In the part of the study reported specifically in this chapter, MDFPP was used to investigate removal of different algal species and to compare the effect of anthracite-sand and anthracite-sand-garnet filter media on direct filtration performance. Natural water from the Biesbosch storage reservoirs was used in filter runs with MDFPP. The maximum filter run length with this set-up was only limited by maximum pressure of 3.0 m available for resistance developed in the filter bed. Filter runs were typically longer than 24 hours.

Anthracite-sand and anthracite-sand-garnet filter beds were used in the experiments with the BSDFPP and the MDFPP. The characteristics of the filter media are given in Appendix 3.1.



Fig.3.2. The bench scale direct filtration pilot plant with four parallel filter columns.

Composition of the anthracite-sand filter beds were identical with the composition of the filter beds used at the full scale conventional water treatment plant Kralingen (Waterworks Europoort), in order to assess if this plant can operate in the direct filtration treatment mode. A shallow polishing garnet layer (0.15 m) was added to anthracite-sand beds of one MDFPP and two BSDFPP filters to study the effect of this relatively easy to implement measure on direct filtration performance. The 0.5-0.8 mm garnet fraction was selected from the commercially available fractions, to allow separation of garnet layer during backwashing, and to limit the increase of total headlosses in the filter bed.

Ferric chloride at a dosage of 1 mg Fe(III)/l, a value selected after preliminary optimisation experiments, was used as a coagulant in MJTA experiments, unless otherwise mentioned. Ferric sulfate prepared at the full-scale water treatment plant Kralingen (Waterworks Europoort, Rotterdam) at a dosage 1-1.5 mg Fe(III)/l, a range selected after preliminary optimisation filter runs, was used as coagulant in pilot plant experiments. The same coagulant was used in the full-scale conventional water treatment plant at the site.

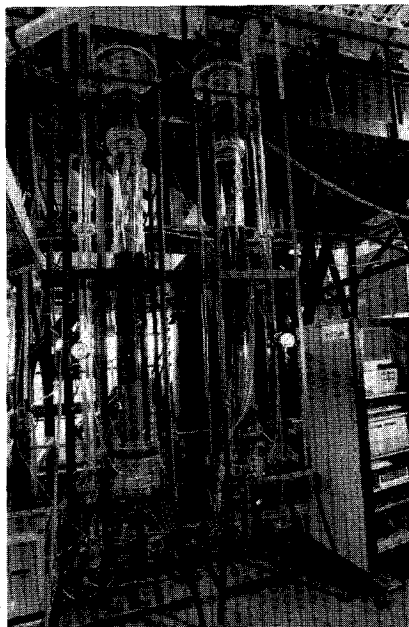


Fig. 3.3. The mobile direct filtration pilot plant with two filter columns.

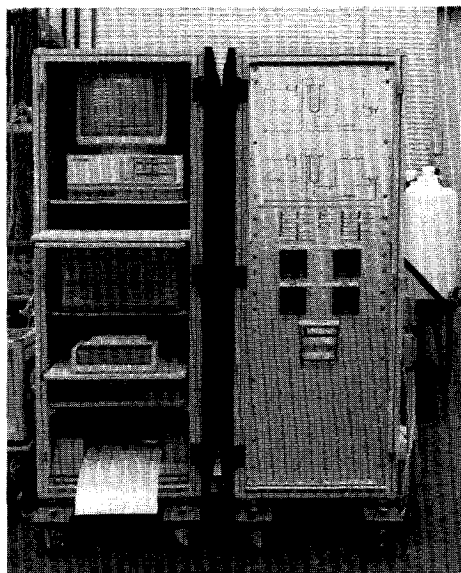


Fig.3.4. Process control, measuring and regulating equipment of the mobile direct filtration pilot plant.

3.2.2. Natural and model water used in experiments

Biesbosch reservoir water

Raw water from Biesbosch reservoirs used in the experiments is characterised by seasonal and even monthly cycles of a limited number of algal genera and species. Figure 3.5 shows the typical yearly distribution patterns (1992, 1993) of dominant algal classes in the Petrusplaat, the last in the series of Biesbosch reservoirs from which raw water is conveyed to the waterworks. The typical distribution pattern of dominant algal species for the late summer and early spring periods is given in Fig. 3.6. In addition to species represented on the graphs, small, green, so-called μ -algae were consistently present in considerable numbers (a few thousand cells /ml). The chlorophyll- α yearly average level of Biesbosch water is about 5 $\mu\text{g/l}$, with the spring peaks reaching values as high as 50 $\mu\text{g/l}$. In addition, Biesbosch water is characterized by low turbidity, less than 4 FTU (most frequently below 1 FTU) and DOC levels between 3 and 4 mg/l.

In the investigation, the removal efficiency for the different algal species belonging to different groups such as Bacillariophyceae-*S. hantzschii*, Cryptophyceae-*Rhodomonas minuta*, Chlorophyceae-*Chlamydomonas* sp., colonies and single cells of μ -algae was examined with BSDFPF and MDFPF. During the early spring period diatoms *S. hantzschii*, *S. astraea* and *Cyclotella* sp. were counted under the common name "centric diatoms". However, the dominating species was *S. hantzschii*.

The removal of large algae, exceeding the size of the commonly applied micro-mesh fabric (35 μm), was not investigated. It was assumed that their efficient removal may be obtained more easily by raw water pre-treatment (microstraining).

Model water with cultured algae

In order to study the validity of the common approach in algae-related water treatment studies based on use of model water with cultured algae, several series of MJTA experiments were conducted with two types of model water. For each set of MJTA experiments two types of model water were prepared by mixing tap water (treated Biesbosch water) with one algal specie grown on two different growth media (5 ml of algal culture per one litre tap water). The algae in both cultures were in the same growth stage. *C. vulgaris* and *S. capricornutum* were selected as representative species. *C. vulgaris* was selected because it is the most frequently used in laboratory investigations. *S. capricornutum* was chosen as an alternative representative of green algae. Algae were cultured on Jaworski (Thompson *et al.* 1988) and Z-8 (Skulberg 1964) growth media as semi-continuous cultures at the Sanitary Engineering Laboratory (Delft University of Technology). Composition of these commonly used growth media is given in Appendix 3.2. Jaworski and Z-8 growth media were selected as growth substrate because it was earlier observed that these particular growth media could influence algal filterability over membrane filters (part of the chlorophyll- α analysis).

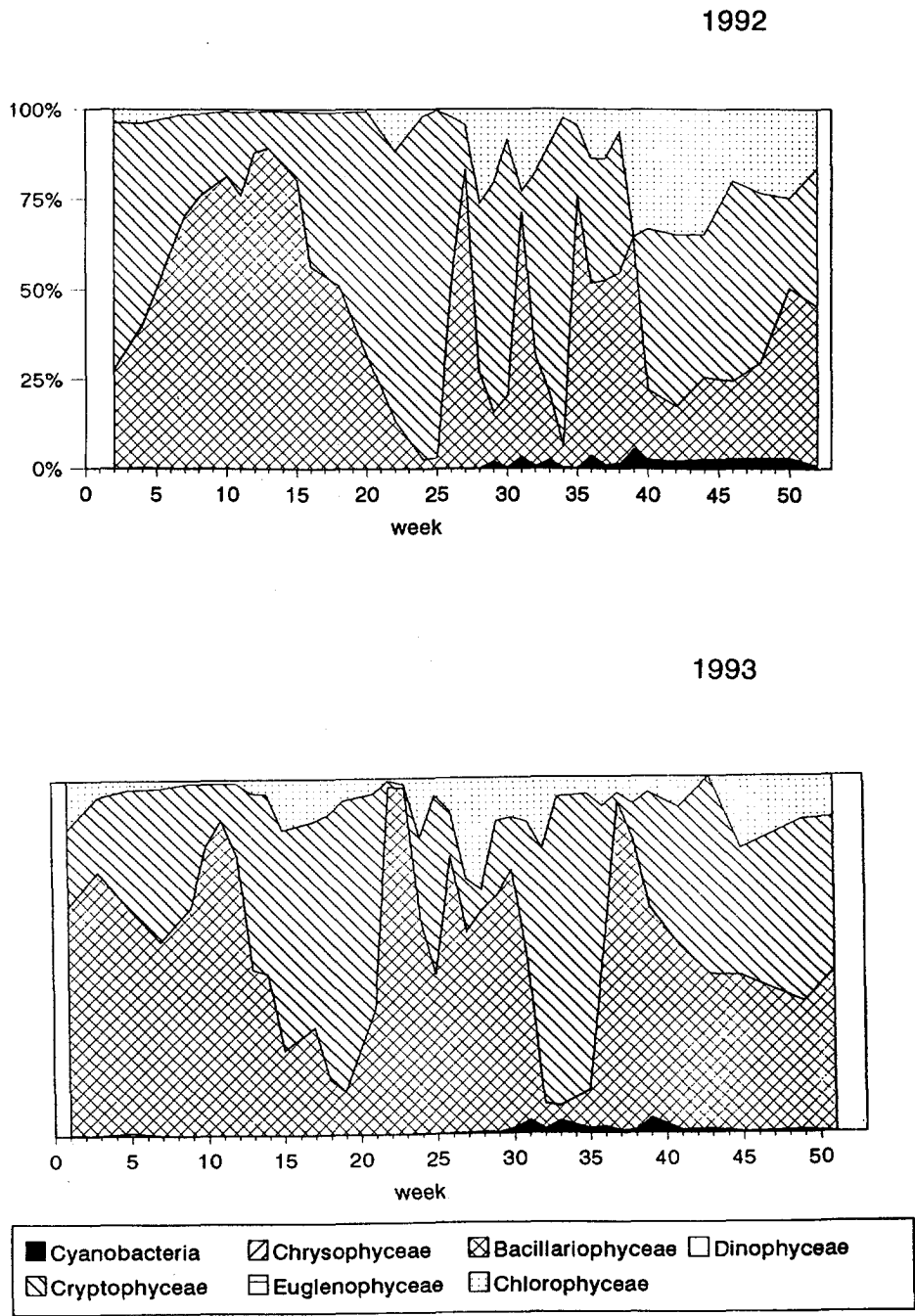


Fig.3.5. 1992 and 1993 yearly distribution patterns of dominant algal classes in Petrusplaat, the last in the series of Biesbosch reservoirs (Ketelaars, unpublished data).

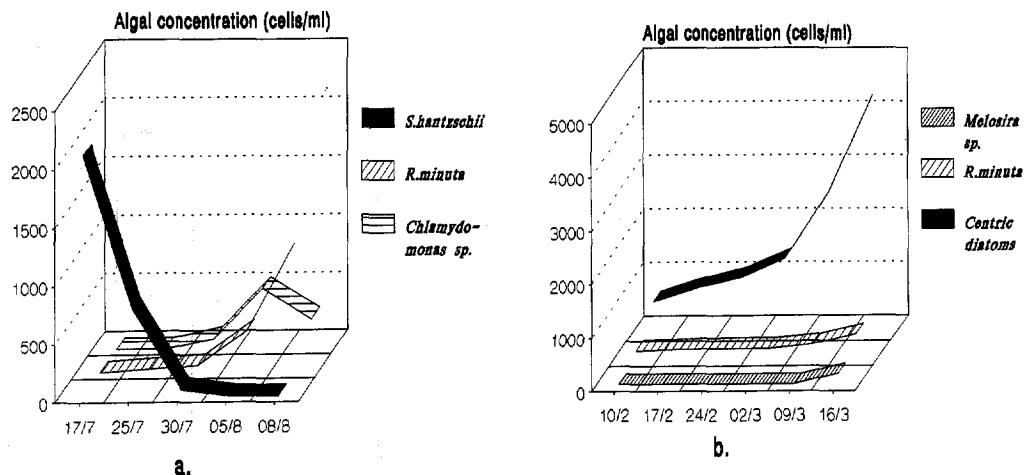


Fig. 3.6. Variation of algal concentration in Biesbosch water, for the periods summer 1991 (a), and spring 1992 (b).

An additional set of MJTA experiments was conducted using natural and cultured *M. aeruginosa*, to compare particle (algae) removal efficiency under identical treatment conditions. This alga was selected as a common blue-green alga, frequently responsible for the unpleasant taste and odour of treated water. The model water was prepared by mixing tap water with *M. aeruginosa* culture, grown on Citiri medium (Appendix 3.2) as a batch culture at the Microbiological Department of the University of Amsterdam. Natural water was taken from the De Gijster, first in series of interconnected Biesbosch reservoirs with the highest *M. aeruginosa* concentration, during a late summer *M. aeruginosa* bloom.

3.2.3. Water quality analysis

Particle (algae) agglomeration and removal in the MJTA experiments were evaluated by Mini-Magic Scan (IAS 25/ IV25, Joice-Loebl Ltd), an image analysis system (Fig. 3.7). The system comprises video camera (with a resolution of 604*288 pixels), mounted on the Nikon Optiphot light biological microscope (equipped with the phase contrast objectives). The analyses were performed on fresh samples of raw water (model or Biesbosch water) and filtrate. The samples were placed in cuvettes, covered with a cover glass and placed under the microscope. The images scanned by the camera were fed to computer and further analyzed by the image analysis program Genias 25 (Joice-Loebl Ltd), in the form of statistically elaborated binary image data. The results were expressed as a cumulative number of scanned particles (algae and iron hydroxide flocs) in 100 scanned view-fields per sample

as a function of particle area (logarithm of the horizontally projected area in μm^2). Consequently, the results obtained with the image analysis system provide an indication of particle concentration and particle size distribution in the examined water samples.

An inverted microscope providing up to 600 magnification was used for plankton counting. Algal enumeration procedure commonly used by Dutch Water Works was followed (minimum 50 counted fields or 400 counted units-cells per sample).

Turbidity was measured with a high precision laboratory turbidity meter (Sigrist Photometer AG, Zurich, Switzerland).

Particle counting in a size range was performed with the HIAC particle counter (model PC-320), that provides high-speed particle size distribution analysis. The instrument was equipped with a 6-channel automatic particle size analyzer with adjustable thresholds for each channel within the size range 3-150 μm . The instrument operates on the light-blocking principle.

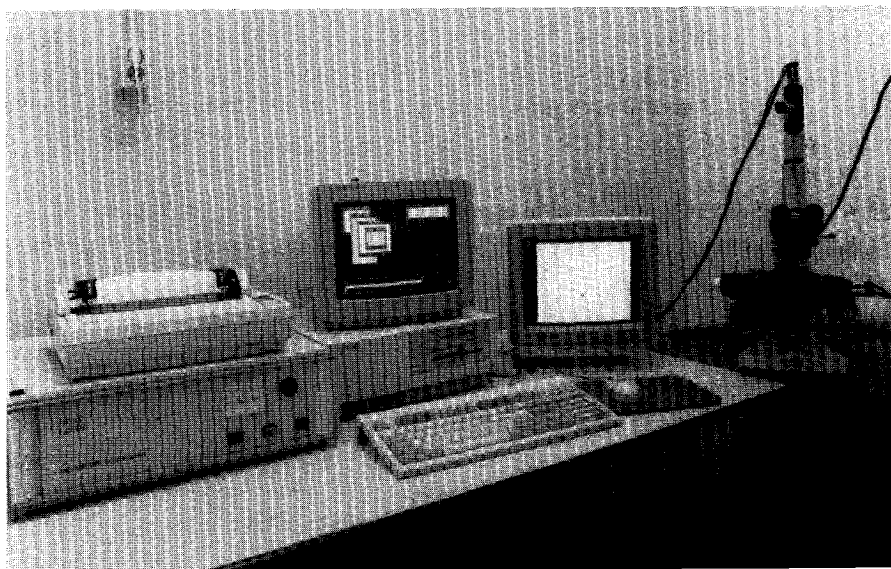


Fig.3.7. Mini-Magic Scan, IAS 25/IV25, an image analysis system (Joice-Loebel Ltd.) used to evaluate particle agglomeration and removal.

Video system

In order to overcome the shortcomings of conventional water quality analysis, and to provide more insight into phytoplankton behavioral response to coagulation, a video system (video camera attached to an inverted microscope) was employed for in situ observation. The system

allows direct observation of algae (in size range 1 to 100 μm) on a monitor, or recording of images on video tape. It provides important qualitative information that cannot be obtained with other techniques (e.g. interaction between algae and oxidant, algal motility, and algae and iron precipitates morphology).

3.3. RESULTS AND DISCUSSION

3.3.1. Influence of Growth Media on Algal Removal in Direct Filtration

Results from experiments with MJTA show that the same algal species in the same growth phase, but grown on a different medium, respond differently to identical treatment conditions. Direct filtration reduced particle (algae) concentration initially present in model water prepared with *C. vulgaris* at stationary growth stage, cultured on Z-8 medium (Fig. 3.8. a). However, identical direct filtration treatment conditions were completely ineffective and resulted in higher particle concentration in the filtrate when the model water was prepared with the same algal species at the same growth stage, but grown on Jaworski medium (3.8.b). Typically, comparison of Fig. 3.8. a and b shows that Z-8 medium produced *C. vulgaris* at a stationary growth phase yields better filtrate quality. However, this discrepancy was not observed during their logarithmic growth stage (Fig.3.8 c, d).

In order to verify the validity of these outcomes, the same set of MJTA experiments was repeated with another type of green alga, *S. capricornutum* grown on the same media (Fig.3.9). Initial particle concentration in both model waters, prepared with Jaworski and Z-8 cultured algae, was reduced more efficiently than earlier experiments in which model waters were prepared with *C. vulgaris* (Fig. 3.8). Higher *S. capricornutum* removal efficiency is to be expected because of its larger size (*S. capricornutum* 5-10 μm , *C. vulgaris* 4-5 μm). However, the overall reduction in the particle concentration, as measured by a number of scanned particles in model water and the MJTA filtrate, was much higher when model water prepared with Z-8 medium grown *S. capricornutum*. During the logarithmic growth stage a value of 50 % reduction was reached for Z-8 medium (Fig. 3.9 c), compared to 25 % for the Jaworski medium grown algae (3.8.d). The difference was even more pronounced in the stationary growth phase, in which a 40 % particle reduction was accomplished for Z-8 medium grown algae (Fig. 3.9 a), compared with a mere 3 % reduction obtained for model water with algae grown on the Jaworski substrate (Fig. 3.9 b). In general the Jaworski-medium grown algae led to poorer direct filtration performance.

MJTA experiments with both Z-8 and Jaworski cultured *C. vulgaris* and *S. capricornutum* were repeated to test the reproducibility of the results. The trends reported here were found to be reproducible.

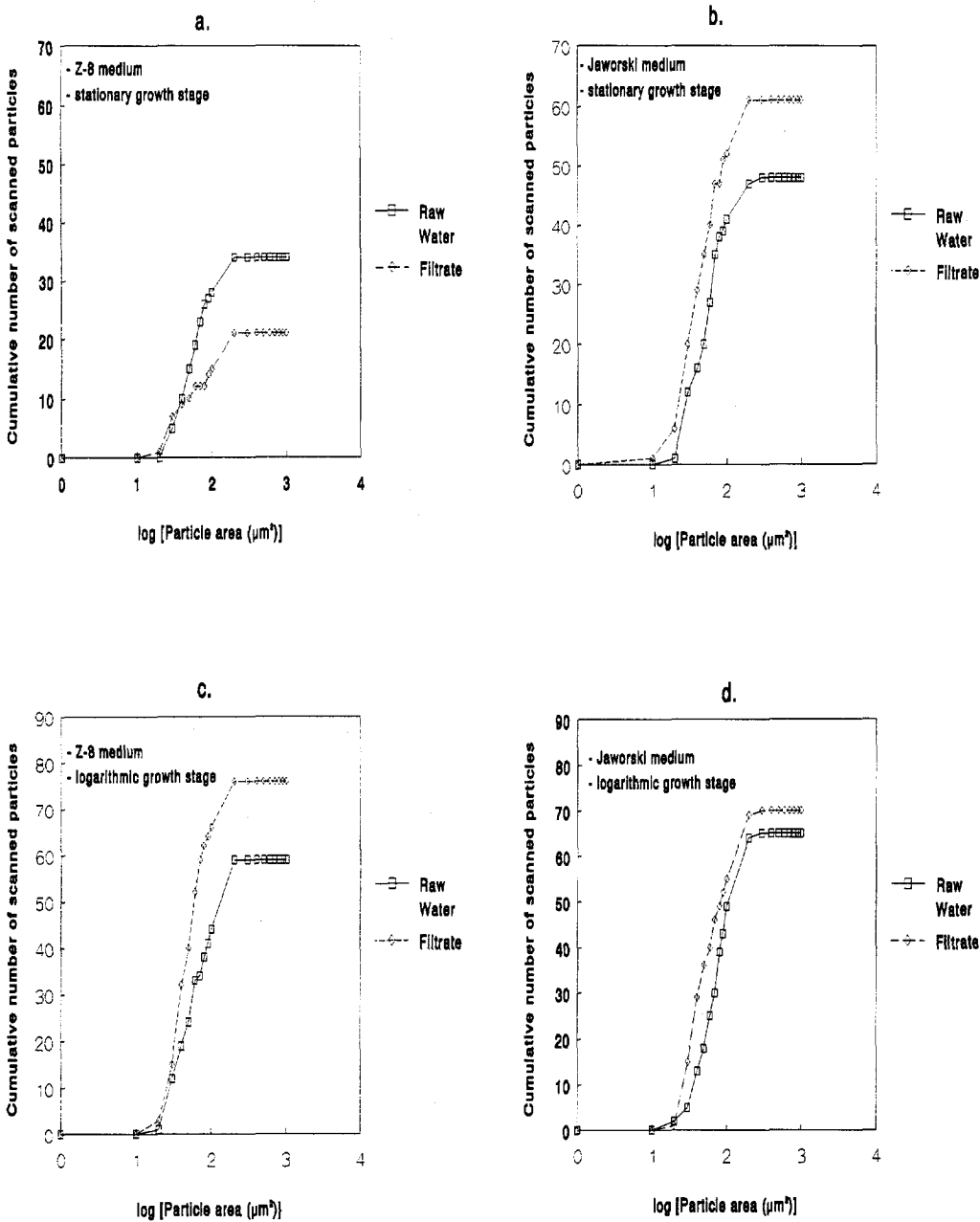


Fig. 3.8. Cumulative number of scanned particles as a function of particle size, expressed as the logarithm of the horizontally projected area in μm^2 , before and after MJTA experiments. *C. vulgaris* in stationary (a, b) and logarithmic (c, d) growth stage, cultured on Z-8 (a, c) and Jaworski (b, d) media.

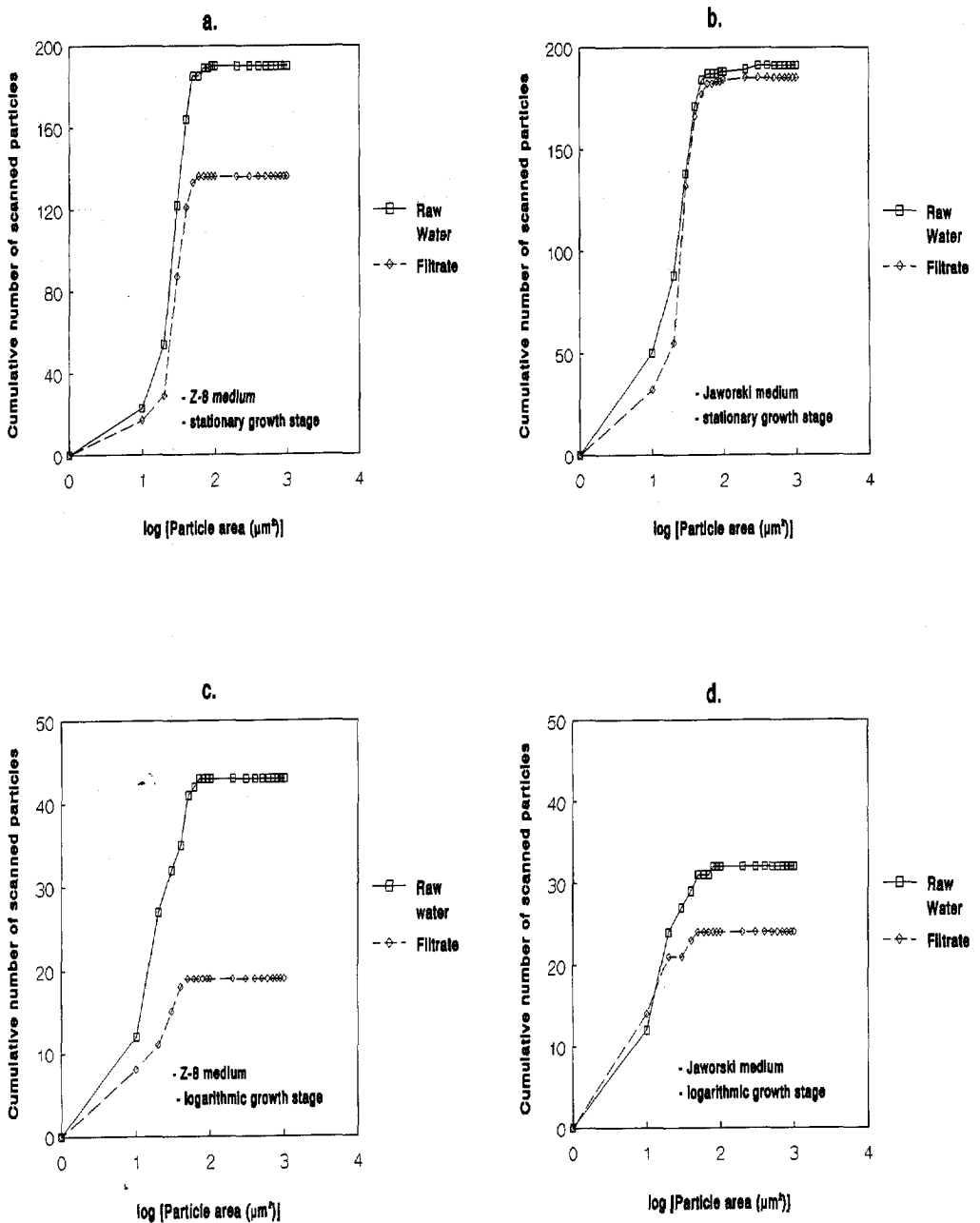


Fig. 3.9. Cumulative number of scanned particles as a function of particle size, expressed as the logarithm of the horizontally projected area in μm^2 , before and after MJTA experiments. *S. capricornutum* in stationary (a, b) and logarithmic (c, d) growth stage, cultured on Z-8 (a, c) and Jaworski (b, d) media.

The observed phenomenon is most likely correlated to a difference in the medium's composition. A considerable difference exists in major and trace elements, vitamin concentration, the composition and concentration of complexing agents. Complexing agents, however, are able to keep Fe in solution by complex formation, thus making less Fe available for floc formation. In the Z-8 medium, a significant part of the complexing agent is likely to be already bound by the high concentration of numerous micronutrients. This is less the case with the Jaworski medium, which is characterized by a low micronutrient level. In addition significant difference in the phosphate concentration in the two model waters (Z-8 medium is prepared with a four times lower phosphorus concentration) may also play an important role. Consequently, the amount of iron available for algal coagulation is likely to be higher in the case of Z-8 medium, producing more favourable coagulation and flocculation (agglomeration) conditions.

Results obtained in the algal-related water treatment studies, in which model water prepared with cultured algae is used, may be strongly influenced by the composition of the growth media used. Consequently, it can be concluded that the extrapolation of results obtained in studies with model water, prepared with cultured algae, to natural waters, or even from one natural water to another is questionable.

An additional set of MJTA experiments was conducted with natural and model *M. aeruginosa* dominated water (Fig.3.10). Coagulant dosages ≥ 3 mg Fe(III)/l resulted in very efficient removal of natural *M. aeruginosa*, while cultured algae at same coagulant dosages could not be eliminated. Different algal removal efficiencies under identical treatment conditions found for natural and cultured algae may also be relate to a likely higher concentration of complexing agents and phosphate in model water. In addition, a significant difference in the appearance of natural and culture *M. aeruginosa* was observed. In natural water, algal cells were found to be grouped in three-dimensional colonies, while the algae in the cultures were in the form of single cells, probably as a consequence of continuous mixing during their culturing. *M. aeruginosa* cells in model water were of a size that is most difficult to remove in filtration (approximately 2 μm). It is obvious that differences in algal size and form can strongly influenced removal efficiencies achieved in direct filtration.

The limited available volume of Biesbosch water with a high concentration of *M. aeruginosa*, as well as difficulties associated with culturing this alga, did not allow duplication of experiments. Nevertheless, results obtained indicate that a straightforward use of model water with cultured algae may lead to erroneous conclusions if results are directly extrapolated to natural conditions. In addition, very efficient removal of *M. aeruginosa* colonies (>98%) and meagre removal of single cells of the same alga (approx. 65%) confirms the experience of waterworks in practice that *M. aeruginosa* causes filtration performance to be poor when colonies break up and algal cells appear in individual form. This phenomenon again emphasizes the importance of adequate agglomeration, by natural or chemical coagulation and flocculation, as a prerequisite for efficient filtration.

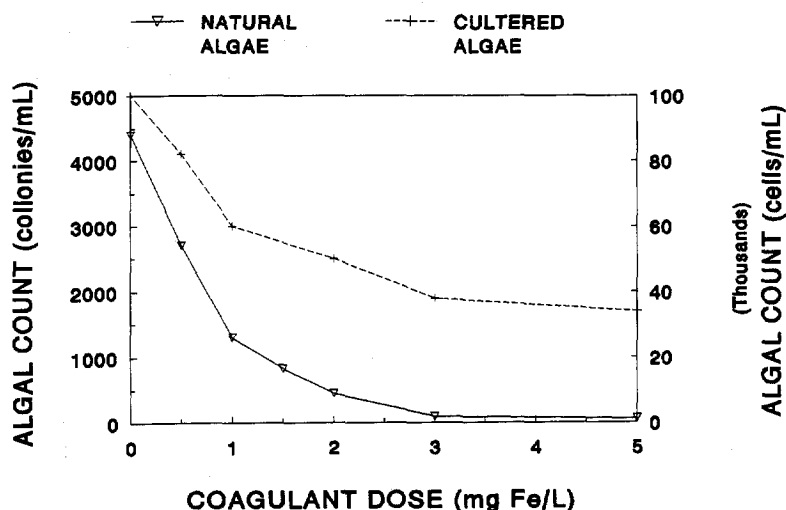


Fig. 3.10. Concentration of *M. aeruginosa* in the modified jar test effluent, as a function of coagulant dose.

3.3.2. Removal of Dominant Algal Species from Biesbosch Water

As a consequence of the applied softening technique in Biesbosch reservoirs, a considerable amount of calcite particles, of a size similar to alga dimensions, were present in the raw water. Microscopic examination demonstrated that complete elimination of calcite particles was systematically achieved in filter runs with BSDFPF and MDFPF, indicating that the flocculation and filtration conditions in the pilot plants were appropriate for removal of common inorganic particles. However, the experiments with natural (Biesbosch water) as well as model water, have shown that algal removal efficiency strongly varies with algal species (Figs. 3.8, 3.9 and 3.11). It was also noticed that the removal efficiency may differ significantly for algal species with similar sizes and shapes, indicating that other algal properties also play an important role. Figure 3.11. shows typical algal removal patterns achieved with MDFPF and BSDFPF during the summer and early spring. Data presented in Fig.3.11 are averages from several filter runs (five during summer and four during the spring period) repeated under identical treatment conditions. Average removal efficiency as low as 5% was found for *R. minuta* during the summer period, making it the most difficult algal species to be eliminated. This alga, 5-10 μm long, is equipped with flagella enabling easy and fast swimming. The movement of flagellated algae at speeds of 50 to 300 $\mu\text{m/s}$ have been reported (Brokaw 1962). Significantly higher removal efficiency, typically about 60 %, of *Chlamydomonas* sp., also a flagellated alga, was found. The difference in behaviour of *R. minuta* and *Chlamydomonas* sp. may be due to a difference in size and possibly cell surface properties, as well as to the distinctive pattern of *R. minuta*'s flagellar movement. In the pilot plant experiments high average removal efficiency (94-100%) was found for *S.*

hantzschii, though it is generally reported to be difficult to agglomerate. This discrepancy is probably related to the absence here of long needles; these were reported by Bernhardt and Clasen (1991) to be the main agglomeration inhibitor. In our experiments, we found diatoms in Biesbosch water to have no needles during the summer and early spring period. Small spherical green algae, Chlorophyceae (less than 3 μm in diameter), also called μ -algae are almost continuously present in Biesbosch water. Their presence in raw water is frequently undetected, since the commonly applied inverted microscopes with magnification of up to 400x are not sufficient for their proper identification and enumeration. In this study, an inverted microscope that provided 600 magnification was used. Removal efficiency of μ -algae was found here to be less than 50 %, with a somewhat higher removal of their colonies in a three-layer filter. These results may be correlated with (1) their inefficient flocculation, and (2) results from filtration studies revealing that minimum removal efficiency may be expected for particles of size 1-3 μm (Yao *et al.* 1971, Westerhoff *et al.* 1991, chapter 2).

The problem of inefficient removal of these algal species is frequently neglected, partly because their concentration in reservoir water is relatively low compared with other species. However, Figure 3.12 indicates that the contribution of these algae to the total algal biomass increased from approximately 6 % in raw Biesbosch water to over 47 % in the filtrate. Consequently, the issue of their efficient removal should be carefully addressed.

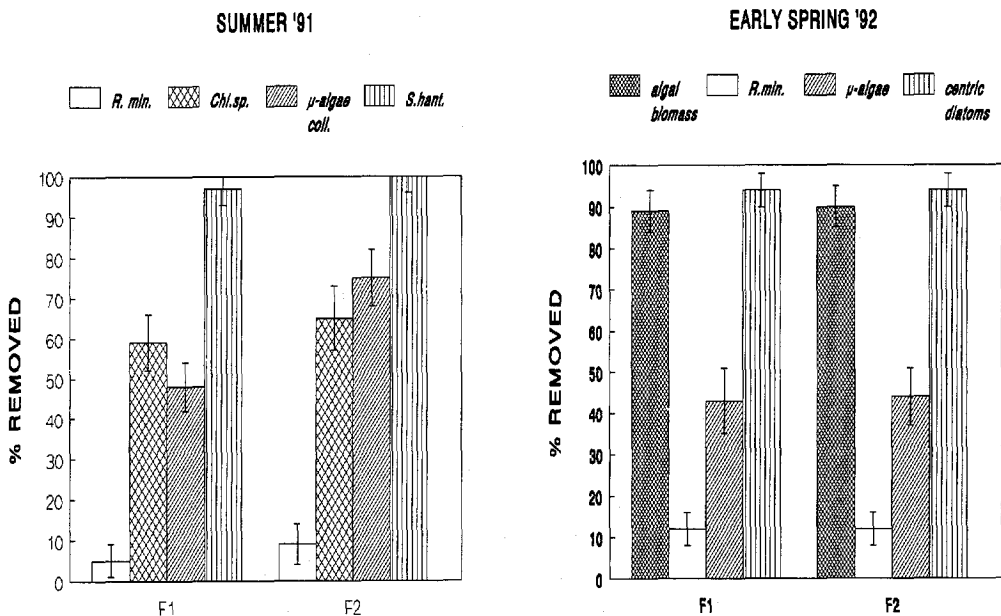


Fig. 3.11. Removal of different algal species obtained in MDFPP and BSDFP, during the summer and early spring period. Coagulant: ferric sulphate, 1.0 mg Fe(III)/l, F1-anthracite-sand bed, F2- anthracite-sand-garnet bed, filtration rate 10 m/h. Algal species: *R. min* - *R. minuta*, *Chl. sp.*- *Chlamydomonas* sp., μ -algae coll. and μ -algae - colonies and single cells of μ -algae, *S. hant.* - *S. hantzschii*, centric diatoms - diatoms like *S. hantzschii* (predominant), *S. astraea* and *Cyclotella*.

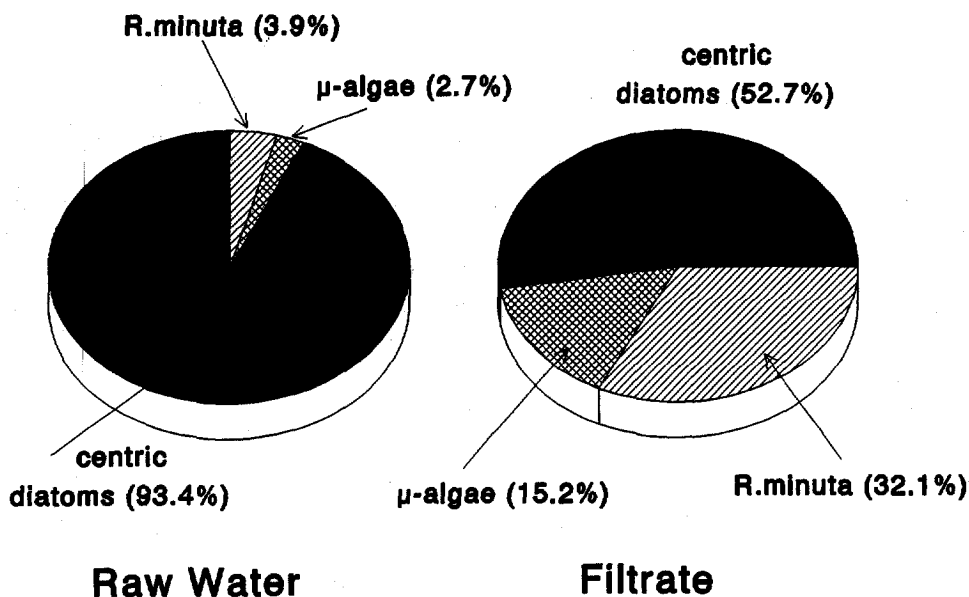


Fig. 3.12. Contribution of different algal species to total algal biomass in the raw Biesbosch water and filtrate.

Microscopic examination (magnification 600X) revealed that the algae in the filtrate were present almost exclusively in the form of single cells. It was also observed that the coagulated raw water, before entering filter media, contains a mixture of iron hydroxide microflocs without algae, larger flocs (40-60 μm) with several algae trapped inside, and a large number of single algal cells. This indicates that where algal removal in direct filtration is poor, it is mainly related to inefficient algae-flocs interaction and agglomeration (low collision efficiency during coagulation and filtration stage).

Inspection with the video system demonstrated that algal motility may be partly responsible for poor algal agglomeration and removal of certain algal species (see the attached video tape). Most of the algae observed in the pilot plant's filtrate that operated in direct filtration treatment mode were highly motile (e.g. *Pandorina* sp., *R. minuta*, *Cryptomonas* sp., *Navicula* sp., *Nitzschia* sp.). To investigate further the relevance of algal motility additional experiments were conducted. First, filtrate of the MDFPP was concentrated with a tangential flow membrane micro filtration system to obtain high concentration of motile algae (for concentration procedure see chapter 4). Subsequently a concentrated water sample was coagulated with 1.5 mg Fe(III)/l. Fresh coagulated samples were examined with the video system. Examination with the video system demonstrated that motile algae are able to escape from flocs by virtue of their motility. The observed phenomenon is not only valid for flagellated algae as earlier assumed by Bernhardt and Clasen (1991) but also for pennate

diatoms like *Navicula* sp. and *Nitzschia* sp., which can glide.

In addition to algal motility, it may be speculated that other algal properties like cell wall composition, algal shape, presence of gas vacuoles, and in particular the presence of the outer mucilaginous layer, may contribute to poor coagulation, flocculation and filtration of these particles.

3.3.3. Dual and three-layer filter media

In comparison with dual filter media, the three-layer filter, consistently produced filtrate of superior quality, as measured by turbidity (Fig.3.13), residual iron (Fig.3.14) and particle count (Fig.3.15). However, the three-layer filter featured equal or only slightly higher algal removal efficiency (Fig.3.11). Graphs given in Figs 3.13, 3.14, 3.15 and 3.16 are the results of a single filter run with MDFPP, conducted during typical spring algae bloom. Filter run under similar treatment conditions (coagulant dosage 0-2.0 mg Fe(III)/l, and filtration rate 5.0-10.0 m/h) were repeated through the year. The trends reported here were found to be reproducible and not influenced by alteration of direct filtration process conditions.

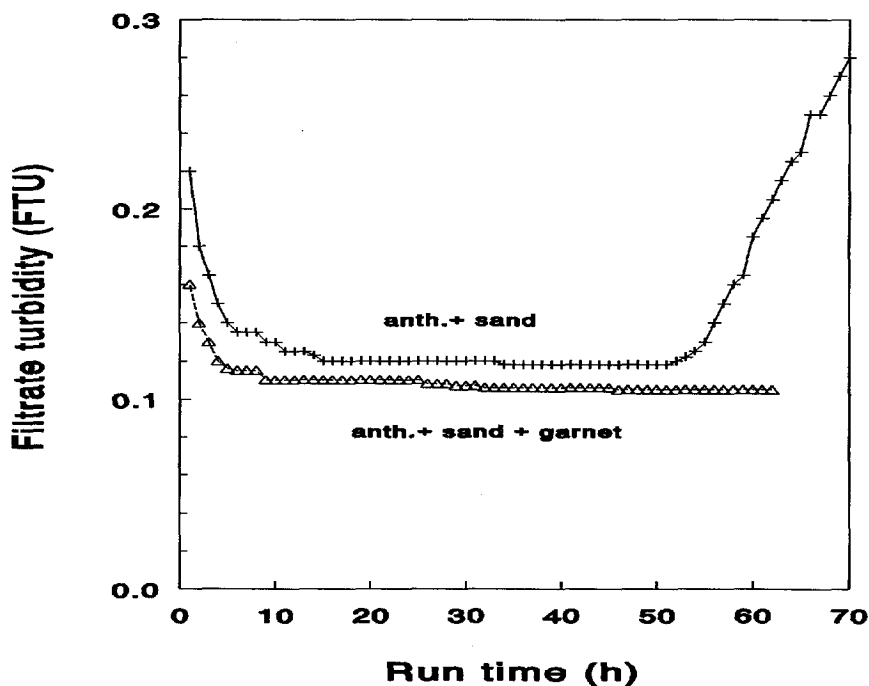


Fig.3.13. Effect of dual and three-layer media on turbidity of the MDFPP filtrate; coagulation with 1.0 mg Fe(III)/l, filtration rate 2.7×10^{-3} m/s.

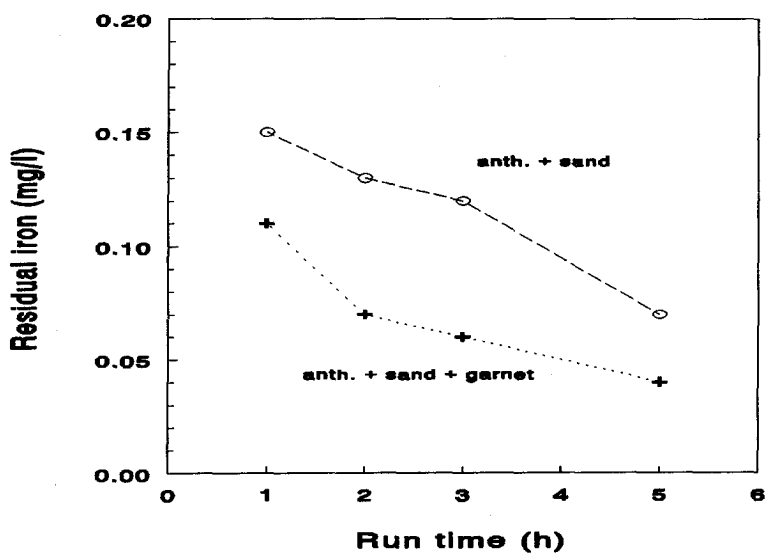


Fig. 3.14. Effect of dual and three layer-filter media on residual iron concentration in the MDFPP filtrate; coagulation with 1.0 mg Fe(III)/l, filtration rate $2.7 \cdot 10^{-3}$ m/s.

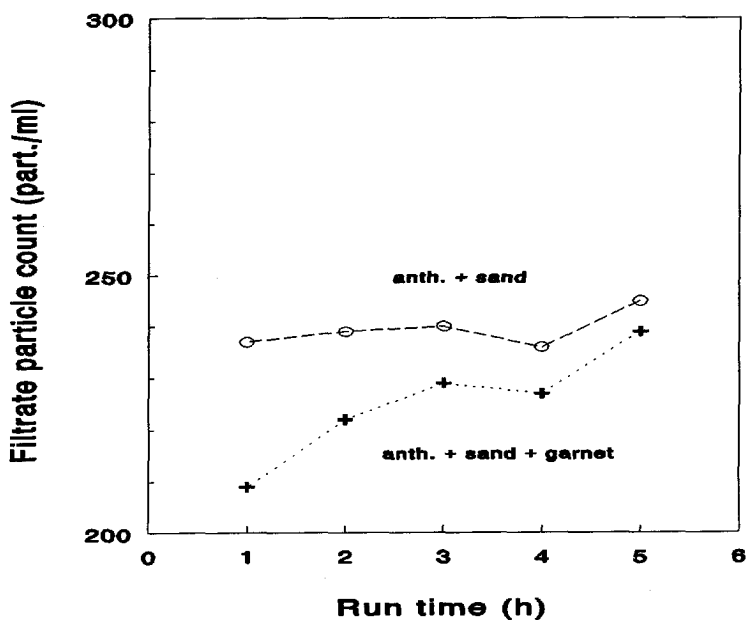


Fig.3.15. Effect of dual and three layer filter media on particle concentration in the MDFPP; coagulation with 1.0 mg Fe(III)/l, filtration rate $2.7 \cdot 10^{-3}$ m/s.

Filter run lengths were a function of the applied coagulant dosage. Coagulant dosage of 1.0 Fe(III) mg/l typically resulted in filter run lengths of 40-50 hours (Fig. 3.16). Filter runs of the filter equipped with anthracite-sand filter media were regularly terminated due to turbidity breakthrough, while the runs of the anthracite-sand-garnet filter were terminated when the maximum allowable head loss of 3.0 meters was reached.

Filtrate turbidity and residual iron clearly improved during initial filter run hours. Relatively long filter ripening periods, up to 10 hours, were required to achieve consistent low filtrate turbidity (0.10-0.12 FTU with anthracite-sand-garnet filter and 0.11-0.14 FTU with anthracite-sand filter). The three-layer filter consistently ripened more rapidly than the dual media filter. By contrast, particle concentration in filtrate slightly increased during initial filter run hours (Fig.3.15). The particles found in the filtrate were predominantly in the size range 3-10 μm . Poor removal of highly motile algae (Fig.3.11) together with the observation with the video system strongly suggest that algae like *R. minuta* contribute significantly to the total particle count in the filtrate. It may consequently be speculated that increase in filtrate particle concentration, during initial filter run hours may be attributed to motile algae that need a specific time to find the way through the labyrinth of filter media and finally end up in the filtrate.

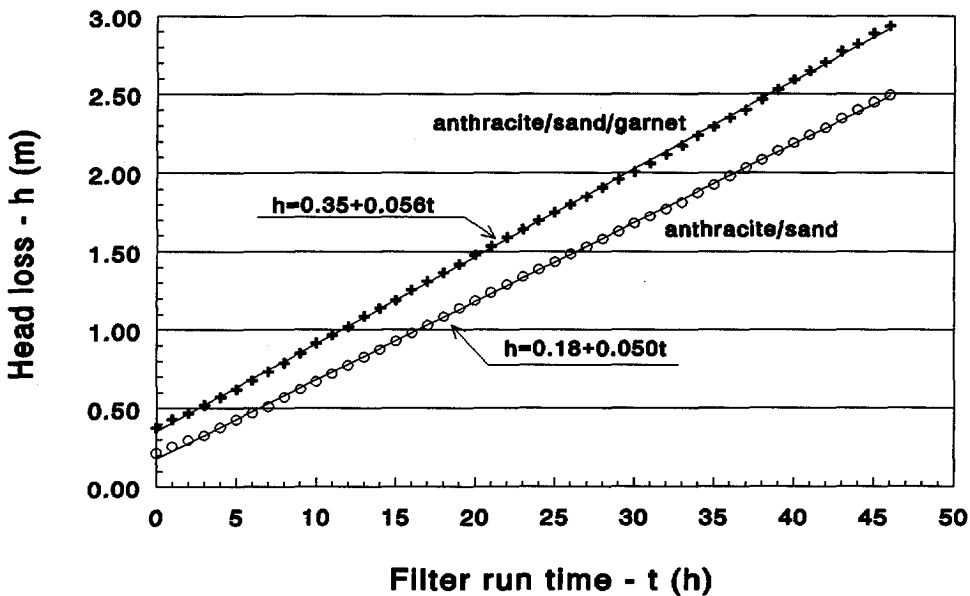


Fig.3.16. Head loss as a function of filter run time for anthracite-sand and anthracite-sand garnet filter beds; coagulation with 1.0 mg Fe(III)/l, filtration rate $2.7 \cdot 10^{-3}$ m/s.

Results from pilot plant experiments demonstrated that straightforward direct filtration, without additional pre-treatment, can achieve only approximately 90% algae removal,

indicating that approximately 10% of the algae that are present in the raw water pass treatment and finish in the drinking water. These results are in agreement with the findings of other researchers (Bernhardt *et al.* 1986). Consequently, one or more of the earlier-mentioned algae-related inconveniences can be experienced. Achieved algal removal efficiency is remarkably lower than the direct filtration particle removal capabilities as assumed in the Surface Water Treatment Rule - SWTR (Von Huben 1991). SWTR assumes that direct filtration can achieve 2.0-log removal* of *Giardia* cysts (particles of a size similar to size of algae commonly present in Biesbosch water) in contrast to 1.0-log removal found in this investigation. Data on algal removal efficiency achieved in the full scale conventional water treatment plant Kralingen, that also treats Biesbosch water were not available. However, comparison of the particle concentrations, measured with the HIAC particle counter demonstrated that a full-scale conventional plant produces filtrate with a seven times lower particle concentration (approximately 240 in the MDFPP filtrate and approximately 35 in the filtrate of the full-scale conventional plant). Data on particle removal efficiency, together with the presence of an additional particle removal barrier, the sedimentation unit, and considerably higher applied coagulant dosages (6.0-8.0 mg Fe[III]/l) strongly suggest that the conventional, full-scale plant achieves much higher algal removal efficiency.

Straightforward direct filtration produces filtrate with much lower turbidity than currently required by the EEC Directives (1.0 FTU) or VEWIN (Association of Dutch Waterworks) guide levels (0.8 FTU, or 0.2 FTU if disinfection is applied). Nevertheless, turbidity levels were higher than the levels achieved in the full-scale conventional treatment plant (direct filtration: 0.10-0.14 FTU, full scale conventional plant: consistently < 0.10 FTU).

The application of straightforward direct filtration in drinking water production cannot therefore be accepted as a viable treatment alternative to conventional treatment, because it produces drinking water of poorer quality (higher turbidity, higher particle and algal concentration). In order to be considered as a viable treatment option, and to consequently benefit from economic attractiveness of the process, direct filtration performance should be improved in terms of filtrate turbidity and, more significantly, particle and algae removal efficiency. Direct filtration should be capable of producing filtrate with consistent turbidity < 0.1 FTU and, in addition, particle and algae removal efficiency should be improved to at least 2.0-log removal unit, consequently fulfilling the requirements established in the SWTR, and, also producing filtrate with chlorophyll- α < 0.1 $\mu\text{g/l}$. However, straightforward direct filtration of Biesbosch water can be a viable and economically very attractive treatment alternative for production of industrial water characterised by somewhat lower quality requirements.

* 1-log removal=90%, 2-log removal=99%, 3-log removal=99.9%

4. CONCLUSIONS

The developed semi-batch experimental set-up MJTA has been demonstrated to be very useful for rapid preliminary testing of a variety of direct filtration treatment conditions. Consequently use of this set-up can reduce the number of long and complex pilot scale filter tests. In addition, two set of direct filtration pilot plant BSDFPP and MDFPP were developed to overcome MJTA limitations. These set-ups allow simultaneous assessment of direct filtration performance under different conditions, continuously throughout the entire filter run.

The results presented show that different particle removal was achieved when two model waters prepared with the same algal species in the same growth stage, but, grown on two different culturing media were exposed to identical direct filtration treatment conditions. Different algal removal efficiencies observed may be related to different concentrations of complexing agents and phosphates in culturing media and consequently in model waters. In addition, different removal efficiencies of cultured and natural *M. aeruginosa* were observed under identical direct filtration treatment conditions. Consequently, extrapolation of the results from model studies that apply algal cultures to natural conditions is highly questionable. Conceivably the better approach is to use natural algae from water bodies intended to be used as water sources.

Algal removal efficiency strongly varies with respect to different algal species. High removal efficiencies, over 94 %, were found for centric diatoms, the dominant algal species in the Biesbosch reservoirs. The most troublesome algal species to eliminate were found to be *R. minuta* and μ -algae. Their poor removal (5-75%) may be mainly related to poor agglomeration, or floc formation. Although the contribution of μ -algae and *R. minuta* to total algal biomass in raw Biesbosch water is small, they represent almost half of the algal biomass in the filtrate.

In comparison with anthracite-sand filter media, the anthracite-sand-garnet filter media consistently produced filtrate of superior quality as measured by turbidity, residual iron and particle count.

Straightforward direct filtration of Biesbosch water, without additional pre- and/or post-treatment, produces filtrate of poorer quality (turbidity, particle and algae concentration) than conventional treatment. Consequently, it is questionable to promote this treatment as an alternative to conventional treatment in production of drinking water. In order to be considered a viable treatment option, particle removal efficiency in direct filtration should be increased by at least 1-log unit, corresponding to a minimum 99% particle (*Giardia* cysts - SWTR) and algal removal efficiency and chlorophyll- α level in filtrate ≤ 0.1 mg/l. In addition filtrate turbidity should be consistently < 0.1 FTU.

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APPENDIX 3.1. Characteristics of the filter beds used in the pilot plant experiments.

| DUAL-MEDIA | | | | | |
|------------|------------------|------------------|-------------------------|-----------------|------|
| Layer | Thickness (m) | Fraction (mm) | d ₆₀ (mm) | U* ¹ | ψ |
| Anthracite | 0.8 | 1.60-2.50 | 2.04 | 1.25 | 0.64 |
| Sand | 0.4 | 0.80-1.25 | 0.97 | 1.17 | 0.99 |

| THREE-LAYER-MEDIA | | | | | |
|-------------------|------------------|------------------|-------------------------|------|------|
| Layer | Thickness (m) | Fraction (mm) | d ₆₀ (mm) | U* | ψ |
| Anthracite | 0.8 | 1.60-2.50 | 2.04 | 1.25 | 0.64 |
| Sand | 0.4 | 0.80-1.25 | 0.97 | 1.17 | 0.99 |
| Garnet | 0.2 | 0.50-0.80 | 0.68 | 1.41 | 0.87 |

$U = d_{60}/d_{10}$

$\psi = d_h/d_s$

$d_s = (W_1/W)d_{s1} + (W_2/W)d_{s2} + \dots + (W_n/W)d_{sn}$

where:

- U - uniformity coefficient;
- ψ - sphericity;
- d_h - hydraulic diameter (derived from Carman-Kozeney equation, after measuring the resistance in a clean filter bed);
- d_s - sieve diameter;
- W - weight of sieved sample of filtering material;
- W₁....W_n - weight of fraction between the consecutive sieves;
- d₁₀ and d₆₀ - the sizes of the sieve through which 10% and 60% of the material will pass;

APPENDIX 3.2. Composition of algae cultivating media

| Element | Concentrations (μM) | | |
|---------|----------------------------------|------------|----------|
| | Jaworski* | Z-8 (25%)* | Citiri** |
| Ca | 84.67 | 61.87 | 63.50 |
| N | 1038.00 | 1500.00 | 3239.00 |
| K | 91.10 | 44.25 | 17.60 |
| P | 191.70 | 43.70 | 17.60 |
| Mg | 203.00 | 25.50 | 25.60 |
| S | 203.00 | 25.70 | 25.60 |
| C | 200.00 | 51.70 | 250.00 |
| Na | 1213.00 | 1546.00 | 5226.00 |

| Trace Elements | Concentration (μM) | | |
|----------------|---------------------------------|----------------------|----------------------|
| | Jaworski* | Z-8 (25%)* | Citiri** |
| B | 40.00 | 1.35 | 0.75 |
| Mn | 7.00 | 0.33 | 0.53 |
| Fe | 5.60 | 10.69 | - |
| Mo | 0.81 | 0.01 | 0.01 |
| Br | - | 0.03 | - |
| Zn | - | 0.03 | 0.01 |
| Cu | - | 0.01 | $0.18 \cdot 10^{-4}$ |
| Cr | - | $0.25 \cdot 10^{-2}$ | - |
| Al | - | 0.02 | - |
| Ni | - | 0.01 | - |
| Co | - | 0.01 | $0.17 \cdot 10^{-2}$ |
| I | - | 0.01 | - |
| Cl | - | - | 7.70 |

* semi continuous cultures

** continuous culture

| Vitamins | Concentration (mg/l) | | |
|----------|----------------------|------------|----------|
| | Jaworski* | Z-8 (25%)* | Citiri** |
| B-12 | 0.04 | - | - |
| B- 2 | 0.04 | - | - |
| Biotin | 0.04 | - | - |

| Complexing agents | Concentrations (μM) | | |
|-------------------|---------------------|------------|----------|
| | Jaworski* | Z-8 (25%)* | Citiri** |
| EDTA Fe Na | 5.60 | - | - |
| EDTA Na | 6.04 | - | - |
| Fe EDTA | - | 1.76 | - |
| Na NTA | - | - | 1800.00 |
| MES | - | - | 25000.00 |

* semi continuous cultures
** continuous culture

Chapter 4

TANGENTIAL FLOW FILTRATION:
A METHOD TO CONCENTRATE FRESHWATER ALGAE *

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* B. Petruševski, G. Bolier, A.N. van Breemen and G.J. Alaerts (1995), *Wat. Res.* Vol. 29, No. 5.

ABSTRACT - The suitability of the application of the tangential flow filtration system (TFF) for the concentration of living freshwater phytoplankton for water treatment studies was examined. We investigated the capability of a TFF system, equipped with a $0.45\mu\text{m}$ pore-size membrane, to concentrate algae from large volumes of reservoir water characterized by low algal biomass. The samples examined were concentrated 5 to 40 times. The assessment criteria of the system's performance were algal recovery rate and cell viability. It was found that large volumes of water could be processed without problems. The algal recovery rate was high and correlated with the applied concentration factor and the prevailing algal species. An overall algal biomass recovery of 70 to 89 percent was found. The assessment of algal viability in the concentrated samples was based on the growth rates and degree of preservation of their complex structure and other properties (e.g. motility, mucilage capsule, surface charge, etc.) that affect their behaviour in water treatment. Algal cells in the concentrated samples and in natural reservoir water were found to be identical, with all delicate cell structures undamaged. Motile species preserved their active locomotion. Algal reproduction capacity was not affected. The results obtained confirm that the TFF system is a powerful apparatus for the preparation of model waters to be used in experimental algal-related water treatment studies.

4.1. INTRODUCTION

The eutrophication of surface water is a worldwide problem, which is increasing in significance, although in some industrialised countries the situation of late stabilized because of pollution abatement and improved water management (Oskam and Van Breemen, 1992). However, it is forecast that fresh surface water will be of increasing importance for the production of drinking water, whilst at the same time tap water is having to meet progressively more stringent quality requirements. The omnipresence of algae is, therefore, a problem in drinking water production. Elimination of algae in the water treatment processes is complex. Similarly, the organic matter produced by algal cells (extra-cellular organic matter - EOM) in its turn negatively influences the performance of flocculation and filtration. These topics require extensive experimental investigation because large number of process variables (algal species, algal growth stage, seasonal changes of algal composition etc.) may influence process efficiency. Several investigations have already been carried out on key parameters of algal coagulation, agglomeration and removal in water treatment processes. Model water prepared with mono-algal cultures was used in most of these investigations. The most widely studied algal species are *Chlorella* sp. and *Scenedesmus* sp., because they are commonly found in natural water and represent the green algae, but also because they are easily cultured under the laboratory conditions. Lusse (1988) achieved an important advancement by developing a specific algal culturing method that best simulates the natural environment.

Studies on algal cultures allow the investigation of fundamental principles and mechanisms of algal agglomeration and the role of algal EOM. However, recent studies have confirmed that the results obtained in water treatment studies with model waters, prepared with cultured algae, may strongly be influenced by the cultivation conditions. In addition, it was

demonstrated that natural and cultured *Microcystis aeruginosa* behaves quite differently in the context of a direct filtration treatment process (Petruševski *et al.*, 1993). Millington *et al.* (1988) reported that growth media composition affects the toxic values to test algae of four chemicals (morpholine, nitrilotriacetic acid, *o*-dichlorobenzene and triphenyl phosphate).

These results also suggest that algae have a tendency to change their properties in response to local environmental conditions. The validity of the extrapolation of results obtained in model studies, in which suspensions were prepared with cultured algae, to natural suspensions is, therefore highly questionable. A better strategy would be to use natural algae from the water bodies which are intended to be used as a raw water source. However, this approach faces experimental difficulties because of the seasonal periodicity of the algal population. Oligotrophic and mesotrophic reservoirs, preferred as raw water sources, have very low concentrations of algae for long periods of the year. As a consequence, the opportunities to conduct experiments are limited to short and partly unpredictable periods of algal bloom. A possible solution to the problem is, there, to concentrate the algae in the water for the purpose of the experiments. However, the concentration technique employed must not change the algal population significantly, nor affect algal viability. In addition, the concentration of dissolved natural organic compounds like humic and fulvic acids that are present in the natural water, and that can control coagulation process, must not be substantially altered. Consequently, the applicability of conventional cell harvesting techniques such as centrifugation and "dead-end" membrane filtration is restricted because of the damage caused to the organisms and the limited volume processing capability. However, the tangential or cross-flow filtration technique (TFF) offers a new opportunity. In TFF, water is kept flowing at elevated speed along a membrane, and is allowed to flow tangentially across the membrane thus keeping the cells in the main circulations flow in suspension. Particles and molecules smaller than the membrane pores pass through the membrane, while the larger ones are retained. TFF may be equipped with a microporous or ultra-filtration membrane with a wide range of pore sizes or molecular cut-offs. Whitehouse (1990) examined the application of TFF equipped with a nominal molecular weight cut-off of 10,000 (pore size 1-2 nm) for the concentration of colloids from the aquatic environment. He found that both organic material and several trace metals were recovered without significant losses. Barthel *et al.* (1989) examined the applicability of the system in oceanographic research for the concentration of live pico- and nanoplankton, and found that large volumes of seawater can be processed for the accumulation of plankton. So far the use of TFF for the concentration of plankton and other particles in the field of water treatment research has not been studied. The technique has found wider application in medicine for the concentration of human cells, viruses and bacteria.

Our aim was to investigate the feasibility of employing TFF for the concentration of algae in natural fresh water for the purpose of bench-scale experiments on coagulation/flocculation, direct filtration, and flotation in water treatment. The suitability of TFF was assessed as to its ability to concentrate algal species in natural water while preserving their properties that enable them to resist treatment and to end up in treated water. Algal characteristics that

influence the algae behaviour in water treatment include active motility, cell locomotion of eukaryotic flagellates or the peculiar gliding motility of certain diatoms, cell wall elongations (e.g. long needles, flagella), cell unification (e.g. as filamentous algae and cell colonies), the presence of a mucilage layer or capsule attached to the cell wall of certain algal species (e.g. *Pandorina* sp.), and negative surface charge.

4.2. MATERIALS AND METHODS

4.2.1 Raw water

Two raw waters were used in the experiments: (i) water from the Petrusplaat reservoir, the last in the series of three Biesbosch water storage reservoirs (volume 13×10^6 m³, 13-15 m mean depth, located in the central part of the Netherlands), during periods of low (January-February) and moderate (beginning of March) phytoplankton concentrations, and (ii) filtrate from a direct filtration pilot plant.

Water from the Petrusplaat reservoirs first was characterized by very low algal concentrations (chlorophyll- α < $1.0 \mu\text{g l}^{-1}$). The predominant algal species were centric diatoms (*Stephanodiscus hantzschii*, *S. astraea* and *Cyclotella* sp.), *Rhodomonas minuta* (Crypthophyceae) and small green algae (size < $2 \mu\text{m}$) referred to as micro-algae. During early spring, the algal biomass increased (chlorophyll- $\alpha \approx 2.5 \mu\text{g l}^{-1}$), but the algal composition did not change significantly. Biesbosch water was used in the experiments designed to investigate the recovery of algal biomass and for cultivation of algae.

The filtrate from the direct filtration pilot plant, treating raw Biesbosch water was used as an alternative source of water with very low concentration of algae. The plant was operated applying ferric sulphate ($1.0 \text{ mgFe[III] l}^{-1}$). The plant achieved very efficient removal of inorganic particles like iron precipitates and calcite particles. Filtrate had in addition, very low algal concentration (chlorophyll- α < $1.0 \mu\text{g l}^{-1}$). Algae present in the filtrate were found to be undamaged, in the form of single cells. The species in the filtrate were typical organisms that are difficult to agglomerate and remove: *R. minuta*, *Navicula* sp., *Phacotus* sp., *Monoraphidium* sp., *Kirchneriella* sp. and centric diatoms. The filtrate from the direct filtration pilot plant was specifically used for investigations with the video system designed to assess the effect of concentration procedure on algal motility.

Water from the Petrusplaat reservoir has a high concentration of calcite particles (CaCO_3) as a consequence of softening with lime or sodium hydroxide. These particles are of a size similar to that of common unicellular algal cells. It may be expected, there, that TFF will also accumulate calcite particles that may trap algae in calcite agglomerates and thus possibly damage algal cells and hinder algal inspection and counting by microscope. Calcite particles were there dissolved prior to concentration by lowering the pH with CO_2 . It was found that too low a pH level has a detrimental effect on the viability of certain algal species; a critical boundary was pH 5 below which *R. minuta* was damaged or even completely destroyed.

High pH values, on the other hand, had little effect on calcite dissolution. Microscopic inspection of the sample proved pH=6 to be optimal (rapid calcite dissolution, no visual cell damage).

Prior to pH adjustment, the raw water was filtered through a standard 35 μm microsieve fabric to eliminate zooplankton, other particles like algae larger than 35 μm , thus reducing the possibility of membrane fouling. The presence of these large algae in the concentrated water samples was not considered essential, because standard water treatment techniques eliminate these organisms very efficiently. Microstraining was followed by pH adjustment with CO_2 gas under continuous pH monitoring until $\text{pH } 6.0 \pm 0.1$. The water was then stirred for approximately 1 hour to promote calcite dissolution.

4.2.2. The tangential flow filtration (TFF) systems

Preliminary experiments were carried out employing two different systems based on TFF, namely one with flat and one with hollow fibre membranes. Preliminary experiments revealed that both TFF systems could efficiently concentrate algae without causing visible cell damage. However, the observation with the microscope demonstrated that the TFF system equipped with the hollow fibre membrane had the drawback that small pieces of membrane fibres were present in the concentrated water. There, the system equipped with plane membranes (Pellicon Cassette System, Millipore Corporation, Bedford, Mass., USA) was selected. This system incorporates a variable speed ($0.16\text{--}13.00 \text{ l min}^{-1}$) positive displacement pump and filter holder which accommodates two membrane cassette packs with a total surface area of 0.93 m^2 (Fig.4.1). Among the available microporous membranes (pore sizes of 0.1, 0.22 and $0.45 \mu\text{m}$), the membrane with $0.45 \mu\text{m}$ pores was selected to enable the concentration of micro-algae, to limit the accumulation of other unwanted water constituents, and to reduce membrane fouling. However, more recent investigations indicated that membranes with smaller pores show in general lower fouling tendency. Pressure of feed water and retentate was 0.8 to $1.2 \cdot 10^5 \text{ Pa}$ and 0.3 to $0.5 \cdot 10^5 \text{ Pa}$, respectively, and the filtrate flow rate was $3.0\text{--}3.5 \text{ l min}^{-1}$, corresponding to a filtrate flux of approximately $200 \text{ l/m}^2/\text{h}$. The actual degree of phytoplankton recovery was assessed for the volumetric concentration factors 5, 10, 20 and 40. The volumetric concentration factor (C) is defined as:

$$C = V_i/V_f$$

where:

V_i = initial volume of water in the process tank before concentration (l);

V_f = the final volume of water in the process tank after concentration (l).

An initial volume of pretreated raw water of 200 litres was used, samples of the retentate were taken when the defined volumetric concentration was attained.

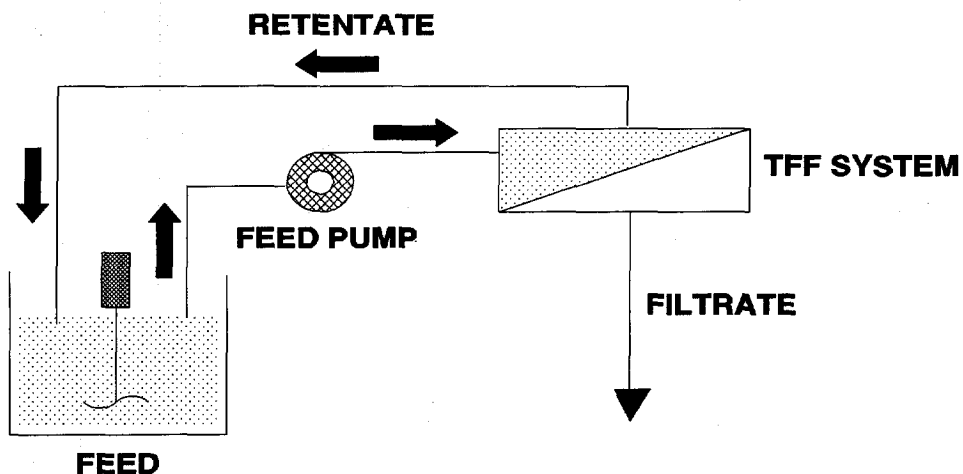


Fig.4.1.a. Process scheme of the TFF Pellicon cassette system.

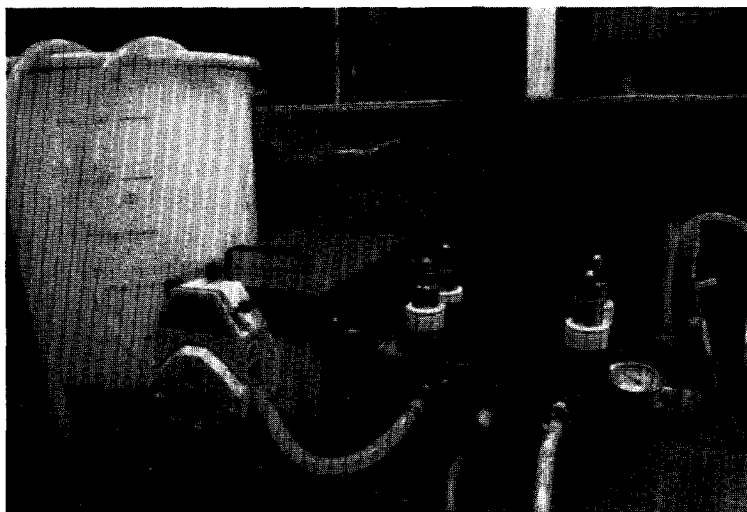


Fig. 4.1.b. Photo of the TFF Pellicon cassett system.

4.2.3. Sample analysis

Video system

Algal viability was assessed with the aid of a video camera attached to an inverted microscope which provided up to 600x magnification. The video system enabled reliable observation of motility.

Electrophoretic mobility

Electrophoretic mobility (EM) of algae and other particles was measured by using a zeta potential meter (Tom Lindstrom AB) under 90 volt potential difference, and equivalent cell length of 6.56 cm. An average of 10 measurements in each direction was taken.

Cultivation of algae

Pre-treated Biesbosch water and concentrated samples were cultured in order to qualitatively assess the viability of concentrated algal cells. Growth experiments consisted of inoculation of a 10 ml sample in 125 ml cultivation medium (Z-8, 25 percent of normal strength, according to Skulberg, 1964) and cultivation at $15 \pm 1^\circ\text{C}$ under continuous illumination and shaking. Algal biomass was measured as optical density at 750 nm.

Chlorophyll- α and concentration of different algal species

Algal recovery rates at different concentration factors were assessed by chlorophyll- α measurements, and by counting algae in raw water and concentrated samples.

Chlorophyll- α was extracted by ethanol and measured by spectrophotometric procedure according to the standard method NEN 6520 of the Dutch Standardization Institute (Nederlands Normalisatie Instituut 1981).

Algae were counted with inverted microscopy at a magnification of 600x. The algae counting procedure commonly used by Dutch water works was followed (minimum 50 fields or 400 counted units-cells per species per sample).

DOC and UV measurement

In order to quantify the extent of physical damage to algal cells (rupture of the cells), and to monitor possible concentration of dissolved organic matter, DOC and UV absorbance at 254 nm were measured. DOC concentrations were determined photometrically with the Auto-analyzer II, following the procedure NPR 6522 of the Dutch Standardization Institute (Nederlands Normalisatie Instituut 1986). UV absorbance at 254 nm was measured with the Perkin Elmer spectrophotometer (model 550 SE).

4.3. RESULTS AND DISCUSSION

Observation with the video system and inverted microscope

At all concentration factors ($C=5-40$) the phytoplankton in the concentrated water looked fresh and was without visible difference from organisms from natural non-concentrated water. The key properties of the algal species and cyanobacteria observed with microscope are listed in Table 4.1. All characteristics including active motility were preserved after TFF concentration. In addition, no damage to the Ciliata structure, their flagella or motility was observed. Interestingly, the TFF concentration procedure created the possibility to observe rare organisms that are difficult to detect in natural reservoir water, such as the protozoön

Amoebae found in the most concentrated sample ($C=40$). The concentration process did not break *Amoebae*'s delicate membrane, and the specimens retained their extraordinary locomotion.

Electrophoretic mobility

Negative surface charge of centric diatoms, as measured by electrophoretic mobility ($1.20 \pm 0.10 [\mu\text{m s}^{-1}/\text{V cm}^{-1}]$ at 90V,) was not influenced by the concentration procedure. Measurement of electrophoretic mobility of motile species (like *R. minuta*) appeared to be very difficult because active algal locomotion was stronger than electrokinetic attractive forces.

Table 4.1. Observed key characteristics of algal species and cyanobacteria before and after concentration procedure.

| Group/species | Observed characteristics |
|--|---|
| 1. Chlorophyta | |
| 1.1. <i>Scenedesmus</i> sp. | - spines on the outer cell - colonies formed by joined algal cells, stacked together by local production of mucilage |
| 1.2. <i>Pandorina</i> sp.; <i>Eudorina</i> sp. | - spherical colonies of algal cells - flagella and high motility - mucilage capsules - fresh green colour |
| 1.3. <i>Chlamydomonas</i> sp. | - two cell flagella; swimming in a typical helical path in forward direction |
| 2. Cryptophyta | |
| 2.1. <i>Rhodomonas minuta</i> | - two flagella which emerge from the side of the cell with one flagellum somewhat longer - high motility with extraordinary spiral movements |
| 2.2. <i>Cryptomonas</i> sp. | - flagella and high cell motility |
| 3. Bacillariophyta | |
| 3.1. <i>Navicula</i> sp.; <i>Nitzschia</i> sp. | - common irregular motility, including frequent stops and reversals |
| 3.2. Centric diatoms | - bristle-like appendages |
| 3.3. <i>Melosira</i> sp. | - filaments formed by joined algal cells |
| 4. Euglenophyta | |
| 4.1. <i>Euglena</i> sp. | - response to light stimuli - active swimming with body rotations |
| 5. Cyanobacteria | |
| 5.1. <i>Anabaena</i> sp. | - filaments |

Cultivation of alagae

Comparison of the growth curves for the algae in the raw and concentrated samples (at $C=20$) (Fig. 4.2) strongly suggests that algal viability was not affected by tangential flow filtration. The appearance of both growth curves was identical and similar to the shape of the growth curve for algal mono-cultures cultivated on Z-8 medium (Bolier and Donze, 1989).

Chlorophyll- α and concentration of different algal species

The chlorophyll- α in the concentrated sample (V_c) indicated significant accumulation of algal biomass. Unfortunately, the biomass recovery for the lowest examined concentration factor ($C=5$) could not be quantified, because of the very low chlorophyll- α concentration in the raw water ($<1 \mu\text{g l}^{-1}$). However, as compared to the chlorophyll- α level in the $C=5$ retentate, recovery ratios for $C=10$ and $C=20$ were found to be 83 and 75%, respectively (Fig.4.3a).

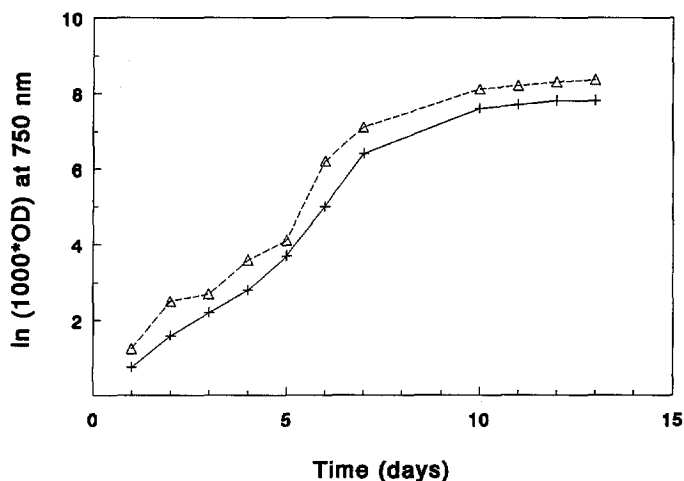


Fig.4.2. Growth curves for algae from natural reservoir water (+) and from a 20X concentrated sample (Δ). Algal biomass measured as optical density (OD) at 750 nm.

A second series of experiments was performed during the early spring period which is characterized by higher algal concentration in the raw water (chlorophyll- $\alpha \geq 2.5 \mu\text{g l}^{-1}$). The concentration procedure induced a limited loss of chlorophyll- α proportional to the concentration factor (Fig.4.3b). At $C=5$, 11% of the initially present algal biomass was not recovered in the retentate. An increase of C to 10 did not cause additional biomass loss. Further accumulation of algae in the retentate corresponding to $C=20$ and $C=40$ increased chlorophyll- α losses to 20 and 30%, respectively. An increase of concentration factor generally results in an increase of non-recovered algal biomass. However, it should be pointed out that complete recovery of algal biomass is not essential for the preparation of model waters.

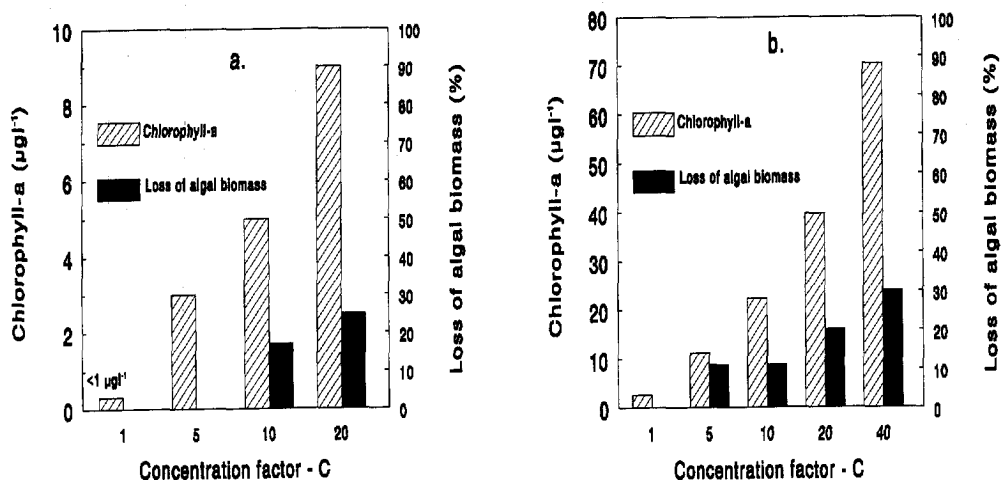


Fig.4.3. Recovery of algal biomass, expressed as chlorophyll- α concentration in the retentate and percentage of biomass lost at different concentration factors C; (a) reservoir water with a very low algal concentration (chlorophyll- $\alpha < 1 \mu\text{g l}^{-1}$), (b) reservoir water with a moderate algal concentration (chlorophyll- $\alpha \approx 2.5 \mu\text{g l}^{-1}$).

Algal cells recovery varies with species and the degree of volumetric concentration, however, the recovery rate was much less sensitive to the concentration factor (Fig.4.4, data presented are averages of duplicates). In general, recovery was found to be high (60-100%). None of the species observed in the raw water was lost during the concentration process. Some of them, like *R. minuta* and *Monoraphidium* sp., are known to be organisms which are very fragile and which are sensitive to both mechanical stress and chemical treatment. Both species recovered efficiently. Very low concentrations of *R. minuta* and *Monoraphidium* sp. in Biesbosch reservoir water (60 and 28 cells ml^{-1} respectively) were increased in the 40-times-concentrated retentate to more than 1500 and 1100 cells ml^{-1} , respectively. Algae in the concentrated sample were viable and undamaged. It is, however, obvious that the initial relative contribution of each individual species to the total algal biomass cannot be completely preserved over the concentration procedure. The concentration procedure would, to a certain extent, increase the relative contribution of the more robust species, that are less sensitive to mechanical stress during pumping and filtration. However, these alterations are of little relevance for water treatment research bearing in mind the pronounced weekly and sometimes even daily variations in the concentrations of particular algal species.

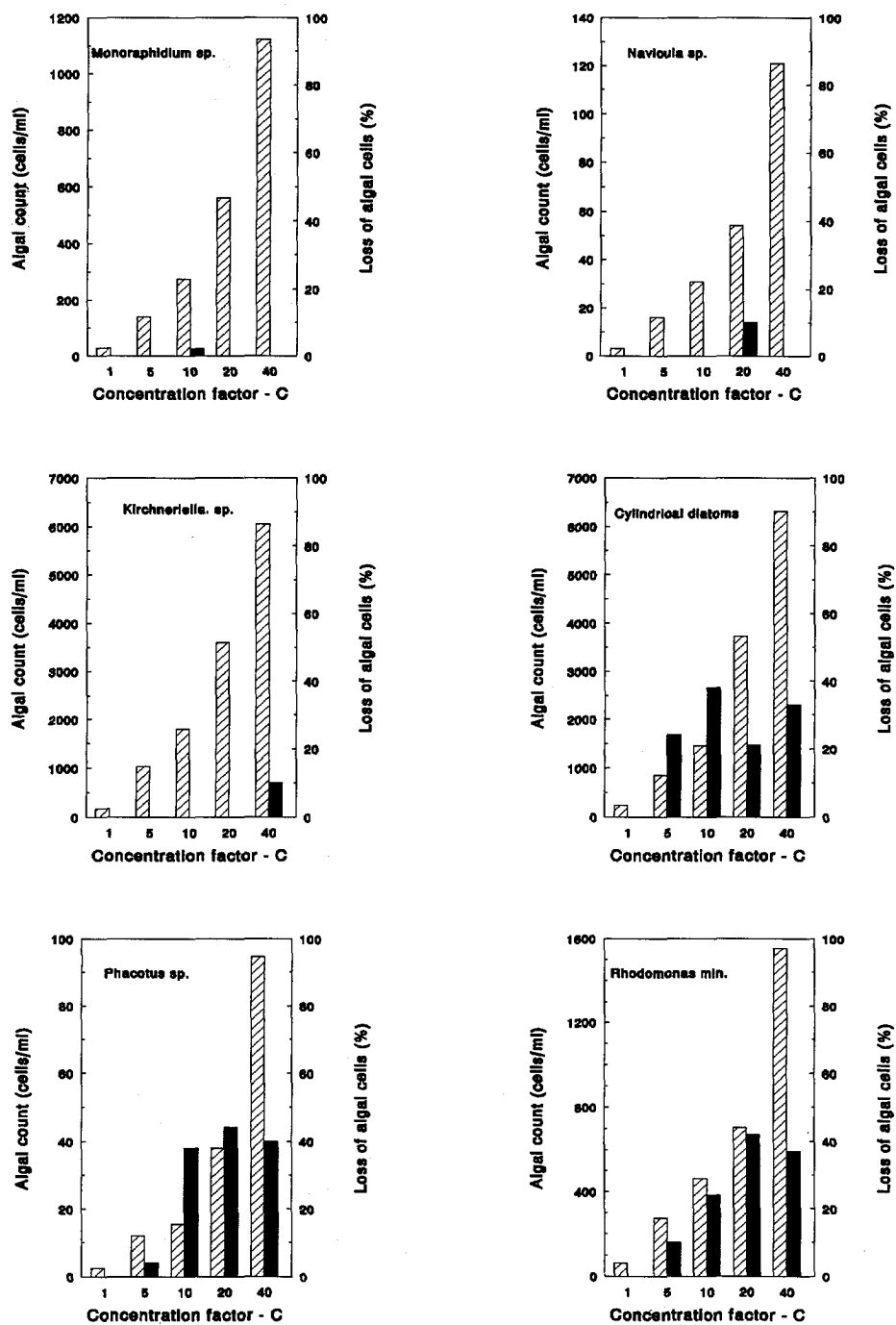


Fig.4.4. Algal concentration in the retentate (striped bars) and percentage of biomass loss (as loss of algal cells (black bars) for different algal species at different volumetric concentration factors C.

The size of some of the successfully concentrated fragile algal cells and the capability of TFF to process large volumes of water indicate that this technique can also be used for other purposes within the field of water research, such as the concentration of *Cryptosporidium* oocysts and *Giardia* cysts.

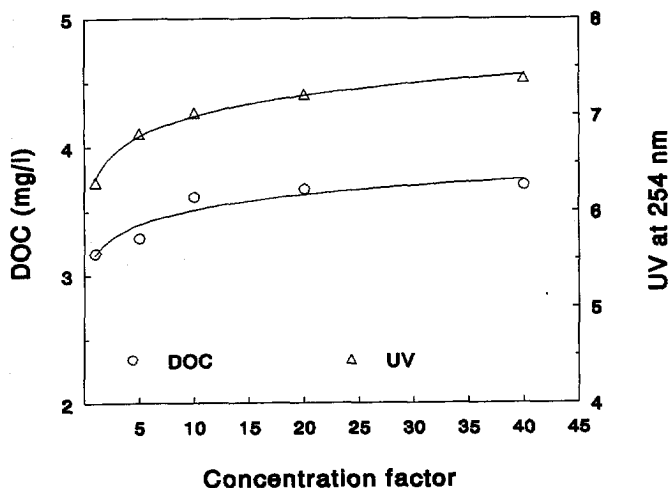


Fig.4.5. Effect of the concentration with TFF at different volumetric concentration factors *C* on the concentration of soluble organic matter (measured as DOC and UV absorbance at 254 nm).

DOC and UV

Dissolved organic carbon (DOC) increased proportionally to UV absorbance (Fig.4.5). The extent of DOC increase and the correlation between DOC and UV absorbance suggest that the increase in the concentration of dissolved natural organic matter should not be attributed to compounds liberated by ruptured algal cells. The increase in DOC can most probably be attributed to the accumulation of UV-sensitive organic compounds (aromatic in structure or with conjugated double bonds). However, the DOC increase is within the limits of the normal annual variation of DOC and UV absorbance in the reservoir water itself. The results presented in Fig. 4.5 are data from a single experiments in which algae present in the pilot plant filtrate were concentrated. The trend of slight DOC and UV increase with the concentration factor were consistently observed in all experiments conducted.

One of the possible drawbacks of the TFF system is inability to concentrate algae-derived EOM. It can be assumed that EOM attached to algal surface will be recovered with recovered algal cells. However, other part of EOM, dispersed and dissolved in the water will most likely be lost with the filtrate. Consequently, model water prepared with the TFF system is likely not suitable for water treatment studies design to assess the effect of algal EOM on treatment performance.

4.4. CONCLUSIONS

TFF can efficiently recover freshwater phytoplankton from large volumes of water. The concentration process causes limited (10-30%) loss of algal biomass, as measured by chlorophyll- α recovery. The recovery is negatively correlated with the concentration factor. Different recovery rates were observed for different algal species. The maximal concentration factor examined ($C=40$) resulted in 60 to 98% recovery of the examined algal species. The procedure did not affect the algal viability, growth capacity and other properties that influence algal fate in water treatment processes (e.g. motility, negative surface charge, cell architecture, etc). The concentrated retentate is representative of the original dilute algal population composition. The TFF device has been proven to be a useful laboratory tool for the preparation of model waters which can avoid some of the problems associated with the use of cultured algae.

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Chapter 5

PRE-TREATMENT IN RELATION TO DIRECT FILTRATION OF IMPOUNDED SURFACE WATER*

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ABSTRACT - Treatment such as microstraining, flocculation and oxidation may diminish plankton caused problems, such as algae passing through filters and rapid filter clogging. The importance of pre-treatment for direct filtration of Biesbosch reservoir water is preliminary investigated. Application of microstrainers as an initial treatment step may eliminate the problem of rapid filter clogging caused by zooplankton and filamentous algae. Pre-flocculation of Biesbosch reservoir water results in enhanced turbidity and particulate removal. The effect is strongly correlated to the flocculation Gt value. Optimum Gt is related to raw water quality and the type of flocculation reactor applied. Batch scale investigation with ozone, as well as batch and continuous pilot scale experiments with potassium permanganate, showed that these oxidants steps enhance algal agglomeration and removal during subsequent filtration. Negative side effects, such as break up of colonies, algal cell lysis, introduction of colour and elevated manganese levels were experienced at higher potassium permanganate dosages. A video system (video camera attached to an inverted microscope) was employed for in situ observation of phytoplankton behavioural response to different treatment conditions.

5.1. INTRODUCTION

Direct filtration is an attractive alternative to conventional chemical treatment for surface water of a high quality (low in turbidity, particle and algae concentration and dissolved organic matter). Lake and reservoir water is often suitable for this type of filtration. The production of drinking water from these sources is, however, often associated with problems related to phytoplankton: algal penetration through filters; interference with the processes of coagulation and flocculation; short filter runs accompanied by decrease in plant capacity and increased consumption of backwash water. Very efficient and economic algal removal is difficult to achieve. Algal penetration in treatment systems which include a chlorination step for disinfection, results in an increase in chlorine demand and formation of trihalomethanes (THMs) and other chlorinated compounds. In a recent review assessing the role of algae as trihalomethane precursors, Wardlaw *et al.* (1991) suggested that THM concentrations arising from natural algal blooms could theoretically exceed the maximum allowable concentrations in drinking water. In addition, algae present in drinking water may introduce natural toxins and have an adverse effect on drinking water taste and odour. Because of their products, algae may be considered easily assimilable organic compounds, and their presence in carbon filters and distribution mains may enhance biological after-growth. Part of the organic matter produced by algae is released from the cell as extra-cellular organic matter (EOM). It is known that if algal EOM is present above a certain concentration, it interferes with the processes of coagulation and flocculation (Bernhardt *et al.*, 1985; Haarhoff and Cleasby, 1989, chapter 2). The aforementioned problems may seriously affect direct filtration feasibility, reducing the treatment efficiency and diminishing its economical attractiveness. A possible remedy may be raw water pre-treatment, in combination with appropriate filter design.

The objective of this chapter is to preliminarily examine the importance of pre-treatment techniques such as microstraining, flocculation and oxidation for direct filtration of Biesbosch reservoir water by conducting batch and pilot plant experiments. In addition to recognised

pre-treatment techniques like microstraining, flocculation and pre-ozonation, the goal of the study is to deal with less conventional pre-treatment processes like pre-oxidation with potassium permanganate and hydrogen peroxide. Similarly, the goal is to review further the literature on different pre-treatment techniques appropriate for direct filtration of impounded surface water. Results from further, more detailed investigation on the effects of pre-treatment with ozone and potassium permanganate on direct filtration performance are given in chapters 7 and 8.

5.2. REVIEW OF LITERATURE ON PRE-TREATMENT OF IMPOUNDED SURFACE WATER

5.2.1. Micro-straining

Micro-strainers are hydraulically cleaned rotary drum strainers, covered with a finely woven metallic fabric, which has extremely small openings (Huisman, 1982). They were originally developed as pre-treatment for slow sand filters. Micro-strainers applied as an initial treatment step in direct filtration treatment schemes, may lower the load on subsequent filters, under certain conditions thus prolonging filter runs. Large algae (e.g. filamentous forms), zooplankton, sand, silt and other inorganic and organic particles exceeding the size of commonly applied microsieve fabric are efficiently removed. The build-up of deposits on the microstrainer fabric also allow the partial removal of particles finer than the nominal pore size. Microstrainer fabric with a nominal mesh size of 35 μm is most frequently used. Finer mesh sizes, although offering higher initial removal efficiency, are not commonly used, due to fast clogging.

Results from full scale application confirm that micro-strainers are generally very efficient at zooplankton elimination. Vrakking and Grimbergen (1982) reported that the microstrainers equipped with 35 μm fabric installed at the Pumping station Andijk, Provincial Waterworks North-Holland, achieved an overall zooplankton removal above 90% (Rotatoria sp. 91.5%, Nauplii 94%, Ciliata sp. 92%). A full scale study at the treatment plant Berenplaat (nowadays part of Waterworks Europoort), which uses Biesbosch reservoir water, found similar removal efficiencies: Rotatoria sp. 98%, Copepoda sp. 90% and Nauplii 97% (Koopman, 1991). The full scale microstrainers at this plant, also equipped with 35 μm fabric, had been freshly renewed and hence showed somewhat higher zooplankton removal rates. In contrast, results from full scale applications show in general lower overall phytoplankton removal efficiency as well as large fluctuations as a function of the predominant algal species (Evans, 1957; Hazen, 1953; Bellinger, 1968). They also demonstrate that large algae (e.g. *Cyclotella* sp., *Asterionala* sp.), filamentous forms (e.g. *Melosira* sp.) and the chain forming species (e.g. *Fragilaria* sp., *Tabellaria* sp.) are easily retained. Reported removal efficiencies range from 80 to 100%. However, retention of small algae such as *Stephanodiscus* sp., *Scenedesmus* sp., *Anabaena* sp., *Tribonema* sp. was found to be poor (14-36 %).

The main advantage of the micro-strainer is its simple, entirely mechanical action. The disadvantage is possible blocking of the mesh caused by certain filamentous species such as *Tribonema* sp. and deposition and growth of calcium carbonate crystals (Ives, 1957).

5.2.2. Pre-flocculation

A direct filtration treatment scheme with a separate flocculation unit is known as a flocc-filtration process in contrast to an in-line coagulation or contact coagulation. Studies on pre-flocculation have been, to date, inconclusive. Monsevizt *et al.*, (1978) found that Gt values in the order of 25,000 to 50,000 optimize performance of direct filtration plant treating high quality lake water. Filtration with pre-flocculation resulted in longer filter runs, reduction of required coagulant (alum) dosage, improved turbidity and plankton removal. Based on laboratory scale experiments, Treweek (1979) recommended a minimum flocculation Gt of 40,000 (flocculation time $t=7$ min at a velocity gradient $G=100\text{ s}^{-1}$). Edzwald *et al.* (1987) reported that effective direct filtration of river water occurred at Gt values from 25,000. They found that headloss was greater for in-line coagulation versus direct filtration with pre-flocculation. In addition, they pointed out that pre-flocculation should not have a significant effect on filter performance in the case of impounded waters, characterised by low turbidity and low to moderate TOC levels, due to slow flocculation kinetics. Bernhardt and Schell (1992) recently reported an optimum removal of turbidity with a laboratory "floc-filtration" test apparatus at G values around 40 s^{-1} , t values of 15-30 min and a Gt range of 30,000-60,000. The values are in reasonable agreement with results from the full-scale direct filtration phosphate elimination plant applying pre-flocculation (Wahnbach process), where the optimum flocculation conditions were found to be $G=30\text{--}60\text{ s}^{-1}$, flocculation time $t=5\text{--}20$ min and Gt range 15,000-40,000. In addition to the Camp number (Gt), they emphasise the importance of the particle concentration in raw water, in terms of floc volume fraction (C) - as proposed by Ives (1968) or floc volume fraction at the start of the flocculation (C_0) (Tambo, 1991). Consequently, instead of Camp number, the GtC or GtC_0 value is proposed as a more appropriate flocculation conditions indicator. In their laboratory experiments, an optimum Gt range of 30,000-60,000 corresponded to a GtC range of 60-120. The GtC or GtC_0 concept may particularly be suitable for comparing results from various studies, using diverse raw waters and applying different treatment conditions (coagulant type and dosage). The effect of pre-flocculation on direct filtration performance is a consequence of particle size distribution alteration via enhanced particle agglomeration. This has a pronounced effect on filter removal efficiency and headloss development in the filter bed. Fundamental studies (Yao, *et al.*, 1971; O'Melia, 1985) showed that the minimum filter removal efficiency occurs with particle diameters of 1 to 3 μm , and that head loss per unit mass of deposited particles in the filter bed is inversely proportional to particle size. Consequently, the need for pre-flocculation is closely correlated to raw water quality and in particular to particles' concentration and size distribution. In addition, the actual effect of a separate flocculation unit should be judged while bearing in mind the characteristics of applied filter media and

correlated mechanisms: particle flocculation in filter pores, and particle-filter grain interaction.

5.2.3. Pre-oxidation

Oxidants are mainly applied in water treatment for disinfection purposes. However, oxidants can interact with impurities in such a way that more efficient removal can be realized by subsequent additional treatment. Algal removal efficiency and overall filter performance may also be improved if an appropriate pre-oxidation step is provided before coagulation (Hodges *et al.*; 1979, Janssens *et al.*, 1987; Langlais *et al.*, 1991). In the past, chlorine was most frequently applied at the beginning of a treatment system, mainly to prevent microbiological growth in the plant. Such an application of chlorine usually offered the additional benefit of enhanced algal flocculation and subsequent removal. However, after the carcinogenic properties of some chlorination by-products (e.g. chloroform) were recognised the use of pre-chlorination became uncommon or even forbidden in some countries (e.g. Germany).

The use of chlorine dioxide as a pre-oxidant, although not producing chlorinated organics, results in the formation of noxious chlorite. This compound, similar to nitrite, produces methaemoglobin in the human body, which leads to "blue baby" disease in infants (Schalekamp, 1986). The World Health Organisation established a provisional guideline value for chlorite of 200 $\mu\text{g/l}$. Furthermore, use of chlorine dioxide as an pre-oxidant is also forbidden in some countries (e.g. Germany).

5.2.3.1. Ozone

As an alternative, ozone has been increasingly used as pre-oxidant. Numerous ozone-related beneficial effects have been reported in literature. These include: improved agglomeration and removal of algae, enhanced removal of other particles and turbidity, reduced required coagulant dosage, shortened filter ripening period, extended filter run length, improved removal of THMs precursors, probable improved removal of the basic and neutral fraction of natural organic matter, improved removal of taste, odour and colour, etc. It is known that pre-ozonation causes a shift in size distribution towards larger particles and the formation of colloidal particles from dissolved organic matter. This improves organic removal during subsequent treatment steps, reduces the coagulant dosage and extends the filter run length (Reckhow *et al.*, 1986; Singer, 1990). The mechanisms in which ozone acts as a coagulant aid are not yet known precisely. Several mechanisms have been proposed in the literature (Jekel 1983; Reckhow *et al.*, 1986; Sukenik *et al.* 1987; Singer, 1990) such as the reaction of ozone with the adsorbed organic coating on the particles surface, the destruction of the EOM present in the raw water and the alteration of the algal cell wall structure, the formation of biopolymers that can assist in the coagulation of particulate matter, the breakup of organic-metal complexes, the polymerization of organic matter, the increased association of metal coagulants with ozonated organic matter, the calcium complexation of ozonated organic matter, etc. Ozone applied as pre-oxidant also splits the algal EOM dissolved in the

raw water or adsorbed on other particles. In addition to the general enhancement of a coagulation process, there is clear evidence that pre-ozonation significantly improves algal agglomeration and removal (Ginocchio, 1981; Jodlowski, 1990). It should be pointed out that the use of ozone does not necessarily have a favourable impact on the agglomeration of all algal species and overall direct filtration performance. Edzwald (1992) reported that pre-ozonation at absorbed dosages of 1-3 mg/l enhanced the agglomeration of *Scenedesmus quadricauda* and *Cyclotella* sp., but not the agglomeration of *Chlorella vulgaris*. He correlated the efficiency of flocculation with the amount of EOM produced by algae. *Chlorella* produces a minor amount of EOM, while *Scenedesmus* and *Cyclotella* produce much more (10 and 36 times as much, respectively). Ozone easily oxidises algal EOM, shifting the molecular weight to lower weight fractions. On the other hand pre-ozonation may reduce the filterability of filamentous algae by breaking up the large filaments. Tobiason *et al.* (1992) found that pre-oxidation of high quality impounded water with ozone (0.5-1.5 mg/l) did not significantly enhance filter performance as assessed by filtered water turbidity and headloss development. Langlais *et al.* (1991) also reported that pre-ozonation failed to show a beneficial coagulating effects with particular raw waters. Coagulating effects of ozone are highly dependent on nature of the raw water (Reckhow *et al.*, 1993), and the optimal dosage of ozone depends also on raw water hardness and total organic carbon TOC (Chang and Singer, 1991).

In addition, Kruithof *et al.* (1993), Kruithof and Meijers (1993) recently showed that the ozonation of Biesbosch waters may lead to the formation of bromate at a level suspected to be hazardous to health. They found that use of ozone for disinfection positively correlates with bromate formation. However, Kruithof *et al.* (1995) reported that at low specific ozone dosages (below 0.3 mg O₃/mg DOC for pre-treated Biesbosch water), the concentration of bromate does not exceed the detection limit of 2 µg/l (experiments conducted in 1991/1992). Different values for maximum acceptable bromate level can be currently found in different guidelines and guideline proposals (the World Health Organisation Guidelines-25 µg/l, proposals for European Community Standards and USEPA Disinfection/Disinfection Byproduct Rule-10 µg/l, Proposal for Dutch Drinking Water Act 0.5 µg/l, and exceptionally 5 µg/l when ozone is used for disinfection purposes). Another negative consequence of pre-ozonation is the considerable increase of assimilable organic carbon - AOC (van der Kooij, 1991) in the oxidised water. However, the increase of AOC may be considered as beneficial effect when the objective of ozonation is to enhance biological activity of activated carbon filtration. A high AOC reduction in the subsequent filtration step was also reported (van der Kooij, 1991). An additional problem related to ozone application is its effect on the metal concentration of filtrate. Edwards and Benjamin (1992) reported that pre-ozonation can increase metal residuals in systems with Fe coagulants by stabilizing coagulant flocs. The problem is more pronounced at low coagulant to total organic carbon (TOC) ratios, at high ozone levels (above 0.3 mg O₃/mg TOC) and when the coagulant is an iron salt.

Though the observations from full scale plants applying ozone, as well as research findings are not consistent, Reckhow *et al.* (1986) outlined that there is a general consensus regarding

the following points:

- (a) low ozone dosages (< 3 mg/l; most often 0.5-1.5 mg/l) are most effective; higher dosages can lead to deterioration of the coagulation process;
- (b) it is important to add the coagulant at the point of ozonation or shortly afterwards, and
- (c) a certain critical concentration of organic matter must be present to observe the coagulation effect of ozone.

It can be summarised that pre-treatment with ozone can improve direct filtration performance in terms of effluent turbidity, filter run length and in particular algal removal efficiency. However, in view of possible side-effects, as well as relatively high investment and operational costs, the final conclusion regarding ozone application should be drawn only after detailed study, preferably including pilot plant experiments. The optimum ozone dosage will probably exhibit a seasonal pattern correlated with phytoplankton concentration as well as prevailing algal species.

5.2.3.2. Potassium permanganate

Another strong oxidant, which is nevertheless not frequently applied as a pre-treatment oxidant for direct filtration of impounded surface waters is potassium permanganate. Traditionally, potassium permanganate is used in water treatment for the removal of dissolved iron and manganese, and taste and odour control.

Application of potassium permanganate as an algicide for algal growth control has been studied and reported by several researchers (Kemp *et al.* 1966; Fitzgerald, 1964 and 1966). Bernhardt and Lusse (1989) reported that the inactivation of zooplankton by potassium permanganate resulted in significantly increased zooplankton removal efficiency in the flocculation filtration system. A few recent studies indicated that potassium permanganate, applied as a pre-oxidant, may behave as a coagulant aid. Jun Ma and Guibai Li (1992) found that the pre-treatment with potassium permanganate resulted in an enhanced coagulation-flocculation process, reducing the coagulant dosages and improving turbidity removal. Petruševski *et al.* (1992) reported that pre-oxidation with potassium permanganate clearly enhanced algal removal efficiency. The effect of potassium permanganate as a coagulant aid may be related to the insoluble manganese dioxide hydrates (for convenience further on notified as MnO_2), formed in the pH range used in water treatment. MnO_2 enhances the flocculation kinetics and acts as adsorbent as a consequence of its large surface area ($300 \text{ m}^2/\text{g}$, [Masschelein, 1989]). Drawbacks, related to the use of permanganate, frequently precluding its use in water treatment, are the violet colour lent to the water and the elevated residual manganese. So far there is no evidence that oxidation with potassium permanganate result in the formation of by-products hazardous to health.

5.3. METHODS AND MATERIALS

5.3.1. Raw water source

In the experiments raw water from the Biesbosch water storage reservoirs was used. These reservoirs provide raw water for the cities of Rotterdam and Dordrecht and a number of waterworks in the Dutch provinces of Zeeland and Brabant. The raw water for these reservoirs is abstracted from the polluted and eutrophic River Meuse. The Biesbosch reservoirs, three in series, act as fully mixed reactors and distinctly improve water quality. Water mixing by air injection at the bottom of deep reservoirs, combined with zooplankton grazing, keeps the biomass of phytoplankton at a low level. Although based on total P and N content (300 and 5000 mg/m³, respectively) a eutrophic state of the reservoirs might be expected, algal biomass expressed as chlorophyll- α corresponds more to mesotrophic or even oligotrophic conditions (Oskam and van Breemen 1992). Water from Petrusplaat, the last of the reservoirs, which is used in the experiments, is characterised by turbidity < 4 FTU (most frequently < 1 FTU), TOC levels 3.2-3.7 mg/l, high pH (9.0), bicarbonate ($[\text{HCO}_3^-] = 123$ mg/l) and salts concentrations ($[\text{Ca}^{2+}] = 50$ mg/l, $[\text{Cl}^-] = 55$ mg/l, $[\text{SO}_4^{2-}] = 65$ mg/l, $[\text{Na}^+] = 52$ mg/l). The average annual chlorophyll- α level is about 5 $\mu\text{g/l}$, although values as high as 50 $\mu\text{g/l}$ have been recorded during spring periods in the past years. The peaks during the spring algal blooms are however, less pronounced since 1990.

Algal population in Biesbosch water features seasonal and even monthly cycles of a limited number of dominant algal species. The early spring period is characterised by high concentrations of diatoms e.g. *Melosira* sp., *Navicula* sp., *Stephanodiscus hantzschii*, *Stephanodiscus astraea*, and *Cyclotella* sp. Late spring and early summer are characterised by the dominance of green algae (*Chlamydomonas* sp., *Pandorina* sp., μ -algae etc.), at levels considerably lower than concentrations recorded during early spring diatom blooms. During late summer and early autumn a second algal peak can be noticed, caused primarily by cyanobacteria (e. g. *Microcystis aeruginosa*). The winter period is characterised by very low algal concentrations and mixtures of different algal species and groups. Throughout the entire year motile flagellated algae of the group Cryptophyceae may be found in the raw Biesbosch water. Their biomass is substantially lower than that of the dominant species, although during short intervals this alga may dominate.

Initial particle (algal) concentration in the raw Biesbosch water during late winter was increased 5-10 times with the help of the tangential flow membrane filtration system (Millipore-Pellicon filter holder equipped with 0.45 μm pore size membranes), in order to obtain more pronounced responses to different treatment conditions (Petrusevski *et al.*, 1995, chapter 4). Concentrated Biesbosch water was used in a number of experiments with the modified jar test apparatus designed to investigate the effect of pre-treatment with potassium permanganate, hydrogen peroxide and ozone.

5.3.2. Experimental set-ups

The effect of microstrainers on algal removal was studied with a bench scale set-up furnished with standard 35 μm micro-fabric. A fixed volume of fresh Biesbosch raw water was regularly passed through a microstrainer fabric. Chlorophyll- α analyses before and after microstraining were done to evaluate the efficiency of microstrainers on phytoplankton removal

The experimental set-ups developed and used for direct filtration modelling are described in chapter 3. In this specific part of the study a modified jar test apparatus (MJTA), and a bench scale direct filtration pilot plant (BSDFPP) were used. MJTA was used in the experiments design to investigate effect of flocculation and pre-oxidation with potassium permanganate, hydrogen peroxide and ozone. BSDFPP was used in filter runs designed to test the effect of pre-treatment with potassium permanganate on direct filtration performance.

In the MJTA experiments examining the role of pre-flocculation, the procedure described in chapter 3 was slightly altered by introducing a flocculation step at different Gt combinations after coagulation (before filtration).

MJTA experiments with potassium permanganate involved addition of different permanganate dosages (1.0-5.0 mg KMnO_4/l), 30 minutes contact time, followed by MJTA procedure as described in chapter 3.

A bench scale ozone dispersing/contact system (Kiwa N.V. Research and Consultancy) was utilized for preliminary experiments design to study effect of pre-ozonation on direct filtration performance. Pre-ozonated raw Biesbosch water (ozone dosages tested ranged from 1.3 to 2.5 mg O_3 consumed /l*) was subsequently exposed to MJTA procedure as described in chapter 3.

MJTA experiments with hydrogen peroxide comprised the addition of hydrogen peroxide (H_2O_2 dosages tested ranged from 10 to 80 mg/l), for 8 minutes contact time followed by the MJTA procedure as described in chapter 3.

The results from the MJTA experiments reported here are results from a single experimental series. MJTA experiments were repeated under identical treatment conditions. The trends reported here were found to be reproducible.

The pilot plant experiments with potassium permanganate involved the operation of three parallel treatment lines (Fig.5.1). Permanganate dosages applied ranged from 0.5 to 2.0

* In this thesis the ozone dosage expressed as mg O_3 consumed/l means difference between the concentration of ozone introduced to a reactor and the concentration of ozone that leaves the reactor with the off gas; residual ozone concentration in water was not measured.

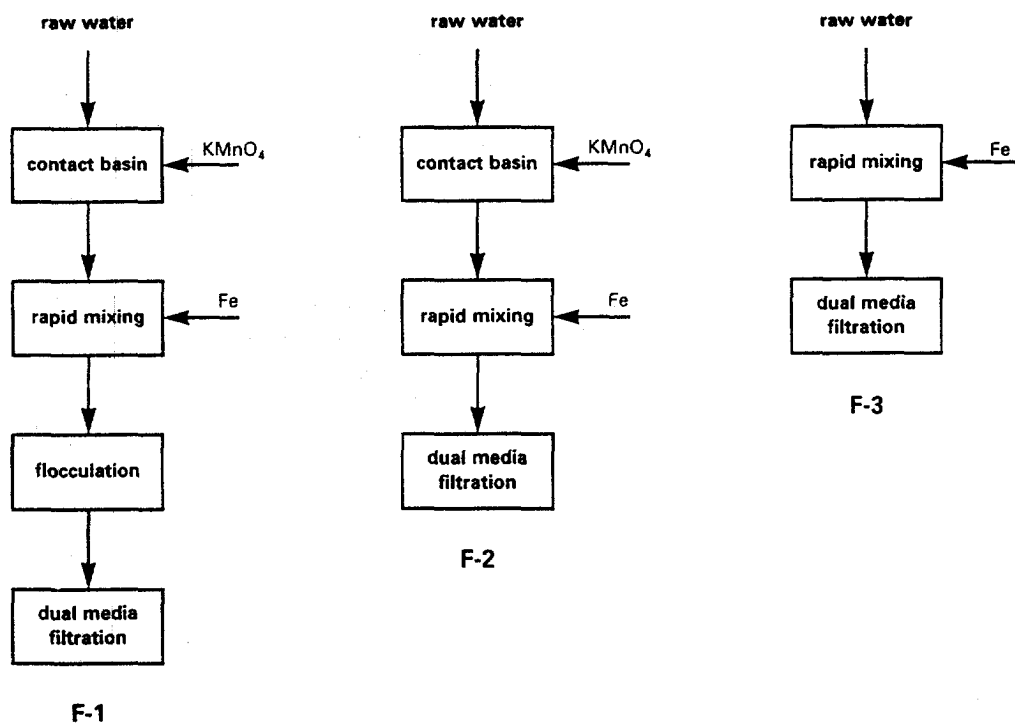


Fig.5.1. Treatment alternatives examined with BSDFPP.

mg KMnO_4/l . Addition of oxidant was followed by a contact basin, allowing 25 minutes nominal hydraulic residence time. A static mixer with high energy input ($G=1400 \text{ s}^{-1}$) was used for rapid mixing of coagulant (ferric sulfate, dosage of 1 mg Fe(III)/l) and raw water. Filters were operated at a constant filtration rate of $2.8 \cdot 10^{-3} \text{ m/s}$. The results from pilot plant experiments with BSDFPP are results from single filter run series. Filter runs were repeated under similar treatment conditions (the permanganate dosage was the only variable, the range tested 0.5 to 2.0 mg/l) and observed effect of permanganate on direct filtration removal efficiency was reproducible.

A granular media flocculator was used to study the effects of pre-flocculation in combination with pre-oxidation with potassium permanganate. The unit, a plexiglass column 100 mm in diameter, 3.0 m high, was packed with gravel (commercial fraction 2.2-3.3 mm), and operated at the rate of $5.6 \cdot 10^{-3} \text{ m/s}$, thus allowing a flocculation time of 2.5 minutes at $G=140 \text{ s}^{-1}$. The coagulation (flocculation) step was followed by filtration through BSDFPP provided with anthracite-sand bed at a filtration rate of $2.8 \cdot 10^{-3} \text{ m/s}$.

Ferric sulphate at a dosage of 1 mg Fe(III)/l , a value selected after preliminary optimisation experiments, was used as coagulant, unless otherwise mentioned. The potassium permanganate stock solution was prepared by dissolving 3.4 grams of analytical grade

KMnO₄ in 1 litre of deionised water. The working hydrogen peroxide solution (6 gr/l) was prepared by dilution of a 30% commercial H₂O₂ solution (Merck) with deionised water.

5.3.3. Water quality analysis

Particle concentration and size distribution were determined by an HIAC particle counter (model PC-320). An inverted microscope, providing up to 600X magnification was used for plankton counting. The algae enumeration procedure commonly followed by Dutch water works was followed (minimum 50 fields or 400 counted units-cells per sample per species). Turbidity was measured by a turbidity meter (Model Sigrist lab 65). DOC was determined photometrically by an Auto-analyzer II. A Perkin-Elmer 550 spectrophotometer was used for measurement of ultraviolet light absorbency at 254 nm wavelength.

In chapter 3 description is given of the video system used for *in-situ* observation of the effect of pre-treatment with potassium permanganate on algae.

5.4. RESULTS AND DISCUSSION

5.4.1. Microstraining of phyto- and zooplankton

Results obtained with a bench scale microstrainer with standard 35 μ m microsieve fabric, in the period September 1991 / April 1992 are shown in Fig.5.2. Typically, comparison of chlorophyll- α level before and after microstraining shows that algal removal efficiency was low. The highest removal rate achieved in the experiments was 50%. Poor algal removal efficiency may be correlated with the size of the dominant algae present in Biesbosch water during the period under consideration. The size of prevailing species such as *S. hantzschii*, *S. astraea*, *R. minuta*, *Chlamydomonas*, is far below the pore size of the microsieve fabric used. Somewhat higher algal elimination, found in week 43, 1991 and week 13, 1992 may be related to the presence of algal species *Pandorina* sp. and *Melosira* sp.. High elimination for these species is a consequence of their size or form (long filaments as in the case of *Melosira* sp., and colonies with lengthy flagella in the case of *Pandorina* sp.).

In addition to algae removal, microstrainers are intended to eliminate zooplankton. The importance of zooplankton for direct filtration performance had been clearly demonstrated during short intervals in spring 1992, when surface clogging of the mobile direct filtration pilot plant was experienced. Relatively short periods (a few weeks) with high concentration of zooplankton (*Daphnia* sp.) commonly follow early spring algae bloom (Fig 5.3). Fig.5.4 shows pressure distribution diagrams in anthracite-sand filter beds obtained in two filter runs with MDFPP. Both filter runs were performed under identical treatment conditions (filtration rate $2.8 \cdot 10^{-3}$ m/s, coagulant dosage 1.0 mg Fe[III]/l) during the period of early spring algae bloom (Fig.5.4.a) and subsequent period of very high zooplankton concentration

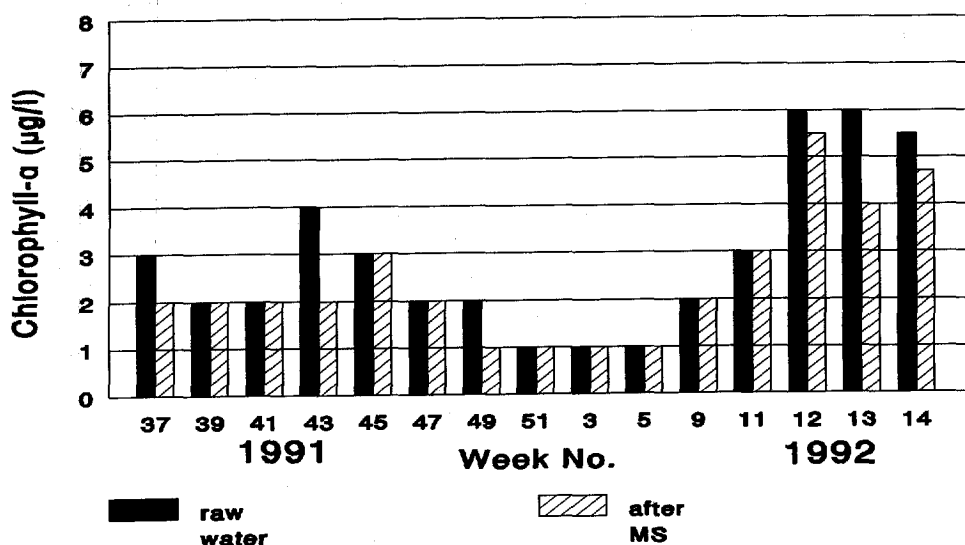


Fig. 5.2. Phytoplankton concentration measured as chlorophyll- α in raw water and after micro-straining (MS) through the bench scale micro strainer with 35 μ m pore size fabric.

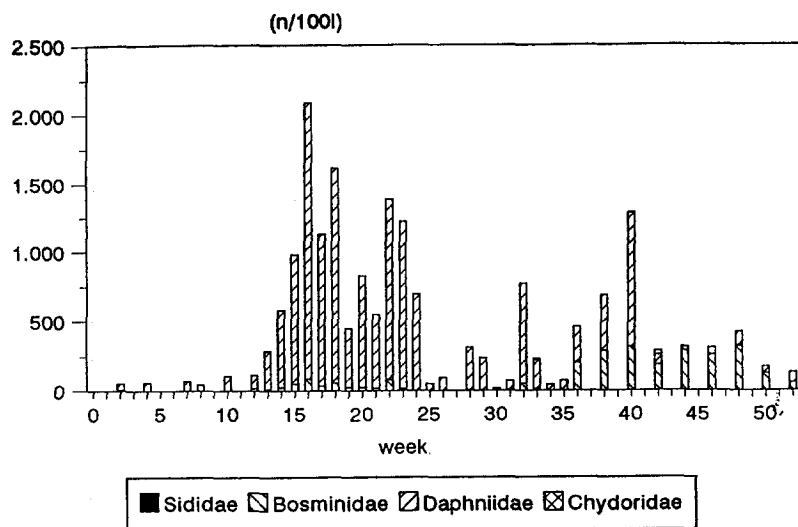


Fig. 5.3. 1992 yearly distribution pattern for Cladocera in Petrusplaat, the last in the series of Biesbosch water storage reservoirs (Ketelaars, unpublished data).

(Fig. 5.4.b). Filters were not preceded by microstrainers. Filter runs usually more than 50 hours long (Fig. 5.4.a.) were reduced during the period with high zooplankton concentration to 35 hours. In addition, the shape of the pressure distribution diagrams shows that a high

concentration of zooplankton (mainly *Daphnia* sp.) resulted in cake filtration (Fig.5.4.b) in contrast to deep-bed filtration commonly achieved during algae blooms. It may be assumed that if microstrainers had been applied the problem associated with the high zooplankton concentration would have been avoided. Previously described experience with zooplankton microstraining at Berenplaat supports this hypothesis.

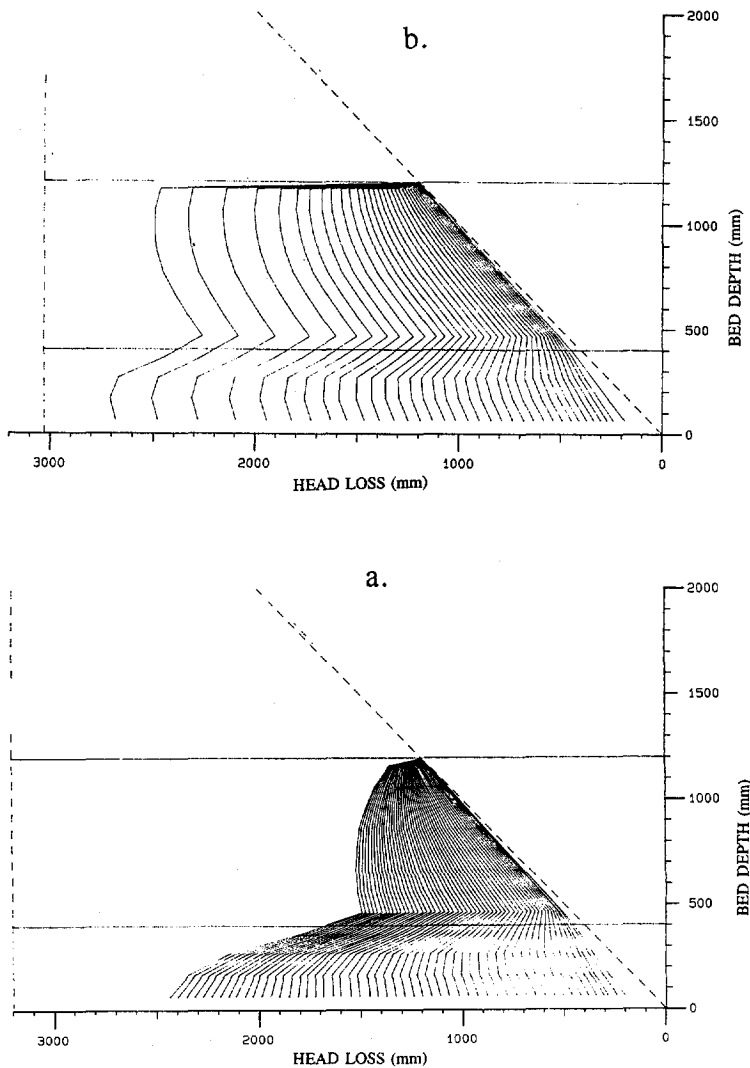


Fig.5.4. Pressure distribution diagrams in MDFPP anthracite-sand filter bed as a function of filter bed depth and filter run time, during (a) early spring algae bloom and (b) period with high zooplankton (*Daphnia* sp.) concentration; treatment conditions: filtration rate $2.8 \cdot 10^{-3}$ m/s, coagulant dosage: 1.0 mg Fe(III)/l.

The high zooplankton concentration during short but numerous periods throughout the year (appendix 5.1.), together with the historical data on water quality (spring blooms of filamentous species e.g. *Melosira* sp. experienced in previous years) indicate that the application of microstrainers as an initial treatment step can be useful in substantially diminishing problems of fast surface filter clogging caused by high concentrations of large or filamentous algae and zooplankton.

5.4.2. Pre-flocculation

The effect of pre-flocculation for direct filtration of Biesbosch water has been preliminary investigated with the MJTA. In these experiments natural Biesbosch water (turbidity 0.6 FTU, particle count 1500 part/ml) was used. Figures 5.5 and 5.6 show the impact of flocculation time - t and the flocculation velocity gradient - G on treatment efficiency in terms of filtrate turbidity, residual coagulant concentration and particle count.

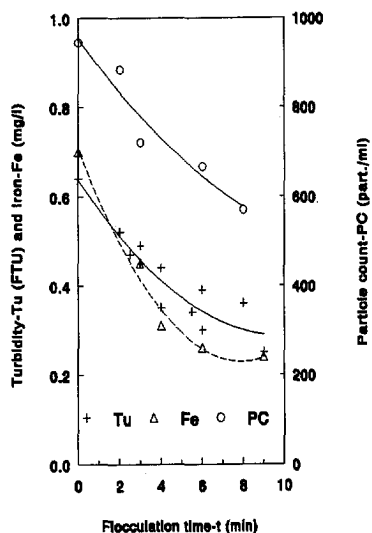


Fig.5.5. MJTA filtrate quality as a function of flocculation time t ; coagulant ferric sulfate: 1.0 mg Fe(III)/l; flocculation $G=100\text{s}^{-1}$; filtration rate $1.8 \cdot 10^{-3}$ m/s.

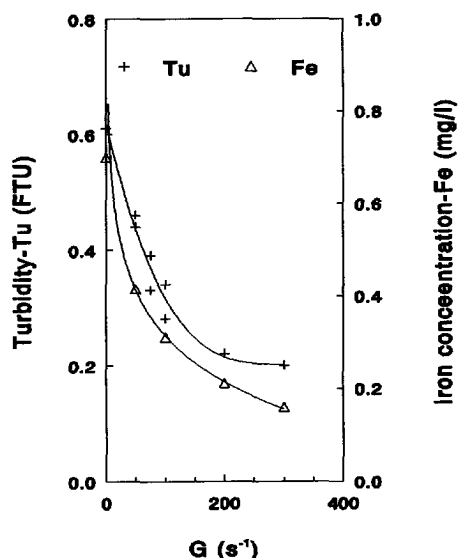


Fig.5.6. MJTA filtrate quality as a function of flocculation G ; coagulant ferric sulfate: 1.0 mg Fe(III)/l; flocculation time $t=360$ s; filtration rate $1.8 \cdot 10^{-3}$ m/s.

An optimum filtrate turbidity of about 0.20 FTU is achieved; In view of a desired higher filtrate quality it should be noted that the obtained values are necessarily sub-optimal as a consequence of constraints related to the MJTA (shallow, and clean filter bed). These values should be considered only as an indicator of direct filtration performance during initial filter run period. Both process variables show a strong influence on filtrate quality. At constant

$G=100\text{ s}^{-1}$, t of about 6 to 8 minutes is required for the formation of filterable flocs. From the graphs, it can be seen that filtrate turbidity improved significantly up to a flocculation time of 6 minutes. Residual iron concentration and particle count show a parallel behaviour, which can be explained by the adsorption of added iron in the form of hydrolysis products on colloidal and suspended particles. Similar results were found in the experiments where the influence of G was examined at fixed flocculation time $t=6\text{ min}$ (Fig. 5.6). Increase of G -value up to 200 s^{-1} resulted in a distinct reduction of filtrate turbidity and residual iron.

A further increase of G -value to 300 s^{-1} reduced residual iron, but resulted in only slightly improved turbidity. G values above 300 s^{-1} , tested in another set of MJTA experiments (Fig. 5.7.) induced deterioration of filtrate turbidity. A likely explanation for this can be that an increase of velocity gradient above an optimum value promotes floc breakup or the formation of less optimally sized flocs. The results of the flocculation experiments are presented in a condensed form in Figure 5.7. From the graph it can be seen that significant improvement of filtrate turbidity is obtained up to Gt -values of about 75,000. Further increase does not seem to be justified. At much higher Gt -levels (above 150,000), deterioration of filtrate turbidity is noticed, likely as a consequence of high velocity gradients and associated floc breakup. The optimum Gt range found in our experiments is considerably higher than the values reported by other researchers, as a consequence of very low initial particle concentration in our case (high quality raw water and low coagulant dosage). It may be estimated that in our experiments a Gt of 75,000 corresponds to much lower $GtC \approx 30$, in contrast to an optimum Gt range of 30,000-60,000 found by Bernhardt and Schell (1992) that corresponds to much higher $GtC=60-120$, due to higher coagulant dosage applied and higher particle concentration in raw water.

The MJTA experiments conducted, indicated the advantageous effect of pre-flocculation on turbidity, particle and iron removal in direct filtration of Biesbosch reservoir water. However, before drawing general conclusions regarding the effect of a separate flocculation unit on direct filtration performance, the limitations of the set-up used should be taken into account. These limitations, namely that the filter beds are shallow, single-layer, unripened, and consequently have very limited ability to simulate flocculation in filter pores, may be of particular relevance for flocculation studies. It may be assumed that the agglomeration that almost exclusively occurs during flocculation stage in the MJTA experiments, in reality partly also occurs during filtration stage, in filter pores of multi layer filter beds. As a consequence, the beneficial flocculation effect observed in MJTA experiments will probably be less pronounced in pilot plant experiments with filters of full bed depth. Consequently, further detailed pilot plant experiments are required to verify results obtained in the MJTA experiments. Nevertheless, the results obtained with MJTA once again demonstrated the importance of particle agglomeration for direct filtration efficiency.

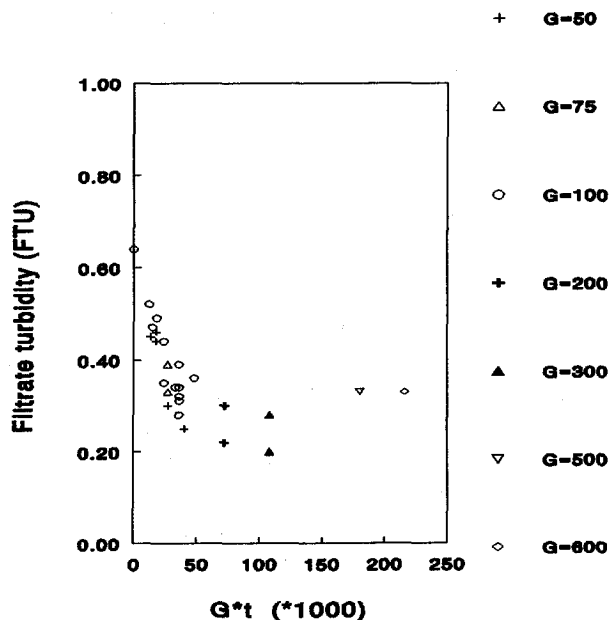


Fig.5.7. MJTA filtrate turbidity as a function of flocculation Gt ; coagulant: ferric sulfate, dose 1.0 mg Fe(III)/l ; filtration rate $1.8 \cdot 10^{-3} \text{ m/s}$.

5.4.3. Pre-oxidation

In order to preliminary examine the influence of oxidants on efficiency of direct filtration applied for Biesbosch water treatment, introductory experiments with ozone, potassium permanganate and hydrogen peroxide were performed (the pre-chlorination option was discarded to avoid THM formation). The results show the general improvement of treatment efficiency with the application of ozone and potassium permanganate. This effect could not be observed with hydrogen peroxide, however. In addition, application of high H_2O_2 dosages may be problematic, because H_2O_2 is a probable mutagen and, consequently the residuals should be low. The USEPA proposed standard for residual H_2O_2 to be $180 \mu\text{g/l}$ (Kruithof, personal communication).

5.4.3.1. Preliminary assesment of pre-ozonation

The ozone dosages tested were 1.3 , 1.8 and $2.5 \text{ mg O}_3 \text{ consumed/l}$, with the corresponding specific dosages 0.31 , 0.43 and $0.66 \text{ mg O}_3/\text{mg DOC}$. Observation with inverted microscope and the video system showed that such dosages have minimal effect on algal cell lysis and release of algal intracellular organic matter. Pre-ozonated samples were exposed to MJTA to investigate the effect of pre-ozonation on direct filtration performance. Pre-ozonation at all dosages improved turbidity removal in subsequent coagulation and filtration steps (Figs. 5.8 and 5.9).

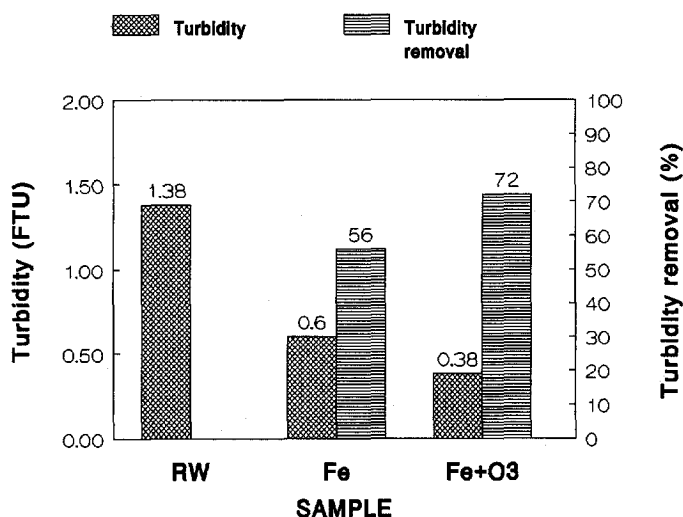


Fig.5.8. Turbidity removal with MJTA; coagulant ferric chloride, dosage 1.0 mg Fe(III)/l; RW-raw water, Fe-sample without O₃ pre-treatment, Fe+O₃ sample pre-treated with 1.0 mg O₃/l.

The observation that pre-ozonation significantly improves turbidity removal could not be documented by algal count, because practically all algae found in the pre-ozonated filtrate were entrapped in flocs making proper algal enumeration impossible. In contrast to oxidised samples algae found in non-oxidised samples appeared to be in the individual form. The modified jar test, featuring only short, clean beds, does not guarantee complete flocs removal. Aggregates of the kind found in the filtrate ($> 20\text{--}30\text{ }\mu\text{m}$) would likely be retained in a ripened filter of normal depth. This shows that for the algal population under consideration, pre-ozonation promotes efficient agglomeration and hence likely improves filtration efficiency. It is interesting to note that pre-treatment with ozone itself resulted in about 50% reduction of raw water turbidity and observable water discoloration. A relation between specific ozone dosage (mg O₃/mg DOC) and treatment efficiency was observed (Fig. 5.8). The optimum turbidity removal was observed for a specific ozone dosage of approx. 0.4 mg O₃/mg DOC confirming values derived from full scale plants that successfully apply ozone as a pre-oxidant (Chang and Singer 1988).

In addition to the reported mechanisms of ozone acting as an algal agglomeration promoter (reaction with the adsorbed organic coating on the algal surface [Jekel, 1983; Singer, 1990]), destruction of algal EOM present in the raw water and attack on the algal cell wall structure [Sukenic *et al.*, 1987], formation of biopolymers that can assist in coagulation of particulate matter [Singer, 1990; Sukenic, 1987]) it observation with the video system demonstrated that

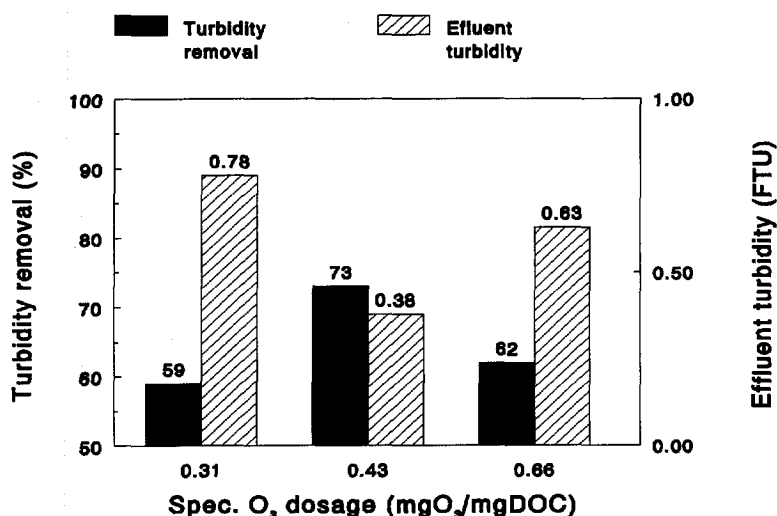


Fig.5.9. Effect of specific O₃ dosage on turbidity removal in MJTA experiments; coagulant ferric chloride, dosage 1.0 mg Fe(III)/l.

immobilization of motile algal species may also play a critical role (see the attached video tape).

Experiments showed that the use of ozone as pre-oxidant to increase particulate and algal removal efficiency seems plausible. More detailed research on the effect of ozone on Biesbosch water, covering different algal species and concentrations, diverse operating conditions is presented in chapter 7.

5.4.3.2. Preliminary assessment of pre-oxidation with potassium permanganate

As an initial research stage, the effect of potassium permanganate was examined with the MJTA. The effect of pre-oxidation at different potassium permanganate dosages on turbidity, particle and algal removal are shown in Figures 5.10 and 5.11. The results indicate a general rise in turbidity as a consequence of permanganate treatment. On the other hand, there is a distinct decrease in algal concentration and the particle count (size range 2.7 - 100 μm) in the filtrate. Examination of MJTA filtrate under microscope demonstrated that the rise in turbidity could be related to brown MnO₂ precipitate. With an increase of permanganate dosage, an increase in the concentration of MnO₂ precipitates in the MJTA effluent could be observed. This was not reflected by the particle number, since the manganous oxide hydrates were present in the form of very small particles of a size less than 2.7 μm , being the

minimum size that can be detected by the Hiac particle counter. The increase in particle count at the higher oxidant dosage of 5 mg/l (Fig.5.10) could be explained by an increase in the number of MnO_2 particles which enhanced flocculation and/or crystallization kinetics to the extent that the particles within the detection zone of the HIAC counter increased in number. However, bearing in mind that the MJTA only features a short and clean filter bed it was believed that MnO_2 aggregates as found in its effluent would be more efficiently retained in a ripened filter of normal depth, thus eliminating this problem of elevated turbidity. Results given in Fig.5.11. reveal the beneficial effect of potassium permanganate on algae removal. The beneficial effect of permanganate was more pronounced on the removal of *R. minuta*, a highly motile alga in comparison with nonmotile centric diatoms. Without permanganate treatment practically no removal of this alga could be achieved. In contrast, pre-treatment with potassium permanganate (>2 mg/l) resulted in complete elimination of *R. minuta*. Observation with the video system demonstrated that permanganate pre-treatment results in immobilization of motile algae.

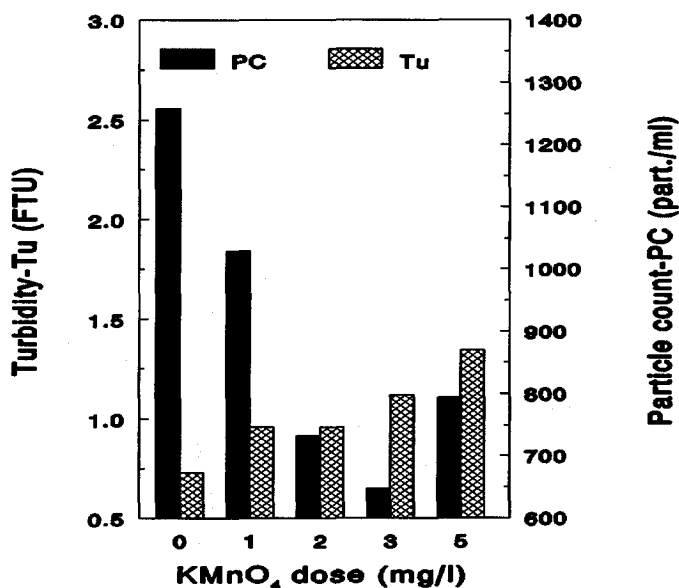


Fig.5.10. Effect of KMnO_4 dosage on MJTA filtrate quality; coagulant: ferric sulfate, dose 1.0 mg Fe(III)/l , filtration rate 1.8×10^{-3} m/s.

Larger-scale, confirmation experiments were carried out with the BSDFPF to verify results obtained in a batch test with MJTA, and to examine whether the MnO_2 precipitates could be more efficiently removed. A few typical results obtained in the filter runs with the BSDFPF are given in Figs. 5.12 to 5.17.

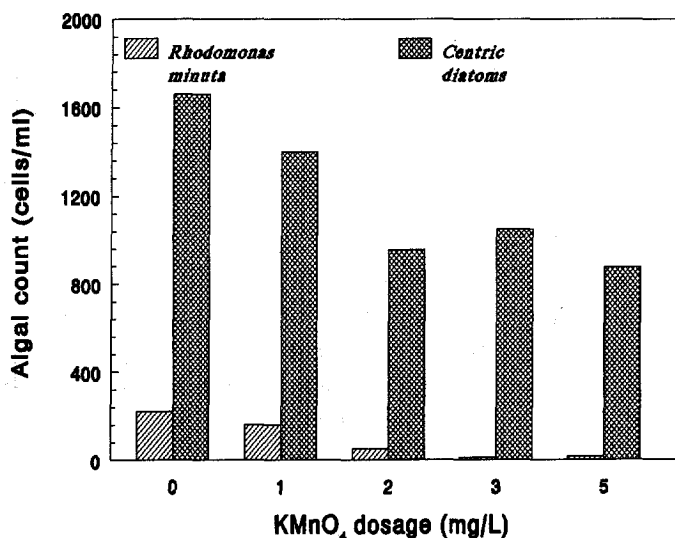


Fig.5.11. Effect of KMnO₄ on algae removal; coagulant: 1.0 mg Fe(III)/l; filtration rate $1.8 \cdot 10^{-3}$ m/s; MJTA experiments with concentrated Biesbosch water: 300 *R.minuta*/ml, 2500 centric diatoms/ml.

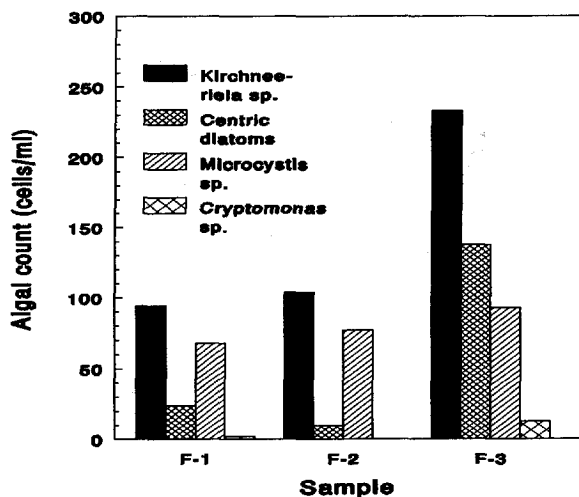


Fig.5.12. Effect of pre-treatment with 2 mg KMnO₄/l on algae removal with BSDFPF; coagulant ferric sulfate, dosage 1.0 mg Fe(III)/l; filtration rate $2.8 \cdot 10^{-3}$ m/s; F-1, F-2 and F-3 refers to treatment lines defined in Fig.5.1.

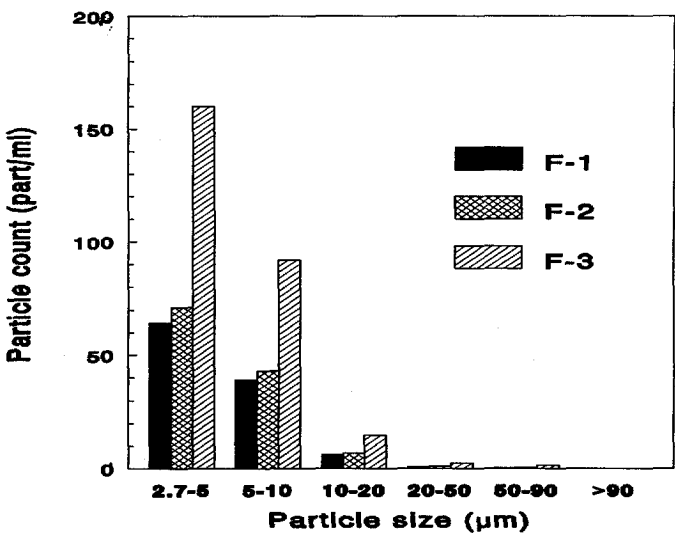


Fig.5.13. Effect of pre-treatment with 1.0 mg/l KMnO_4 /l on particle count and particle size distribution of BSDFPF filtrate; coagulant: ferric sulfate, dosage 1.0 mg Fe(III) /l; filtration rate 2.8×10^{-3} m/s; F-1, F-2 and F-3 refers to treatment lines defined in Fig.5.1.

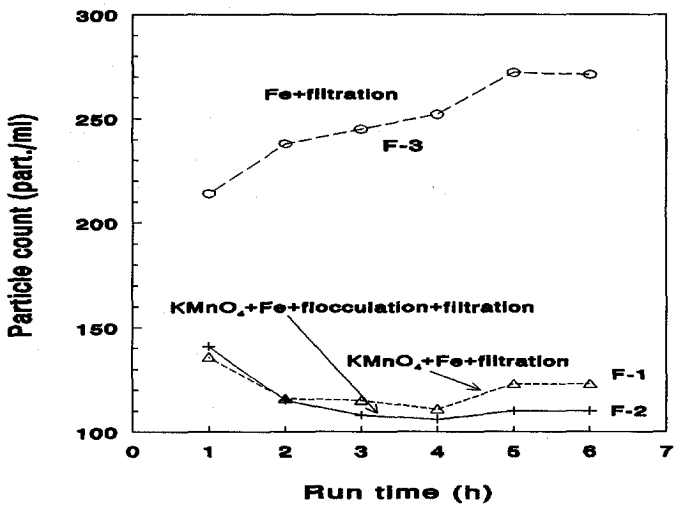


Fig.5.14. Effect of pre-treatment with 1.0 mg KMnO_4 /l on particle concentration in BSDFPF filtrate; coagulant: ferric sulfate dosage 1.0 mg Fe(III) /l; filtration rate 2.8×10^{-3} m/s; F-1, F-2 and F-3 refers to treatment lines defined in Fig.5.1.

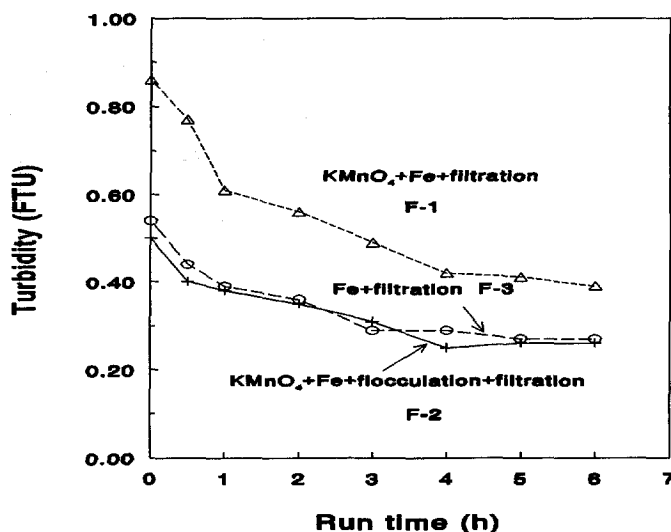


Fig.5.15. Effect of pre-treatment with 0.5 mg KMnO_4/l and flocculation on BSDFPP filtrate turbidity; coagulant: ferric sulfate, dosage 1.0 mg $\text{Fe(III)}/\text{l}$; filtration rate 2.8×10^{-3} m/s; F-1, F-2 and F-3 refers to treatment lines defined in Fig.5.1.

The results obtained confirmed the beneficial effects of potassium permanganate on particle and algae removal observed earlier in the experiments with the MJTA. In addition, the observation that permanganate treatment results in elevated filtrate turbidity was also confirmed in filter runs with BSDFPP. Similar trends observed in both experimental set-ups, namely improved particle and algae removal and the adverse effect on filtrate turbidity as a consequence of permanganate pre-treatment, confirmed that MJTA can provide a reliable indication of direct filtration response to oxidative pre-treatment. The results obtained with BSDFPP can be summarised as follows:

- pre-oxidation with potassium permanganate at all dosages tested (0.5-2.0 mg KMnO_4/l) improved algal and particle removal; pre-oxidation typically halved particle concentration in the filtrate; these findings were confirmed by algal enumeration as well as HIAC particle count (Fig.5.12-5.14);
- the filtrate turbidity levels (Fig.5.15) were higher for pre-oxidised samples (treatment scheme F-2); the difference is more pronounced at the beginning of the filter run, and diminishes with filter bed ripening; increased residual Mn concentration (Fig.5.16) together with the reduced concentration of particles $> 2.7 \mu\text{m}$ (Figs.5.13 and 5.14) suggest that the elevated turbidity is probably caused by MnO_2 precipitates, mainly in a size range 0.45- $2.7 \mu\text{m}$; pre-flocculation (treatment scheme F-1), showed beneficial impacts on turbidity removal, by reducing or eliminating the increased turbidity (Fig.5.15);

- (c) total manganese concentration increased as a consequence of pre-oxidation. A strong positive correlation with potassium permanganate dosage emerged (Fig.5.16). Potassium permanganate dosages of 1 and 2 mg/l elevated manganese level in the filtrate significantly above the maximum admissible concentration (according to the European drinking water directive 50 $\mu\text{g/l}$); oxidation with 0.5 mg/l resulted in filtrate manganese below 50 $\mu\text{g/l}$, however, the observed levels were still unacceptably high from an operational view point. Analysis revealed that almost all the manganese present in the filtrate was retained on the 0.45 μm membrane suggesting that manganese was present in the form of MnO_2 precipitates;
- (d) a light violet colour in the filter effluent was observed only at high potassium permanganate dosages (>2mg/l);
- (e) oxidation by potassium permanganate resulted in only minor improvement of removal of dissolved organic matter, as measured by DOC and UV at 254nm (Fig.5.17);

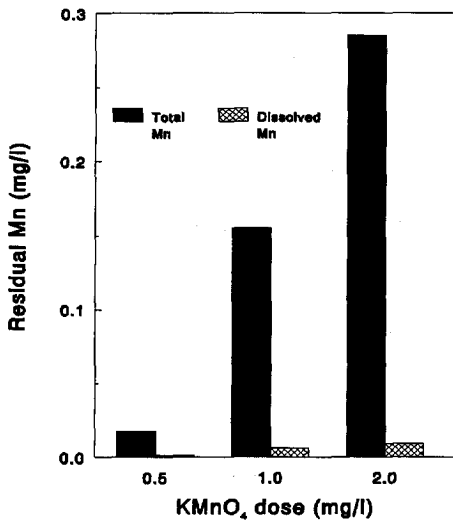


Fig.5.16. Effect of KMnO_4 dosage on residual Mn in BSDFPP filtrate; coagulant: 1.0 mg Fe(III) /l, filtr. rate 2.8×10^{-3} m/s.

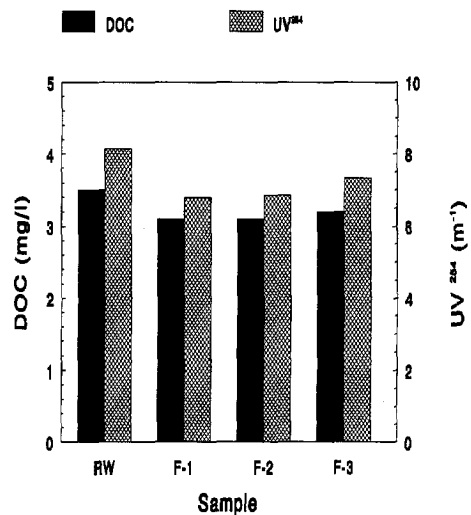


Fig.5.17. Effect of treatment mode on DOC and UV^{254} ; coagulant: 1.0 mg Fe(III) /l, KMnO_4 : 2.0 mg/l (F-1 and F-2).

In-situ observation with the video system showed that the interaction between phytoplankton and oxidant depends on dosage and differs for particular algal species. High permanganate dosages (above 2 mg/l) resulted in hyperactive motility and an extraordinary motion pattern of *R. minuta*. Some of these organisms even completely burst releasing the intra-cellular organic matter into the surrounding water. However, it should be noted that *R. minuta* is an extremely sensitive organism, and that similar phenomena were not observed with the other algal species. It was also noticed that potassium permanganate dosages above 2 mg/l may

break up colonies of *Microcystis* species. Consequently, algal cells appear in the individual form, thus reducing removal efficiency. Manganese oxide precipitates were also observed on algal surface. Algae present in the filtrate were entrapped in cloudy flocs, incorporating very fine MnO_2 precipitates.

Enhanced algal removal in the experiments with potassium permanganate can be attributed to a combination of different mechanisms such as: immobilization or killing of motile algal species, precipitation of manganese oxides on the algal surface and enhanced flocculation kinetics. The beneficial effect of potassium permanganate, under certain conditions, can be counteracted by hyperactivity and bursting of *R. minuta* and the breaking up of natural algal agglomerates.

Even though pretreatment with permanganate demonstrated a strong beneficial effect on particle and algae removal in direct filtration, this treatment will not be operationally feasible if the problem of elevated residual manganese (and turbidity) in the filtrate is not resolved. More comprehensive research on the effect of pretreatment with potassium permanganate on direct filtration of Biesbosch water is presented in chapter 8.

5.5 CONCLUSIONS

Plankton-related problems, such as algal penetration through the treatment process, rapid clogging, and short filter runs may seriously affect the attractiveness of direct filtration. These difficulties may be reduced or even eliminated if an appropriate pre-treatment precedes direct filtration.

Microstraining applied as an initial treatment step may be considered as raw water conditioning with respect to changing particle size distribution in order to improve filter performance. Short filter runs, caused by zooplankton and filamentous algae can be extended. Spring blooms of filamentous algae in Biesbosch reservoir water, followed by high zooplankton concentration, suggest that the application of microstrainers, as an initial treatment step, can be useful in diminishing the problems of fast surface filter clogging.

In the MJTA experiments conducted, pre-flocculation improved turbidity, particle and iron removal. The beneficial effect was correlated with the flocculation G , t and Gt values. Gt values of about 75,000 resulted in the lowest filtrate turbidity, particle count and residual iron. However, in view of the MJTA limitations that may be of particular relevance for flocculation-related direct filtration studies, further detailed pilot plant experiments are required.

Pre-oxidation with ozone or potassium permanganate, enhances algal removal efficiency in direct filtration. Whether the beneficial effect will be observed depends on raw water characteristics (e.g. concentration and composition of DOC, water hardness, prevailing algal

species and, presumably, total phytoplankton concentration) as well as applied treatment conditions (e.g. oxidant dosage). Laboratory and pilot scale investigations, are essential in providing a final judgment for each particular raw water source. Experimental results should be the basis for the selection of a proper type of oxidant, as well as optimal operational conditions. Keeping in mind the importance of phytoplankton concentration and the distinct response of different algal species, experiments should be done throughout the entire year, covering the phytoplankton annual cycle. However, algal bloom periods should be focused. Experiments with Biesbosch reservoir water using potassium permanganate and ozone in wide dosage ranges showed that both oxidants have a beneficial impact on agglomeration and removal of various algal species. On average, 50 % reduction of algal concentration in the treatment line with pre-oxidation was found. Elevated residual manganese was observed at all applied KMnO_4 dosages. Other negative side effects, such as break up of algal colonies, colour (potassium permanganate) in the filtrate, etc. were only pronounced at higher oxidant levels (mainly $\geq 2 \text{ mg KMnO}_4 / \text{l}$). Consequently, the minimum required oxidant dosage should be carefully determined and more efficient removal of residual manganese should be achieved in order to diminish these inconveniences and to maintain the direct filtration's economic and operational attractiveness.

Video technology, used in combination with the tangential flow filtration system, is able to overcome some of the shortcomings of conventional analytical techniques and to provide greater insight into phytoplankton behavioral responses to different treatment conditions, notably with respect to algae-oxidant interaction, and algal motility. Observation with the video system demonstrated that permanganate pre-treatment (dosages investigated $\geq 1.0 \text{ mg/l}$) resulted in immobilization of motile algae. Potassium permanganate dosages $> 2.0 \text{ mg/l}$ may however break up colonies of *Microcystis* sp. and consequently worsen algae removal in direct filtration.

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Chapter 6

OPTIMISATION OF COAGULATION CONDITIONS FOR DIRECT FILTRATION
OF IMPOUNDED SURFACE WATER*

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ABSTRACT - The optimal values of coagulation parameters such as coagulant dosage and pH, are influenced by the pre-treatment process preceding coagulation and the solid-liquid separation process. The optimal coagulation conditions established for one treatment scheme usually cannot be extrapolated to a different treatment scheme. This paper specifically discusses the optimal coagulant conditions for direct filtration without separate flocculation (also known as in-line coagulation or contact coagulation) of Biesbosch reservoir water, characterised by a seasonally high algal load, and compares these values with the optimal conditions for conventional treatment that has a sedimentation step before filtration. Both treatment systems incorporate ozonation, however at a different place in the treatment scheme. Direct filtration, in comparison to conventional treatment, achieved comparable or higher turbidity and particle removal with 4 to 6 times lower coagulant dosages. An increase of coagulation pH above 7.9 resulted in distinctly improved treatment performance. The results also demonstrate that, in addition to turbidity, the particle count is an essential parameter for the determination of optimal coagulation conditions for direct filtration and for assessment of actual plant removal efficiency in a specific particle size range.

6.1. INTRODUCTION

Coagulation commonly requires considerable amounts of chemicals, usually iron or aluminium salts, which results in an excessive production of sludge and high treatment costs. To reduce these costs the amount of chemicals should be limited; this is also in agreement with the growing concern to reduce environmental contamination. These requirements, however, conflict with increasingly rigorous water quality standards that require drinking water to be of very high quality. Therefore, it is necessary to select effective treatment processes that require fewer chemicals, and to optimise process conditions. In addition, many types of relatively clear water require specially designed treatment to remove relatively small amounts of organic particles (notably algae) and their dissolved by-products. Different solid-liquid separation processes, such as sedimentation, flotation, or filtration, follow coagulation. Pre-treatment such as oxidation and microstraining nowadays frequently precedes coagulation. Irrespective of the separation process, it can be assumed that the critical step is the coagulation of the colloidal and other dispersed material into flocs of the appropriate size and characteristics. The pre-treatment plays an important part in the overall coagulation process. The optimal coagulation conditions established for one treatment scheme are not necessarily the best for other treatment configurations. Therefore, the optimal coagulation conditions should pertain to the combination of the pre-treatment preceding coagulation and the selected solid-liquid separation process.

The objectives of this chapter are to describe the effect of pre-oxidation with ozone and potassium permanganate on the treatment performance of direct filtration, and to define experimentally the optimal coagulant dosage and pH value for direct filtration as applied to Biesbosch reservoir water. This study focuses on the direct filtration process which does not include a separate flocculation unit, known as in-line coagulation or contact coagulation, and which includes coagulation with iron salts for the removal of natural particulate matter, mostly algae. Optimal coagulation conditions are compared with the optimal coagulation

conditions for conventional treatment with flocculation and sedimentation. The use of turbidity as a lump parameter to quantify particle removal and treatment performance, and to describe process mechanisms, is complemented by a particle count. Results obtained from batch and continuous flow set-ups, which are used to model direct filtration are presented.

6.2. COAGULATION WITH METAL COAGULANTS

The salts of aluminium and iron are frequently used as coagulants in water treatment practice. The coagulation of colloidal and suspended particles with these chemicals is achieved through two main destabilisation mechanisms: (a) adsorption followed by charge neutralisation and (b) enmeshment in metal hydroxide precipitates. Although a number of process variables such as water quality, metal coagulant dosage, and intensity and time of rapid mixing determine the predominant coagulation mechanism, the coagulation pH is in most cases of critical importance. The significance of the solution pH for the efficiency of coagulation with metal coagulants is well described. pH directly influences the charge of aquatic colloids and algae, controls the stoichiometry kinetics of the chemical reactions and in particular the kinetics of hydrolysis of metal coagulants. In addition, pH determines the species, the concentration and the charge of the metal hydrolysis products, and controls solubility of the metal hydroxide precipitate. However, coagulation related water treatment studies most frequently discuss the effect of the coagulation pH on the species and charge of the polymeric metal hydrolysis products, because the charge neutralisation of negatively charged natural particles through the adsorption of positively charged metal hydrolysis products is often considered a controlling coagulation mechanism. Electrophoretic mobility (EM), colloid charge density and streaming current are used to determine the charge of the aquatic colloids and other natural suspended particles as well as charge neutralisation by positively charged metal-hydroxo complexes.

The best coagulation results achieved through the adsorption and charge neutralisation mechanism were reported when the charge of the particles was strongly reduced or neutralised, defined as electrophoretic mobility or charge density that approaches zero (Bernhardt *et al.* 1986, Klute 1990). Bernhardt *et al.* (1986) conclude that it is necessary to adjust the coagulation pH below the isoelectric point (IEP), the point at which the average charge of the iron hydrolysis product is zero, in order to flocculate negatively charged particles with hydrolysing metal coagulants through adsorption coagulation. It has also been reported that the flocculation of bacteria and small spherical algae, as a consequence of their negative surface charge, also follows the principle of adsorption and charge neutralization coagulation (Ives 1959, Tilton *et al.* 1972, Bernhardt and Clasen 1991, 1992). Efficient charge neutralisation was achieved in the acidic pH range, where positively charged metal hydrolysis species predominate. The coagulation of algal suspensions at higher pH levels required higher coagulant dosages as a consequence of the increased negative charge density of algal cells (Bernhardt and Clasen 1992). The IEP for iron hydroxo-complexes is most frequently reported to be in the acidic pH range, between 6 and 7 (Stumm and Morgan 1962,

Bernhardt *et al.* 1986). The position of the IEP and the charge of the hydrolytically formed iron precipitates strongly depend on the content of anions and cations in the water (e.g. Ca^{2+} , HCO_3^- , SO_4^{2-}). The presence of anions such as SO_4^{2-} and HPO_4^{2-} causes a shift of IEP to lower pH values (Stumm and Sigg 1979), while Bernhardt *et al.* (1986) found that an increase of Ca^{2+} coupled with the absence of HCO_3^- can move the IEP to the neutral pH range, or even prevent charge reversal. Coagulation at pH values below the IEP will increase the average positive charge of the metal hydrolysis species formed, thus enhancing the coagulation through charge neutralisation. Coagulation through adsorption and charge neutralisation generally requires lower coagulant dosages and longer reaction times than coagulation through enmeshment in the metal coagulant precipitate, particularly when the colloidal concentration is low. The amount of metal coagulant required to achieve efficient coagulation through charge neutralisation is stoichiometrically correlated with the colloidal surface charge density (Stumm and O'Melia 1968, Alaerts and van Haute 1981, Bernhardt *et al.* 1986). However, macromolecular organic matter that bears a very strong negative charge and is present in the natural waters can adsorb onto inorganic particles, thus controlling their stability and consequently the required coagulant dosage (Bernhardt *et al.* 1986, Jekel 1983, Edzwald 1993). The formation of positively charged metal coagulant hydrolysis products and their adsorption on the natural particles present in the raw water is an extremely fast process. Metal polynuclear complexes are formed in a fraction of second, while their adsorption to a colloidal particle surface is completed in a few seconds (Hahn and Stumm 1969). Accordingly, high mixing intensity and very fast dispersion of the coagulant in the raw water are essential for efficient coagulation through charge neutralisation (Klute 1990).

Coagulation through enmeshment of the impurities in the metal coagulant precipitates, known as sweep coagulation, prevails at higher pH values, above IEP, where the metal hydrolysis products have a negative surface charge. When iron coagulant is added to water, the initial monomeric hydrolysis products are formed: $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}(\text{OH})_3$. The process of precipitation begins with the condensation of monomeric $\text{Fe}(\text{OH})_3$ into polymeric $\text{Fe}_n(\text{OH})_{3n}$ which may act as nuclei for continuing condensation of other monomeric $\text{Fe}(\text{OH})_3$ molecules (Hsu and Raone 1972); in the case of aluminium coagulant a different mechanism has been proposed where precipitated Al forms micro-crystalline gibbsite which subsequently agglomerates as a large floc (Alaerts and van Haute 1981). The colloids and other impurities present in the raw water may be entrapped in the amorphous metal hydroxide precipitates or may serve as the nuclei for this precipitation. The surface charge of the aquatic colloids does not play an important role when sweep coagulation is the prevailing coagulation mechanism, and, accordingly, charge neutralisation is not prerequisite for efficient coagulation. The optimal coagulant dosage is inversely related to the concentration of aquatic colloids: a low concentration of colloids requires a large amount of coagulant to increase the rate and efficiency of collisions in the flocculation; a suspension with a high colloid concentration requires lower metal coagulant dosages (Packham 1965). Sweep coagulation is considered to have a considerably lower efficiency (Klute 1990). Recently, Bernhardt and Clasen (1992) reported that efficient flocculation of algal cells through sweep coagulation can be achieved

at low aluminium dosages which do not cause charge neutralisation. They reported that the algal cells were embedded in the aluminium hydroxide flocs.

In drinking water treatment practice, coagulation is achieved primarily by sweep coagulation, given that the commonly used dosages of metal coagulants significantly exceed the solubility limits of their metal precipitates, but this is simultaneously aided by charge neutralisation. Rapid precipitation of metal hydroxide occurs at pH values common for drinking water treatment practice.

6.3. EXPERIMENTAL PROCEDURE

Raw water from Biesbosch water storage reservoirs was used in the experiments. Quality of Biesbosch water is specified in chapter 5. Initial particle (algal) concentration in the raw water used in the study, during periods with very low concentration of algae, was increased with the aid of the tangential flow membrane filtration system (Millipore-Pellicon filter holder equipped with membranes of $0.45\ \mu\text{m}$ pore size), in order to obtain a more pronounced response to different treatment conditions (Petrusevski *et al.* 1995, chapter 4). This concentration procedure increased algal concentration while at the same time preserving the relative composition and representative character of the water sample.

The experimental apparatus used in this study was located at the water treatment plant Kralingen, Rotterdam. The set-ups developed and used to establish optimal coagulation conditions and to model direct filtration are described in chapter 3, namely: a modified jar-test apparatus (MJTA), a bench scale continuous direct filtration pilot plant (BSDFP) and a mobile fully automated direct filtration pilot plant (MDFPP).

The MJTA procedure consisted of pH correction with HCl or NaOH, addition of coagulant followed by 30 seconds rapid mixing at $G=1000\ \text{s}^{-1}$, and seven minutes of slow mixing at $G=10\ \text{s}^{-1}$ to simulate the retention period of coagulated water in the filter supernatant, followed by filtration at a constant filtration rate of $1.8 \cdot 10^{-3}\ \text{m/s}$. The standard jar test procedure was slightly altered in the experiments designed to study the effect of coagulation pH and contact time on the concentration of particles $> 2.7\ \mu\text{m}$ in coagulated suspension. The adjusted procedure comprised: the addition and rapid mixing of ferric sulfate at $G=1000\ \text{s}^{-1}$ and $T=30\ \text{s}$ at different coagulation pH values, followed by flocculation at $G \approx 10\ \text{s}^{-1}$ and varying contact time.

In the experiments which examined the influence of pre-oxidation, coagulation was preceded by pre-ozonation or the addition of potassium permanganate.

Raw Biesbosch water was used in MJTA experiments. In the MJTA experiments with pre-ozonation raw Biesbosch water was pre-concentrated to obtain an algal concentration that corresponds to levels during spring algae bloom (chlorophyll- α approx. $20\text{--}30\ \mu\text{g/l}$).

In the pilot plant experiments with BSDFPP and MDFPP, natural water from the Biesbosch storage reservoirs was used.

Coagulant and raw water were mixed using a static mixer with high energy input ($G=1400\text{ s}^{-1}$) and short mixing time ($t < 1\text{ s}$). The coagulation step was followed by filtration through the BSDFPP or the MDFPP provided with dual (anthracite-sand) or multi-layer filter media (anthracite-sand-garnet) at a constant filtration rate of $2.8 \cdot 10^{-3}\text{ m/s}$.

A semi-batch and a continuous-flow ozone reactor were developed to study the interaction between ozone and Biesbosch reservoir water flocculation. The semi-batch ozone reactor was used in the experiments with the MJTA. A glass jar of 5.5 L was used as a reaction vessel. The continuous counter-current flow ozone reactor was developed to study the effect of pre-ozonation on the performance of direct filtration pilot plants. The reactor, a vertical, transparent PVC column, 0.133 m in diameter and 4.5 m in height provided a contact time of typically 150 s.

The addition of potassium permanganate as the alternative pre-oxidant, as a 0.006 M solution, was followed by 25 minutes of average hydraulic detention time.

Ferric sulfate solution for the experiments with the MJTA was prepared from analytical grade $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$. Ferric sulfate for the pilot plant experiments was prepared at the water treatment plant Kralingen-Rotterdam by oxidation of ferrous sulfate by oxygen. The same coagulant was used in the full-scale conventional treatment plant (Kralingen). Synthetic cationic polymer Superfloc C-573 (Cytac Industries B.V.) was used as a secondary coagulant in the experiments with potassium permanganate.

Particle concentration and particle size distribution in a size range of 2.7-150 μm were determined by a HIAC particle counter, model PC-320 (Hiac/Royco, Pacific Scientific). Turbidity was measured by a laboratory Sigrist 65 turbidity meter. The total residual iron was determined by atomic absorption spectrometry at the wavelength of 248.3 nm using an oxidizing air-acetylene flame for high iron concentrations ($> 0.1\text{ mg/l}$) (NEN 6460), or a graphite furnace with pyro-coated tube with a char temperature of 1400°C and an atomization temperature of 2300°C for low iron concentrations (5-200 $\mu\text{g/l}$) (Schuit 1993). In both cases, samples were acidified with nitric acid to $\text{pH}=2$. For the determination of dissolved iron, samples were filtered through a 0.45 μm membrane filter before acidification.

Results from the MJTA experiments are averages from two series of experiments performed under identical process conditions, with raw water of similar quality.

6.4. RESULTS AND DISCUSSION

6.4.1. Coagulant dosage

Preliminary investigations showed that the direct filtration alone could not achieve adequate removal of particulate matter, especially with respect to algae, although it produced water of very low turbidity (< 0.13 FTU) and residual iron (≤ 0.05 mg Fe[III]/l). Pre-treatment with ozone or potassium permanganate was shown to be an important prerequisite to improve turbidity and particle removal in direct filtration (Petruševski *et al.* 1993b, chapter 5).

The experiments conducted with the MJTA provide an indication about the optimal dosages of coagulant and oxidant, namely ozone or potassium permanganate (Fig.6.1).

Ozone was applied at a neutral pH of 7.5 and the coagulation was introduced at pH 8.0.

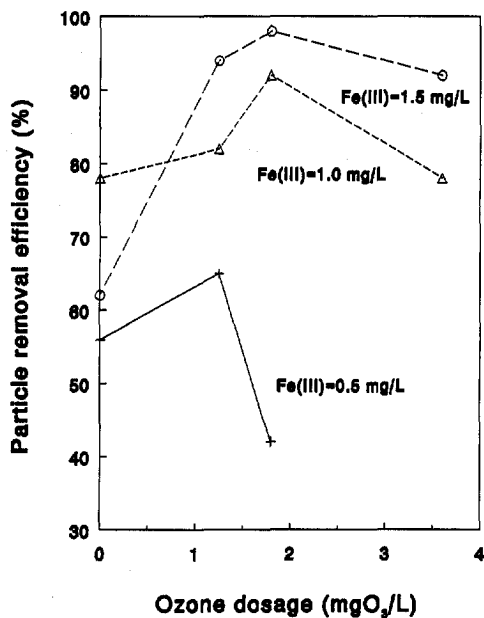


Fig. 6.1. Effect of coagulant and ozone dosage on particle removal efficiency with MJTA.

Pre-treatment with 1.8 mg O₃/l improved particle removal efficiency from 62 to 98% when 1.5 mg Fe(III) was applied as a coagulant. At lower coagulant dosages (≤ 1.0 mg Fe[III]/l), the beneficial effect of ozone was less pronounced (particle removal efficiency improved for approximately 20%).

The exceptionally high removal efficiency of 98% was already obtained with the MJTA, though this features only a simple semi-batch experimental set-up with a shallow, non-

ripened, single-layer filter bed. The results show that there is an optimal ozone dosage for each coagulant dose, and that overdosing of ozone (above approx. 1.8 mg O₃ consumed/l) has a detrimental effect. The highest coagulant dosage tested (1.5 mg Fe(III)/l) was found to produce the filtrate of best quality in terms of turbidity and particle concentration. Higher coagulant dosages were not tested because of the rapid build-up of excessive head loss in the filter bed and associated short filter runs (coagulant dosage of 2.0 mg Fe(III)/l reduced filter run length of MDFPP filter with anthracite-sand-garnet bed to 16 hours). In addition, the examined dosage of 1.5 mg Fe(III)/l was sufficient to achieve the targeted filtrate quality with the BSDFPP and the MDFPP (turbidity ≤ 0.1 FTU and with a very low particle concentration that corresponds to particle removal efficiency > 99%).

Electrophoretic mobility showed that the iron flocs formed at this pH carry a negative surface charge. Therefore, agglomeration of algae and other particles was likely to be achieved through sweep coagulation because those particles also are negatively charged and would repel the flocs. The mechanisms behind the beneficial coagulating effect of ozone are not yet clarified. A number of mechanisms have been proposed, such as the reaction of ozone with the adsorbed organic coating on the particles' surface (Jekel 1983, Singer 1990), the destruction of the algal extra cellular organic matter (EOM) present in the raw water and alteration of the algal cell wall structure (Sukenic 1987), and the formation of biopolymers that can assist in the coagulation of particulate matter (Sukenic 1987, Singer 1990). However, microscopic observations demonstrated that immobilisation of motile algal species such as *Rhodomonas minuta*, *Cryptomonas* sp., *Chlamydomonas* sp., and *Navicula* sp. also plays an important role in the case of Biesbosch reservoir water (Petruševski *et al.* 1993a) (see also chapters 3 and 5). A similar optimum coagulant dosage of approximately 1.5 mg Fe(III)/l was also found with potassium permanganate as the pre-oxidant. However, the application of cationic polymer as a secondary coagulant was required (chapter 8) in this case to achieve efficient removal of the manganese dioxide hydrate precipitates formed in the process, thus producing filtrate with very low residual manganese concentration (< 10 μ g Mn/l). The high particle and turbidity removal efficiency achieved in this case should probably be attributed to two distinct coagulation mechanisms that occur simultaneously: charge neutralisation achieved with the cationic polymer, and enmeshment in the iron precipitates (see chapter 8). In addition, potassium permanganate enhances the coagulation process by immobilising the motile algae and increasing flocculation kinetics. Results from more detailed research dealing with the effect of ozone and KMnO₄ on direct filtration are given in chapters 7 and 8.

The results presented in Fig. 6.2. show that in-line coagulation, in comparison to conventional treatment, can achieve comparable or higher treatment efficiency, in terms of filtrate particle concentration, with coagulant dosages that are 4 to 6 times lower (1-1.5 mg Fe(III)/l in direct filtration and 5-6 mg Fe(III)/l in conventional treatment). This would be true for the particle larger than 2.7 μ m. Fig. 6.2 presents the average values from five series of simultaneous experiments with conventional and direct filtration units, performed throughout the year and thus covering various algal species. Both conventional and direct filtration treatment lines

incorporate ozonation; however, in the conventional treatment line ozonation follows sedimentation, whereas in the direct filtration scheme ozonation precedes coagulation.

Essentially the same high treatment efficiencies were achieved when potassium permanganate was used as the pre-oxidant (99.8% removal with ozone, 99.6% removal with potassium permanganate in contrast to 98.7% removal achieved by conventional treatment).

The lower coagulant dosages associated with the direct filtration schemes are assumed to be related to the oxidants acting as a coagulant aid, and to the differences in the floc characteristics that are required for efficient removal in conventional treatment and in direct filtration.

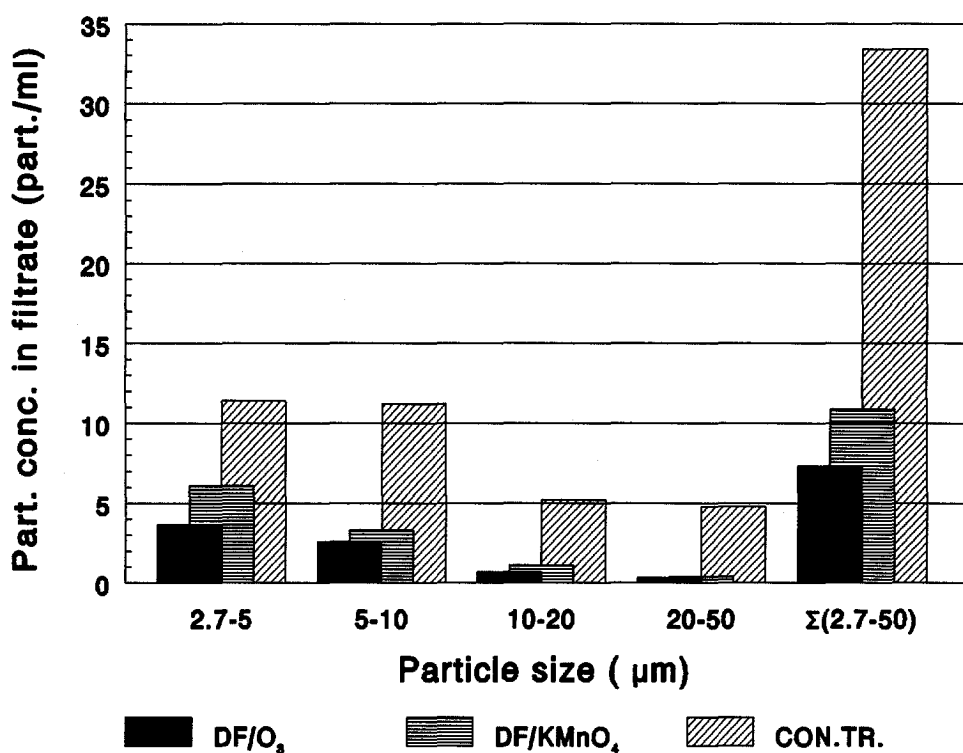


Fig.6.2. Effect of treatment process on particle concentration in filtrate as a function of the size of the particles. Legend: **DF/O₃** - oxidation with O₃ (0.9-1.8 mg/l)*, coagulation with 1.5 mg Fe(III)/l and filtration; **DF/KMnO₄** - oxidation with KMnO₄ (0.7mg/l), coagulation (1.5 mg Fe(III)/l) + 1.0 mg Cationic polymer/l and filtration; **CON.TR.** - conventional treatment: coagulation (6.0 mg Fe(III)/l), sedimentation, oxidation with O₃ (2-3 mg/l)* and filtration.; an average particle concentration in raw water 2540 particles/ml.

* applied ozone dosages varied throughout the year

6.4.2. Coagulation pH

It is known that iron salts are efficient as coagulants over a wide pH range (4 to 8). Also, coagulation with Fe(III) salt at acid pH (4 to 6) is generally thought to enhance coagulation efficiency through charge neutralisation. In contrast, MJTA and MDFPP experiments, showed that coagulation pH has a distinct but opposite effect on filtrate quality: coagulation at pH = 7.9 to 8.8 produced filtrate of lower turbidity, particle count (Figs. 6.3a, 6.4 and 6.5) and residual iron concentration (Fig.6.3b). Typically, increase in coagulation pH above 7.9 halved the filtrate turbidity, residual iron and particle count. Results given in Fig.6.3. are results from a single series of MJTA experiments. This trend was systematically observed in series of experiments under similar experimental conditions.

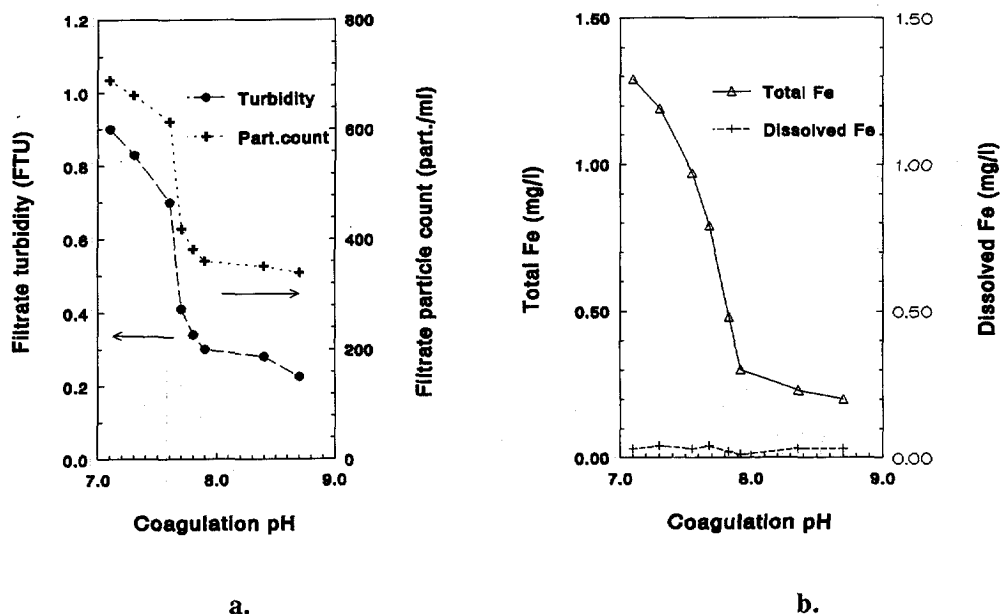


Fig.6.3. Effect of coagulation pH on the quality of MJTA filtrate; coagulant: ferric sulfate, 1.5 mg Fe(III)/l; Fe passing through 0.45 μ m membrane was considered as dissolved.

The effect of coagulation pH on filtrate quality was demonstrated in the filter run with the MDFPP in which the coagulation pH was altered during the course of the run by the addition of HCl or NaOH (Fig.6.4). It was observed that filtrate turbidity, particle count and residual iron increased when coagulation pH was reduced by HCl addition. Filtrate quality improved when coagulation pH was increased by addition of NaOH. The observed enhanced treatment efficiency, with an increase in coagulation pH, with the simple in-line coagulation, consisting of coagulation with ferric sulfate and multi-media filtration (Figs. 6.3 and 6.4) did not change when this process was upgraded with pre-oxidation and the application of cationic

polymer as a secondary coagulant (Fig.6.5).

Trends observed earlier with the semi-batch unit MJTA were similar to those obtained with the larger scale MDFPP (Fig.6.5); MJTA has proved to be a useful device for preliminary assessment of the effect of different treatment conditions on the performance of in-line coagulation.

However, the coagulation pH values examined in these experiments remained above IEP for the iron hydroxo-complexes; in the experiments with the Biesbosch reservoir water the IEP was found to occur between pH 5 and 6. Bearing in mind the results of other researchers (Bernhardt *et al.* 1986, Klute 1990) it may be assumed therefore, that further reduction of coagulation pH to close to or slightly below the IEP, would favour adsorption coagulation and possibly change the trend shown in Figs 6.3, 6.4 and 6.5 thus improving filtrate quality.

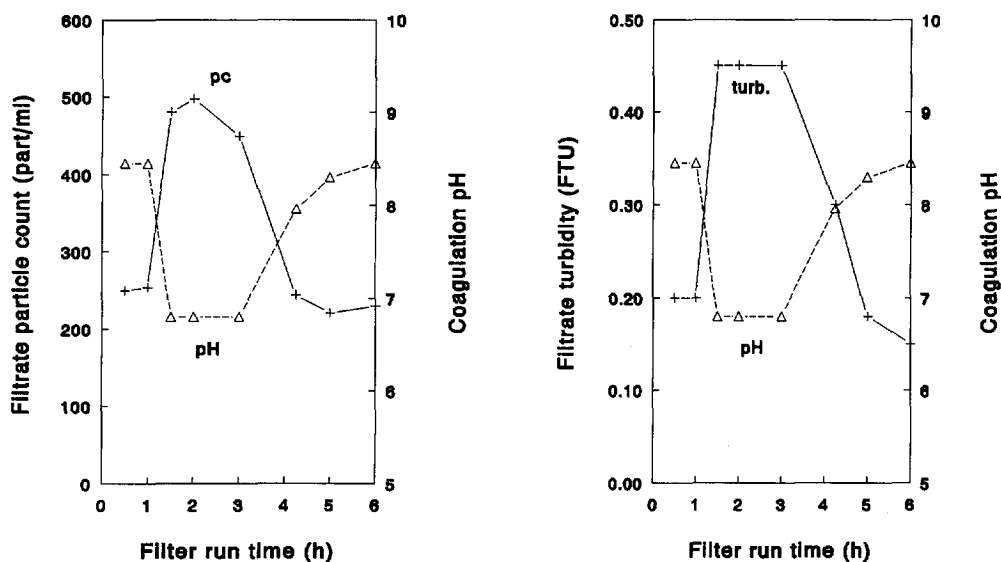


Fig.6.4. Effect of the coagulation pH on the quality of MDFPP filtrate in continuous operation; coagulant: ferric sulfate, 1.5 mg Fe(III)/l. pH is varied during the filter run by adding HCl or NaOH.

However, such low coagulation pH values were not applied here because they were considered unfeasible from a practical view point as the Biesbosch water has a high pH, high salt concentrations and high buffering capacity. Coagulation at low pH would require high acid dosages with associated high cost and an additional increase of the salt concentration.

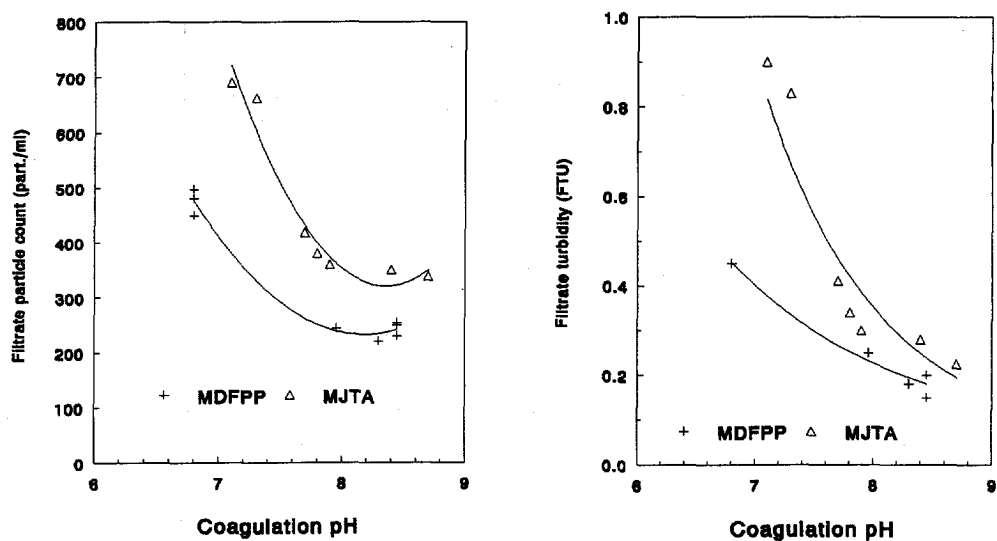


Fig.6.5. Effect of coagulation pH on the particle count and turbidity; experiments with MJTA and MDFPP; coagulant: ferric sulfate, 1.5 mg Fe(III)/l.

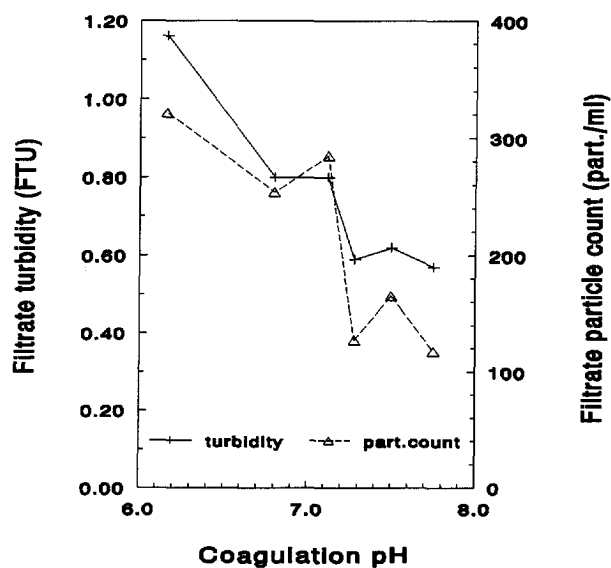


Fig. 6.6. Effect of coagulation pH on the quality of MJTA filtrate. The treatment process comprises: pre-oxidation with 0.6 mg/l KMnO_4 , coagulation with ferric sulfate (1.5 mg Fe(III)/l) and cationic polymer (1.0 mg/l), and filtration.

Fig.6.3b shows that the filtrate's total iron concentration dramatically increases with decreasing coagulation pH, especially below pH 7.9. At the same time, the concentration of "dissolved" iron* was very low (≤ 0.02 mg Fe[III]/l) and independent of pH, suggesting that the iron in the filtrate was essentially in suspended form. A parallel trend observed for both the filtrate turbidity and particle count (Fig.6.3.a) as well as the response of the residual iron concentration (6.3.b) implies that turbidity and particle count are primarily affected by the concentration of ferric hydroxide micro-flocs in the filtrate. Coagulation pH, therefore, seemed to strongly influence the growth kinetics and filterability of the iron hydroxide micro-flocs.

Additional MJTA experiments were designed to study the effect of coagulation pH and contact time on the concentration in the coagulated suspension of particles larger than $2.7\text{ }\mu\text{m}$, consisting of a mixture of hydroxide precipitates and algae. The results (Figs.6.7 and 6.8.) demonstrate that coagulation at pH=8.3 significantly increases the concentration of particles, comprising natural particles and formed ferric hydroxide micro-flocs larger than $2.7\text{ }\mu\text{m}$. It is observed that with decreasing coagulation pH the total concentration of particles of size $> 2.7\text{ }\mu\text{m}$ decreases (Figs. 6.7 and 6.8) but the concentration of particulate residual iron (difference between total iron and "dissolved iron", thus iron precipitates $> 0.45\text{ }\mu\text{m}$, Fig. 6.3.b) increases. This indicates that the concentration of ferric hydroxide micro-flocs in the size range $0.45\text{-}2.7\text{ }\mu\text{m}$ increases with decreasing pH. This may be expected to have a negative effect on overall filter removal efficiency, because filtration studies demonstrated that presence of particles of diameter $1\text{-}3\text{ }\mu\text{m}$ is accompanied by minimum filter removal efficiency (Yao *et al.* 1971, O'Melia 1985).

Despite numerous investigations, little is known about the kinetics of ferric hydrous oxide precipitation and the size distribution of the precipitates (Matijevic and Scheiner 1978). However, our results suggest that the size distribution of hydroxide precipitates formed under the given kinetic conditions varies with the solution pH leading to substantial effects in the filtration step. Results also indicate that flocculation when ferric sulfate is the sole chemical under the conditions investigated (low coagulant dosage and low particle concentration in natural water) has slow agglomeration kinetics (Fig.6.7): practically no increase was observed in the concentration of particles larger than $2.7\text{ }\mu\text{m}$ or particle size distribution change within the contact time feasible for in-line coagulation (up to 15 min). Prolonged reaction time gradually did result in a significant increase in large particle concentration and in a change of particle size distribution at both low (4.0) and high (8.3) coagulation pH (Fig.6.7). Agglomeration of hydroxide precipitates and raw water colloidal and suspended matter in the acid pH range, below the IEP where the positively charged iron hydroxocomplexes predominate, can be attributed to coagulation through adsorption and charge neutralisation. Coagulation through this mechanism requires a longer reaction time when the concentration of the colloids in suspension is low. The time required to achieve a

* iron present in the filtrate after filtration through a $0.45\text{ }\mu\text{m}$ membrane filter; actually consists of dissolved and colloidal ($< 0.45\text{ }\mu\text{m}$) iron.

filterable particle suspension of an adequate size distribution with many large particle aggregates appears to be inappropriate for in-line coagulation. The flocculation observed with an equally prolonged reaction time at the high coagulation pH value (8.3) can be attributed mainly to sweep coagulation. At coagulation pH values of 6.6 and 7.9, conditions favoured neither sweep coagulation, nor adsorption and charge neutralisation, consequently resulting in ineffective agglomeration (Fig. 6.7).

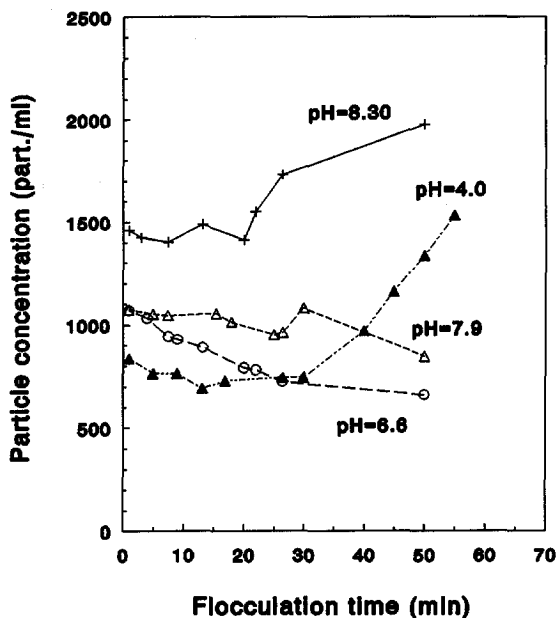


Fig.6.7. Effect of coagulation pH and flocculation time on particle concentration in coagulated raw water; treatment comprises coagulation with ferric sulfate (1.5 mg Fe (III)/l) and flocculation at $G \approx 10 \text{ s}^{-1}$.

Figs 6.7 and 6.8 compare the concentration of particles of size $> 2.7 \mu\text{m}$ in the coagulated suspensions. The former concentration (Fig. 6.8) is created by direct filtration treatment, supported by pre-oxidation with potassium permanganate, and the application of cationic polymer as a secondary coagulant, and the latter concentration (Fig. 6.7) was created by the straightforward direct filtration with ferric sulfate. Pre-oxidation and the application of cationic polymer increased the concentration of particles larger than $2.7 \mu\text{m}$ formed after coagulant addition. Subsequently, this enhanced the floc agglomeration kinetics and led to the higher performance of direct filtration treatment supported by pre-oxidation and the application of double coagulant.

In addition to the effect of coagulation pH on the size distribution of the iron precipitates, the property of Fe to form an array of complexes in natural water in function of pH may also play an important role. Iron may be bound in natural water to organic substances (e.g. humic acids) and form insoluble, highly dispersed colloids (Stumm 1967). These complexes are difficult to filter and easily pass through filters due to their colloidal size. Moreover, Stumm (1967) demonstrated that in natural systems with a high concentration of calcium ions (as is the case in Biesbosch water), Fe^{3+} ions, although usually forming stronger complexes with humic matter than Ca^{2+} , can be replaced by Ca^{2+} ions. This effect strongly depends on the solution pH and is in particular pronounced at $\text{pH} > 8$. Stumm demonstrated that in the presence of excess Ca^{2+} ions even EDTA (which also binds strongly to Fe^{3+}) cannot keep Fe^{3+} ions at solution when $\text{pH} > 8$. Similarly, it may be assumed that in experiments with Biesbosch reservoir water, the amount of Fe^{3+} bound to the organic complexes and present in the form of dispersed colloids, and thus difficult to filter out, reduces with increasing pH. At $\text{pH} > 8.0$ Fe^{3+} is likely to be completely replaced by Ca^{2+} ions in metalo-organic complexes, thus stimulating hydroxide precipitation and shifting particle size distribution towards larger particles and thus enhancing filterability of the iron flocs and aggregates.

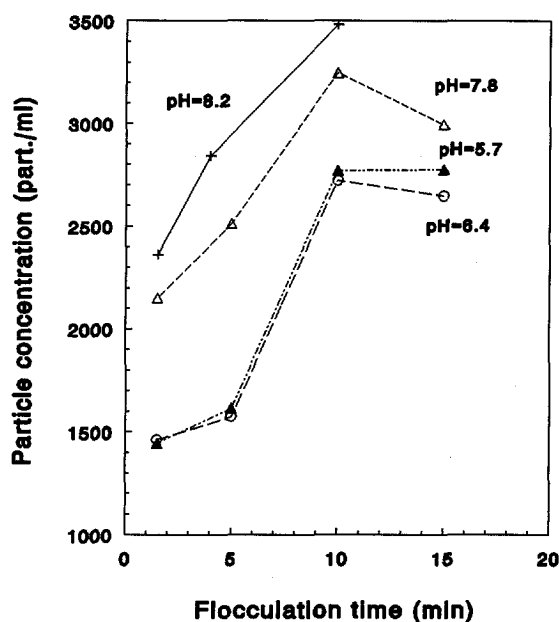


Fig. 6.8. Effect of coagulation pH and flocculation time on particle concentration in coagulated raw water; treatment comprises pre-oxidation with 0.6 mg/l KMnO_4 /l, coagulation with ferric sulfate (1.5 mg Fe(III) /l) and cationic polymer (1.0 mg/l) as coagulant aid, and flocculation at $G \approx 10 \text{ s}^{-1}$.

6.4.3. Turbidity and particle concentration as indicators of process performance

Coagulation efficiency is most frequently judged in the light of its ability to allow a certain percentage of turbidity removal in the subsequent floc separation step. Requirements for efficient turbidity reduction are usually not strict: in some studies a turbidity reduction of only 50% was considered sufficient to characterise the coagulation as effective (Johnson and Amiratharajah 1983). This approach cannot be accepted when coagulation is part of the direct filtration treatment schemes for drinking water production. Rapid sand filtration that follows coagulation is usually the last particle removal barrier and, therefore, the efficiency of coagulation should be judged in the light of its ability to facilitate the production of water that, at least, fulfils stringent drinking water quality standards (e.g. turbidity ≤ 0.2 FTU the recommendation of VEWIN, The Association of Dutch Waterworks or ≤ 0.1 FTU guide level in USA).

In addition to turbidity, the particle count and size measurement are valuable indicators of filtrate quality, particularly given the growing concern regarding pathogenic microorganisms such as *Giardia* and *Cryptosporidium*. Efficient elimination of their cysts and oocysts is becoming increasingly important in view of recent outbreaks of giardiasis and cryptosporidiosis and the low efficiency of disinfection by chlorine and ozone at common concentrations, particularly for inactivation of oocysts. However, Figs 6.9a and 6.9b indicate that turbidity, which is most commonly used to gauge optimised coagulation, is a poor indicator of particle concentration and hence of cysts and oocysts. Fig. 6.9a shows that a better correlation between turbidity and particle concentration can be established when higher turbidity values up to 1 FTU are included (correlation coefficient = 0.80). However, the correlation is very poor (correlation coefficient = 0.49) in the turbidity ranges of interest for drinking water production (Fig. 6.9b). In addition, the results also demonstrated that very low turbidity is not a guarantee of low particle concentration. Several hundreds of particles, in the size range of *Giardia* and *Cryptosporidium* cysts and oocyst (2.7-20 μm), were detected in filtrate of very low turbidity (≤ 0.2 FTU). This can be attributed to poor light-scattering properties of particles greater than 1 μm and consequently inability of nephelometric turbidimetry to detect these particles (Ives, personal communication). Therefore, it may be concluded that, in addition to turbidity, particle count and size measurement are essential parameters to determine the overall optimal process conditions in direct filtration because of their higher degree of specificity. Particle count supported by particle size measurements may nowadays be useful, easy-to-introduce, and relatively inexpensive analysis technique that can provide continuous information about actual plant removal efficiency in a specific particle size range. Such information can probably be used as a useful preliminary indicator of actual plant capacity to remove cysts and oocysts of pathogenic microorganisms, and consequently whether or not the requirements established in the Surface Water Treatment Rule are being met.

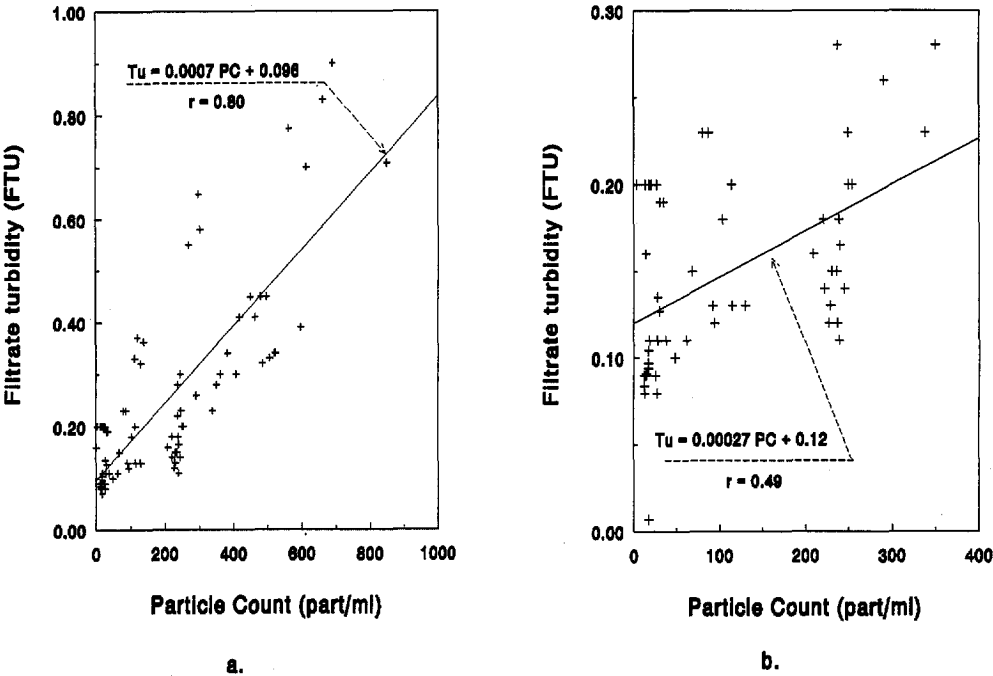


Fig.6.9. Correlation between turbidity and concentration of particles larger than 2.7 μm .

6.5. CONCLUSIONS

The optimal coagulant dosage established for in-line coagulation of Biesbosch water is considerably lower than the coagulation dosage required for conventional treatment of the same raw water. Direct filtration supported by pre-oxidation with ozone or potassium permanganate achieves similar or higher turbidity and particle removal efficiencies in comparison to conventional treatment with several times lower coagulant dosages. Consequently, the optimal coagulation conditions are closely correlated with the pre-treatment, notably pre-oxidation, that precedes coagulation and the selected solid-liquid separation step. The performance of in-line coagulation, in terms of filtrate turbidity, particle and residual iron concentration, under the conditions investigated (coagulation with low dosages of ferric sulfate 1-1.5 mg Fe[III]/l, and raw water with low colloid and particle concentration) improves with an increase of coagulation pH. The optimum results were obtained at pH 8.0-8.8.

The optimal coagulation conditions for in-line coagulation supported by ozone or permanganate pre-treatment as applied to Biesbosch water comprise coagulation with 1.5 mg Fe(III)/l and coagulation pH of approx. 8.0 to 8.3.

The particle concentration and particle size measurement used in addition to turbidity will provide a more reliable indication to establish the optimal coagulation conditions and to assess actual plant removal efficiency in a specific particle size range.

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Chapter 7

PRE-OZONATION: KEY FOR EFFICIENT PARTICLE
AND ALGAE REMOVAL IN DIRECT FILTRATION*

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*Part of this Chapter was published by B. Petruševski, A. N. van Breemen and G.J. Alaerts (1994).
Proc. IOA Regional Conference, Zürich, Switzerland.

ABSTRACT - The effects of Biesbosch reservoir water pre-ozonation on particle and algae removal in direct filtration were investigated. Both bench-scale and pilot-plant experiments have shown that pre-ozonation dramatically improves turbidity, particle and algae removal. The results show that an optimal ozone dosage exists, and that the overdosing has a detrimental effect on treatment performance. Positive correlation between optimal ozone dosage and algal concentration was established. A very short time interval between ozonation and coagulant addition appeared to be of utmost importance to achieve high process performance. Use of hydrogen peroxide in combination with ozone at low H_2O_2/O_3 ratios (0.2 and 0.4) did not improve further the flocculation process; at higher H_2O_2/O_3 ratios (0.6 and 0.8) the flocculation process was disrupted. Application of cationic polymer as a secondary coagulant in combination with ferric sulfate (1.5 mg $Fe[III]/l$) and pre-ozonation (1.8 mg O_3/l) provided nearly complete elimination of algae and other particles larger than 1 μm . SEM micrograms demonstrated that ozone alters algal surface properties and provokes algae to release biopolymers. Observations with a video system showed that ozone dosages ≥ 1.0 mg/l completely arrest active locomotion of motile algae. Finally, a model is proposed explaining efficient particle and algae removal.

7.1. INTRODUCTION

7.1.1. Particle removal in direct filtration

Direct filtration is an economically and environmentally highly attractive process for treatment of impounded surface waters. However, the production of drinking water from these sources may be seriously affected by problems related to phytoplankton, the most serious one being algal penetration through the treatment system. Optimised straightforward direct filtration treatment of Biesbosch water can achieve an average of typically 90% or 1.0-log algae removal (Petruševski *et al.* 1993, chapter 3). Similar removal efficiencies are reported by other researchers (Bernhardt and Schell 1986). Algal penetration in treatment systems, which include a chlorination step for disinfection purposes, results in an increase in chlorine demand and formation of trihalomethanes (THMs) and other halogenated by-products. Algae present in the drinking water may introduce natural toxins and have an adverse effect on drinking water taste and odour. Their products may be considered as easily assimilable organic compounds, and their presence in carbon filters and distribution mains may enhance biological after-growth. Poor removal of algae also suggests that removal of other particles in algal size range, such as cysts and oocyst of pathogenic microorganisms like *Giardia* and *Cryptosporidium*, may be inefficient as well.

Direct filtration should achieve at least 1-log higher particle and algae removal to be considered as a viable replacement of conventional treatment of Biesbosch water (chapter 3). Algae removal in excess of 99%, may result in chlorophyll- α levels in filtrate below 0.1 $\mu g/l$ (the interim standard of the German Association of Drinking Water Reservoirs), assuming that chlorophyll- α level in Biesbosch water is ≤ 10 $\mu g/l$. Higher chlorophyll- α levels during occasional short spring blooms are primarily caused by very large filamentous algae like *Melosira* sp. that can be very efficiently removed by microstraining (chapter 5) and filtration.

Given the similarity in size it may be further assumed that 99% algal removal efficiency will correspond to comparable (2.0-log) removal of *Giardia* cysts. Improved removal efficiency of *Giardia* cysts will consequently be of help in achieving 3.0-log *Giardia* cysts removal or inactivation, the requirement established in the Surface Water Treatment Rule (US EPA 1989) for waters that are not highly contaminated (5-log and 6-log removal or inactivation are required for highly and extremely contaminated water sources respectively; these waters are in general not suitable for direct filtration application).

Given the wide-spread occurrence of *Cryptosporidium* oocysts in surface water and in the large Biesbosch reservoirs (Ketelaars *et al.* 1995) and the fact that traditional disinfectant such as chlorine and ozone* are ineffective in eliminating oocyst infectivity at levels commonly used in water treatment (Parker *et al.* 1993, Pontius 1993), direct filtration should very efficiently eliminate particles in the oocysts size range (4-6 μm). However, no specific standards are currently established.

Algae-related inconveniences are not only associated with direct filtration; other treatment processes are vulnerable as well. However, due to the simplicity of direct filtration, which involves only one particle removal step, algae related problems, and more recently *Giardia*- and *Cryptosporidium*-related problems are most pronounced when this treatment option is selected.

Oxidants like chlorine, chlorine dioxide, ozone and potassium permanganate applied as a pre-treatment can interact with particulate matter (e.g. algae) in such a way that more efficient removal can be realized by subsequent additional treatment (Hodges *et al.* 1979, Janssens *et al.* 1987; Sukenik *et al.* 1987; Langlais *et al.* 1991, Petruševski *et al.* 1993b, chapter 5). As a consequence of hazardous properties of some chlorination by-products (e.g. chloroform), pre-oxidation with chlorine or chlorine dioxide has become uncommon nowadays and even forbidden in some countries (e.g. Germany). As an alternative ozone, and more recently potassium permanganate (Petruševski *et al.* 1994) have been increasingly proposed as a pre-treatment.

7.1.3. Objectives

The objective of this chapter is to ascertain the effect of pre-ozonation on particle and algae removal and overall performance of subsequent in-line coagulation (direct filtration without separate flocculation) applied to the Biesbosch reservoir water. The paper quantifies and details pre-ozonation effects and attempts to describe the involved process mechanisms. It emphasizes the importance of pre-treatment for direct filtration of impounded surface water from the Biesbosch storage reservoirs, characterised by seasonally high algae load.

* Ozone is effective in eliminating *Cryptosporidium* oocysts infectivity, however high dosages required may be associated with high bromate concentrations in waters containing bromide.

7.2. EXPERIMENTAL PROCEDURES

7.2.1. Raw water source

In the experiments, raw water from Biesbosch water storage reservoirs was used. Characteristics of Biesbosch water are given in previous chapters.

Initial particle (algal) concentration in the raw water was artificially increased for a number modified jar test experiments (MJTA), using a tangential flow filtration system (Millipore-Pellicon filter holder equipped with membranes of 0.45 μm pore size) in order to simulate seasonal fluctuation of algal concentration (Petrusevski *et al.* 1995, chapter 4).

7.2.2. Experimental set-ups

The experimental set-ups developed and used to establish optimal treatment conditions and to model direct filtration: MJTA, a bench scale continuous direct filtration pilot plant (BSDFPP) and a mobile fully automated direct filtration pilot plant (MDFPP) are described in chapter 3.

Pre-concentrated Biesbosch water (particle count: 2900 part./ml, turbidity: 1.1 FTU) was used in the MJTA experiments. Natural water from the Biesbosch storage reservoirs, after being conveyed over a distance of 30 kilometres, at the site of water treatment plant Kralingen (Rotterdam) was used in pilot plant experiments.

A semi-batch (batch for water phase and continuous flow for gas phase) and a continuous flow ozone reactor were developed to study the interaction between ozone and Biesbosch reservoir water (Figs. 7.1, 7.2, 7.3 and 7.4). Ozone was produced from air using a LABO LO laboratory ozonator (Trailgaz). The semi-batch ozone reactor was used in the experiments with the MJTA. Two glass jars of 5.5 and 8.5 L, vigorously mixed with magnetic stirrers, were used as reaction vessels. A preliminary step was to produce a diagram that establishes a correlation between the volume of ozonated air introduced to the reactor and the concentration of ozone transferred to water. Consequently, it was possible to easily and accurately ozonate raw water with targeted ozone concentrations by measuring the volume of ozonated gas introduced to the reactor. The continuous flow, counter-current ozone reactor was developed and used in the pilot plant experiments. The reactor, a 4.5 m high vertical, transparent PVC column, 133.5 mm in diameter, provided a theoretical detention time of 2,5 minutes. Ozonated gas was discharged from the ozone generator at a pressure of $0.8 \cdot 10^5$ Pa and introduced into the reactor through the fine bubble porous-glass diffuser (Fig.4). Ozone transfer efficiency greater than 99 percent was achieved. Ozone concentrations in produced and off-gas were determined by iodometric methods (APHA 1985).

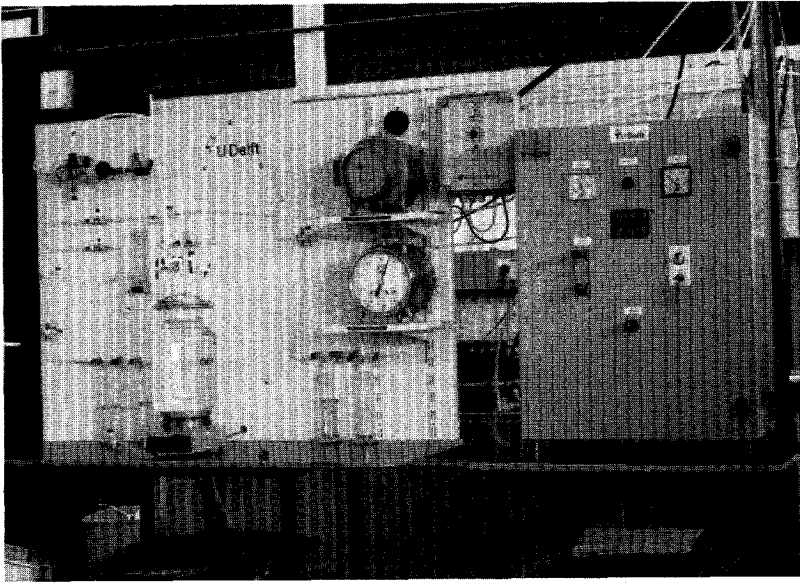


Fig.7.1. Semi-batch ozone reactor developed and used for pre-ozonation studies.

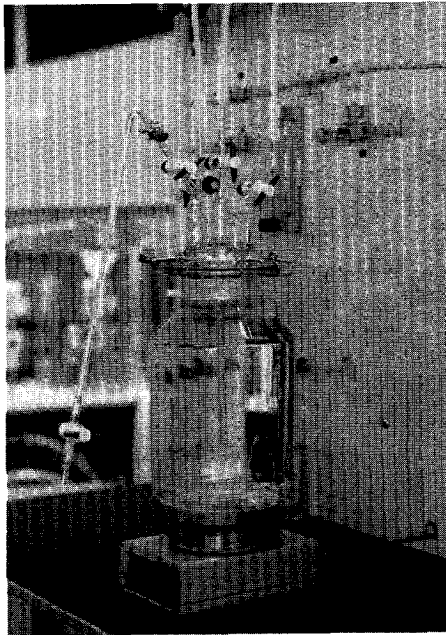


Fig.7.2. The 5.5 l glass jar used as reaction vessel.



Fig.7.3. Vertical, transparent PVC column used as a continuous counter-current ozone reactor.

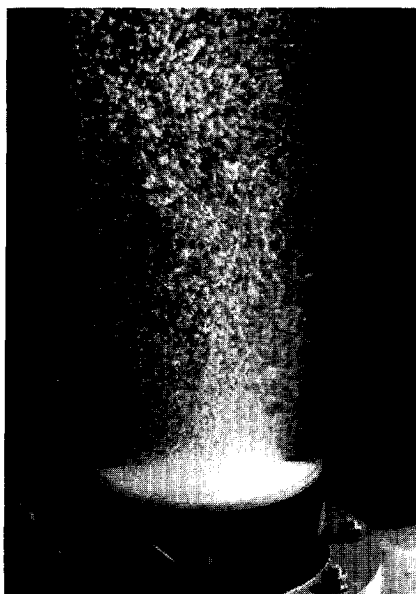


Fig.7.4. Discharge of ozonated gas through fine bubble porous-glass diffuser.

Mixing of the coagulant, ferric sulfate, and raw water in the pilot plant experiments, was achieved with a static mixer with a high energy input ($G=1400\text{ s}^{-1}$, at filtration rate $2.8\cdot 10^{-3}\text{ m/s}$) and short mixing time ($t<1\text{ s}$). In the BSDFPF experiments designed to test treatment performance at different filtration rates, static mixers of different sizes were used to limit the variations in rapid mixing intensity to $\pm 20\%$. Preliminary experiments that were designed to examine the effect of rapid mixing conditions on direct filtration performance (results not included) demonstrated that even much higher variation of mixing intensity, under applied conditions (sweep coagulation) did not show strong effect on direct filtration performance.

The coagulation step was followed with filtration through the BSDFPF or the MDFPF provided with anthracite-sand-garnet filter bed, at a constant filtration rate of $2.8\cdot 10^{-3}\text{ m/s}$, unless otherwise mentioned. Filter media characteristics are specified in chapter 3.

7.2.3. Coagulants

The ferric sulfate solution, used in the experiments with the MJTA, was prepared from analytical grade $\text{Fe}_2(\text{SO}_4)_3\cdot n\text{H}_2\text{O}$. Ferric sulfate, used in the pilot plant experiments, was prepared at the water treatment plant Kralingen-Rotterdam, by the oxidation of ferrous sulfate by oxygen. Four types of polymers were used as coagulant aids or secondary coagulants: Wisprofloc P and Wisprofloc N, as representatives of cationic and non-ionic natural (starch) products, respectively, and Superfloc C-573 and Superfloc A100 as representatives of cationic and anionic synthetic products.

7.2.4. Water quality analyses

Particle counting in a size range $3\text{--}150\text{ }\mu\text{m}$ was performed with the HIAC particle counter (model PC-320). Turbidity was measured by a turbidity meter (Model Sigrist lab 65). Algae were enumerated with inverted microscopy at a magnification of 600x. The standard Dutch waterworks practice for algal enumeration was followed (minimum 50 fields or 400 counted units-cells per sample per species). Chlorophyll- α was measured using the standard spectrophotometric procedure based on the Dutch standards (NEN 6520, 1991).

7.2.5. Video system and scanning electron microscopy

The video system used to provide insight into phytoplankton response to ozonation is described in chapter 3.

The effect of ozone on the morphology of algae has been examined with high resolution scanning electron microscopy (JEOL 6300 F). The examined material was fully hydrated to prevent preparation and observation artifacts. Raw and ozonated water samples were filtered through microporous membrane filter ($0.22\text{ }\mu\text{m}$), the surplus water being sucked away by filter paper. Accordingly, water surrounding algae was removed, but cells were not dehydrated. The filter was mounted on a clamp holder and subsequently frozen in liquid nitrogen. The sample was brought into a cryo-transfer unit (CT 1500 HF, Oxford Instruments, UK), consisting of a high vacuum ($1\cdot 10^{-6}\text{ Pa}$) cryo-preparation chamber and a cryo-holder, inside the SEM. The specimen was placed inside the cryo-chamber at -85°C ,

and sputter coated (Denton) with 3 nm platinum. SEM observation of the coated specimen was carried out at 5 KV and - 180°C.

7.3. RESULTS AND DISCUSSION

7.3.1. Optimization of pre-ozonation and coagulation conditions

Figure 7.5 show the results from the series of MJTA experiments conducted to assess the effect of pre-ozonation on particle removal efficiency and to optimize coagulation and ozonation conditions.

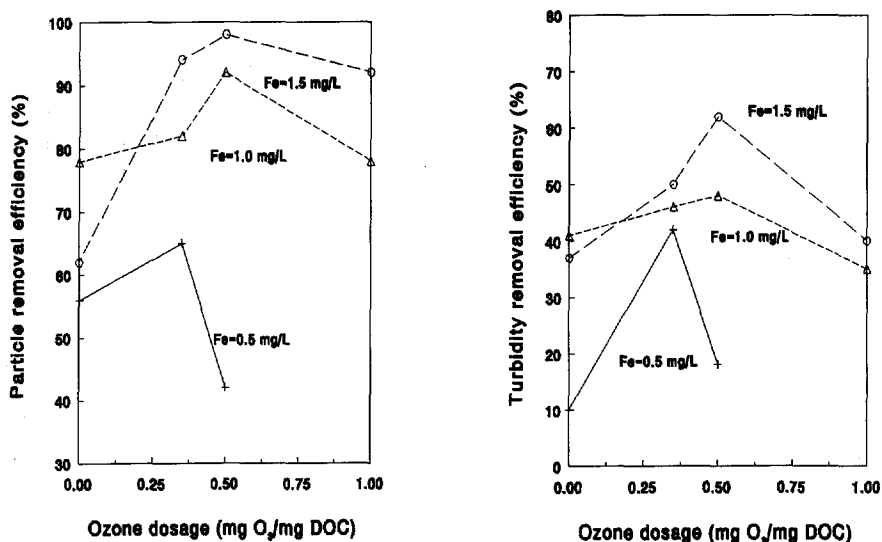


Fig.7.5. Effect of ozone and coagulant dosage on particle and turbidity removal with MJTA;

In these experiments pre-concentrated Biesbosch reservoir water was used with an algal concentration that corresponds to spring algal blooms. These results strongly suggest that pre-treatment with ozone distinctly improves particle removal efficiency. Exceptionally high removal efficiencies (> 90 percent) were obtained even with the MJTA, a simple semi-batch experimental set-up that features a shallow, non-ripened, mono-layer filter bed. The results also clearly show that an optimal ozone dosage exists, and that the overdosing of ozone has a detrimental effect on treatment performance. The optimum particle removal efficiency of 97 % was achieved at the specific ozone dosage of 0.5 mg O₃/mg DOC (1.8 mg O₃ consumed/l). The highest tested dosage of coagulant of 1.5 mg Fe(III)/l was found to produce the filtrate of best quality in terms of turbidity and particle concentration. Higher coagulant dosages were not tested in a view of excessive head loss in the filter bed and associated short filter runs, but also because the examined dosage of 1.5 mg Fe(III)/l was sufficient to achieve

the targeted filtrate quality (turbidity ≤ 0.10 FTU, low particle-algae concentration) in the pilot plant experiments. Pre-ozonation increased the optimum coagulant dosage from 1.0 to 1.5 mg Fe(III)/l, however, the filtrate produced was of considerably higher quality. Turbidity removal followed a similar pattern: pre-ozonation improved filtrate turbidity, and an increase of the ozone dosage above the optimal level increased filtrate turbidity (Fig.7.5). An ozone dosage of 0.5 mg O₃/mg DOC followed by coagulation with 1.5 mg Fe(III)/l resulted in highest particle and turbidity removal. In these experiments ozone was applied at pH=7.5 and the coagulant introduced at pH 8.0. Graphs given in Fig. 7.5 are results from a single series of MJTA experiments. The experiments were repeated to test the reproducibility of the results. The trends and very high particle removal efficiency reported here were found to be reproducible.

The algal population in the Biesbosch water as in other impounded surface water shows strong seasonal, and even weekly fluctuations (Fig.7.6).

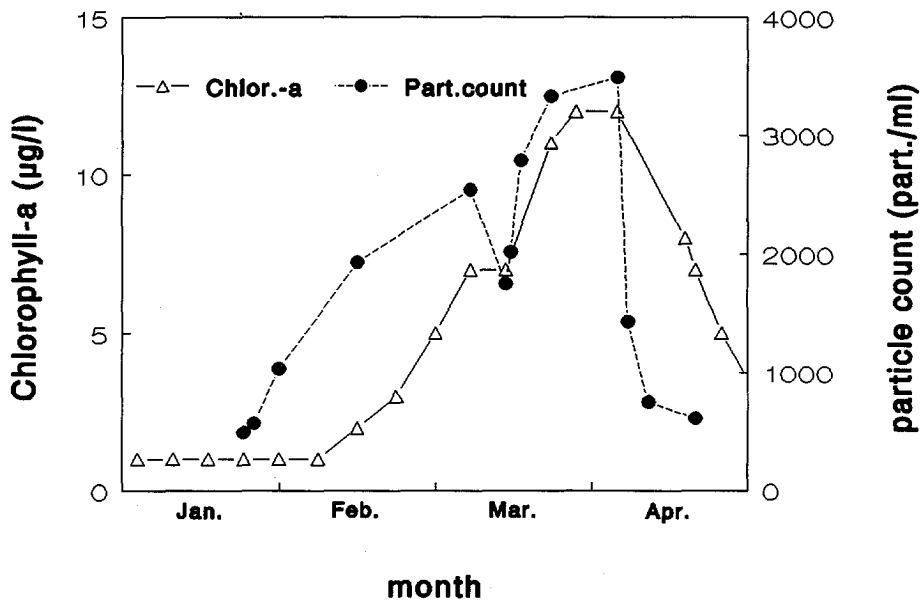


Fig.7.6. Variation of chlorophyll- α and particle concentration in Biesbosch water for the period winter-spring 1994.

Accordingly, an additional set of experiments was designed and conducted to assess the effect of algal concentration on the required ozone dosage. In our experiments we increased the concentration of algae in raw Biesbosch water with the tangential flow filtration system to different previously defined concentration levels. The experiments were conducted with the semi-batch ozone reactor and the MJTA. The pre-ozonated model water (pre-concentrated raw Biesbosch water) was exposed to the standard MJTA procedure (chapter 3). Ferric sulfate dosage was 1.5 mg Fe(III)/l and ozone dosage was altered from 0 to 3.6 mg O₃ /l. The results obtained are synthesized in Fig.7.7. The graph shows that an increase in particle

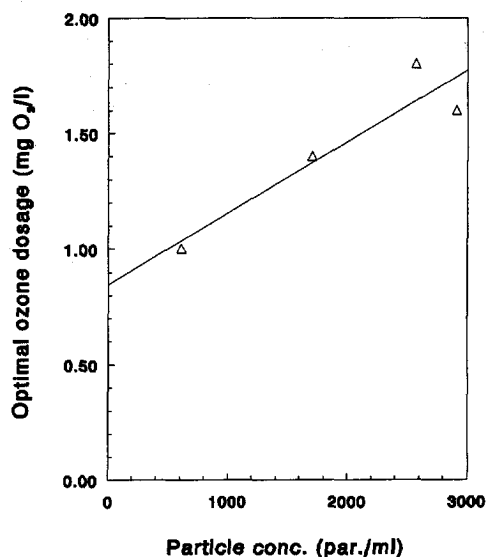


Fig.7.7. Effect of particle-algal concentration on optimal ozone dosage.

(algae) concentration raises the optimal ozone dosage. A good correlation between the optimum ozone dosage and a particle (algae) count was found (correlation coefficient 0.92). Consequently, during the period of a low algae concentration, from November till March, significantly lower ozone dosages, up to 1.0 mg O₃/l, can be applied, thus reducing the operational costs and the risk linked with the formation of the health hazardous ozonation by-products (e.g. bromate). The highest ozone dosage of 1.8 mg O₃/l, required during short algal blooms is still below the minimum ozone level of 2.0 mg/l, reported to lead to the formation of bromate in Meuse water above the bromate detection limit (2 µg/l at the time when reported experiments were conducted, Kruithof *et al.* 1992, 1995). It should be emphasised that the short term nature of these experiments did not allow for the study of the effect of different algal species on optimal ozone dosage. Required ozone dosage might to some extent change due to differing properties of algal species; these differences include size, type and amount of produced extracellular organic matter (EOM), surface and other properties (like motility). However, the results obtained may be considered valid due to the presence in the experiment water of the two most important algal groups: centric diatoms (such as *S. hantzschii*, *S. astraea* and *Cyclotella* sp.) which are responsible for spring algal blooms and motile species (like *R. minuta*, *Navicula* sp.) which are the most difficult to remove.

The results obtained also indicate that in addition to chlorophyll- α , the particle count is a valuable indicator of algal concentration, that can be easily and routinely used to establish required ozone dosage.

Relatively low ozone dosages (≤ 1.8 mgO₃/l) coupled with short associated contact time (2-3 minutes) were required to introduce ozone-related beneficial coagulation effect. This together with the results from the recent studies on bromate formation in Biesbosch water under

different treatment conditions (Kruithof *et al.* 1995) indicate that bromate formed as a consequence of pre-ozonation will be bellow existing standards and likely below the detection limit (2 µg/l).

7.3.2. Point of Coagulant Addition

The effect of the time lag between ozonation and coagulant addition on the coagulating effects of ozone was studied in a separate set of experiments. Pre-concentrated raw Biesbosch water was pre-treated with 1.8 mg O₃/l in the semi-batch ozone reactor and then exposed to the standard MJTA procedure. The results (Fig.7.8) show that a delay in coagulant addition following pre-ozonation, has strong negative effects on process performance - the longer the time period between pre-ozonation and coagulant addition the higher were the filtrate particle count and turbidity. The beneficial coagulating effects of ozone were found to be strongest for a very short time interval of about one minute between pre-ozonation and coagulant addition. Such a short time lag between ozonation and coagulation resulted in filtrate with the lowest particle concentration and turbidity. The experiments were repeated under similar conditions. The trend reported here were found to occur each.

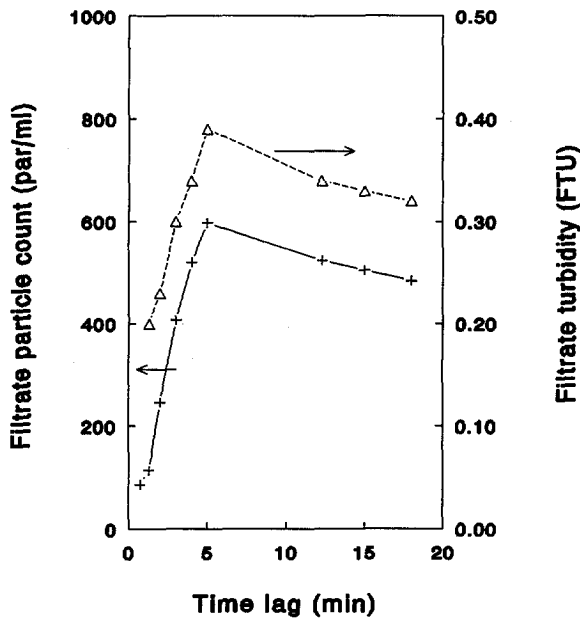


Fig.7.8. Effect of time lag between ozonation and coagulation; MJTA experiments with concentrated Biesbosch water: 4050 part/ml, turbidity 0.9 FTU; ozonation: 1.8 mg O₃/l, coagulation: 1.5 mg Fe(III)/l.

The reason why this process design parameter plays such important role is unclear. Jekel (1983) proposed that one of the process mechanisms that contribute to the beneficial coagulating effect of ozone is ozone reaction and partial removal of natural organic matter adsorbed on particle surfaces. This organic layer stabilises particles and interferes with coagulation process. It may be speculated that ozone-induced removal of organic matter from the particle surface takes place instantly and that this process is reversible. After a specific time it is likely that organic matter present in water may again adsorb on particle surface, thus again hindering the coagulation process and resulting in increased particle count in the filtrate.

The results obtained were used as useful process design criteria for design of continuous flow ozone reactors aimed at improving particles agglomeration and removal by subsequent treatment.

7.3.3. Advanced oxidation process: combination of ozone and hydrogen peroxide

The effect of a advanced pre-oxidation process, the combination of ozone and hydrogen peroxide, on coagulating ozone effects was examined in separate set of MJTA experiments. In these experiments pre-concentrated Biesbosch water was pre-treated with ozone (1.8 mg O_3 consumed/l) and hydrogen peroxide in a wide dosage range to achieve H_2O_2/O_3 ratio between 0 and 0.8. Hydrogen peroxide was introduced in semi-batch reactor two minutes after the start of ozonation process. It was considered that this sequence of addition and a delay in peroxide addition would allow to benefit from both: the direct molecular ozone reactions and subsequently from the radical type reactions. The pre-oxidation step was followed by coagulation with ferric sulfate (1.5 mg $Fe(III)/l$) and filtration. The results given in Fig. 7.9 show that the addition of hydrogen peroxide at H_2O_2/O_3 ratios up to 0.6 did not have a strong effect on filtrate quality in terms of particle concentration and turbidity. It may be assumed the ozone introduced to the reactor was mostly consumed before peroxide addition because of relatively low ozone dosage applied and high instantaneous raw water ozone demand. Unfortunately, the residual ozone concentrations in the water were not monitored. Higher ozone dosages that would result in higher residual ozone concentrations and consequently more ozone available for reaction with peroxide were not tested because of the bromate-associated problems. An increase of hydrogen peroxide dosage above 0.6 mg/l disrupted the flocculation process thus increasing filtrate turbidity and particle count. These results also substantiate hypothesis that the initial direct molecular highly selective ozone reactions are most important regarding the coagulating effects of ozone. The subsequent the radical-induced reactions may even lead to a formation of products which have an adverse effect on coagulation process.

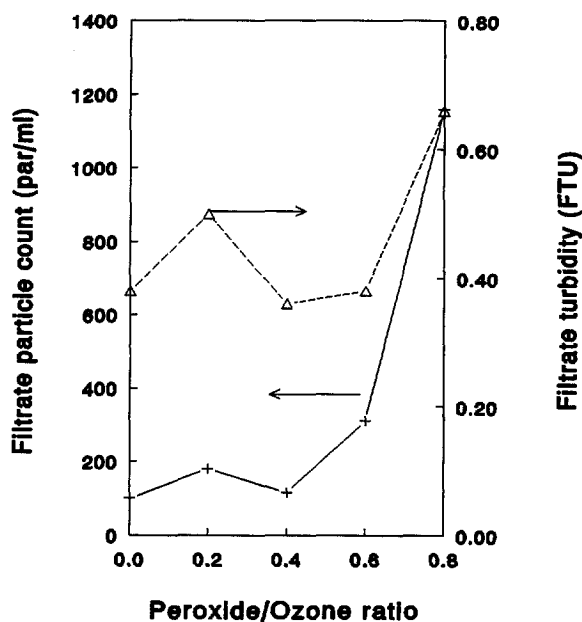


Fig.7.9. Effect of hydrogen peroxide-ozone ratio on the MJTA filtrate turbidity and particle count; pre-concentrated Biesbosch water: 4500 part./ml, turbidity 1.2 FTU; treatment: 1.8 mg O_3 /l, 1.5 mg $Fe(III)$ /l.

7.3.4. Pre-ozonation and coagulation with dual coagulant: ferric sulfate and polymer

The microscopic examinations of the coagulated suspension have shown that pre-ozonation enhanced agglomeration of algae and other particles, and consequently significantly improved their removal. However, some particles, predominantly spherical, green non-motile algae, smaller than $3\ \mu m$, further on referred to as μ -algae, were found in the MJTA filtrate. The applied treatment although significantly improved by pre-ozonation was still inadequate to eliminate these particles completely. It may be speculated that the agglomeration kinetics under experimental conditions (sweep coagulation with low coagulant dosage ($\leq 1.5\ mg\ Fe(III)/l$) and relatively low particle concentration in raw water), was not sufficient to agglomerate these very small particles. Fundamental studies (Yao *et al.* 1971; O'Melia 1985) have shown that a filter has a minimum removal efficiency for particle diameters of 1 to $3\ \mu m$. The increase of agglomeration kinetics brought about by applying higher coagulant dosages were considered impractical because of the drawback, significantly reduced filter run length and very high removal efficiency of particles $> 3\ \mu m$ already achieved at coagulant dosage of $1.5\ mg\ Fe(III)/l$.

Appropriately, the next set of experiments was designed and performed to assess the capability of polymers applied as coagulant aids to enhance the agglomeration kinetics of small algae and already formed micro-flocs, and accordingly to improve their removal in a

filtration step. The preliminary MJTA experiments were conducted with four different types of polymers. The experimental procedure included pre-ozonation at an optimal ozone dosage of 1.8 mg O₃/l, coagulation with ferric sulfate (1.5 mg Fe(III)/l), addition of a polymer (0.15 mg/l) and filtration at a constant filtration rate through small scale filters. All polymers tested showed a strong beneficial effect on particle removal efficiency. However, application of cationic polymers resulted in higher particle removal efficiency. The superiority of cationic polymers was even more evident regarding turbidity removal. These results confirmed that the coagulation of small spherical, non-motile algae with a regular shape, follows the charge neutralisation principle. The use of cationic polymers reduced their stability induced by their negative surface charge. The best results were achieved with synthetic cationic polymer Superfloc C-573 and therefore, this particular polymer was selected for further experiments. Subsequent MJTA experiments were designed to study the effect of polymer dosage on a process performance. The effect of different polymer dosages (0-1.0 mg/l) on filtrate turbidity and particle concentration are given in Fig. 7.10. These results show that increase of polymer dosages above 0.15 mg/l reduces filtrate particle concentration and residual iron concentration. Direct filtration treatment supported by pre-ozonation and coagulation with ferric sulfate (1.5 mg Fe(III)/l) and cationic polymer (>0.60 mg/l) almost completely eliminated particles which can be detected by the HIAC particle counter (the size range 2.7-150 μ m). It should be pointed out that these results were obtained with a very simple experimental set-up the MJTA, that features only short and clean beds, thus even higher removal efficiency can be expected in full scale applications.

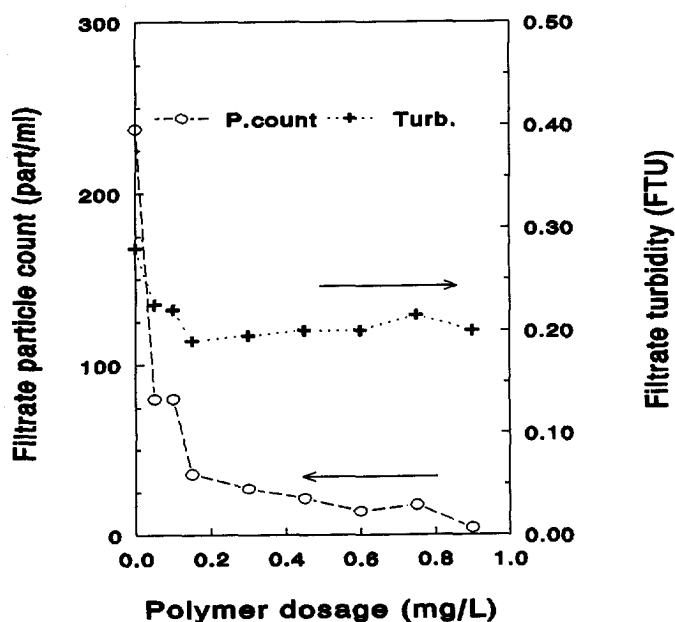


Fig.7.10. Effect of cationic polymer dosage on the MJTA filtrate quality; pre-concentrated Biesbosch water: particle count 4500 particles/ml, turbidity 1.2 FTU.

7.3.5. Pilot plant experiments

Confirmation experiments were performed with pilot plant installations, the MDFPP and the BSDFPP, to verify the results obtained with the MJTA. The BSDFPP provided the potential to establish and assess in parallel four direct filtration treatment systems operated under different conditions. The treatment alternatives examined are shown in Fig.7.11. Biesbosch water used in this experiment had turbidity of 0.63 FTU, particle count of 1150 particles/ml (particle size range 3-150 μm) and temperature 8 °C.

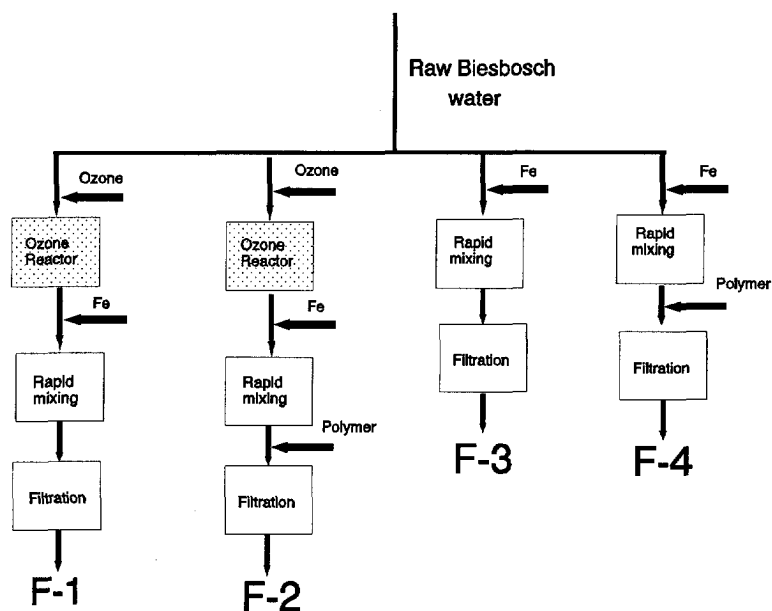


Fig.7.11. Alternatives examined with the BSDFPP; ozone 1.8 mg O_3/l , coagulants: 1.5 mg $\text{Fe(III)}/\text{l}$, polymer 0.6 mg/l; filtration: anthracite/sand/garnet beds, filtr. rate $2.8 \cdot 10^{-3}$ m/s.

The ferric sulfate dosage was 1.5 mg $\text{Fe(III)}/\text{l}$. Cationic polymer was introduced as a secondary coagulant (0.6 mg/l) in treatment lines F-2 and F-4. The treatment lines F-1 and F-2 received pre-ozonated raw water (1.8 mg consumed O_3/l). Pre-ozonation improved particle removal efficiency by more than 1.0-log removal unit in comparison with treatment trains without pre-ozonation (Fig. 7.12). The direct filtration treatment train that included pre-ozonation and coagulation with dual coagulants (ferric sulfate and cationic polymer) achieved particle removal efficiency of 99.7 percent (approximately 3.0-log removal units). Filtrate of very low turbidity (<0.1 FTU) was easily achieved in all pre-ozonated treatment lines. Microscopic examinations revealed that only very low concentration of μ -algae is present in the filtrate of direct filtration treatment line F-1. Microscopic filtrate examination demonstrated that the use of cationic polymer as a secondary coagulant (treatment line F-2) provided nearly complete elimination of algae and other particles larger than 1 μm .

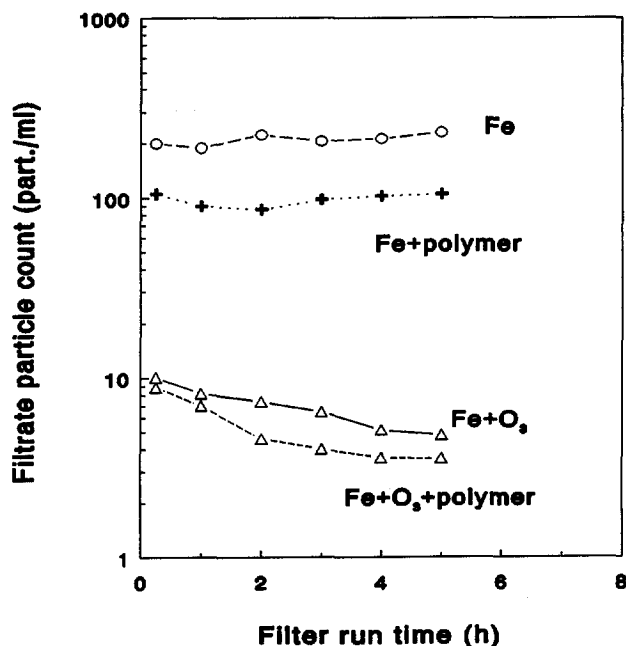


Fig.7.12. Effect of treatment mode on the BSDFPP filtrate particle concentration.

The supplementary filter runs were performed with the larger scale pilot filtration unit the MDFPP, which is considered to reflect more closely full scale applications. Raw Biesbosch water was pre-ozonated (1.8 mg O₃ consumed/l) and coagulated with 1.5 mg Fe(III)/l. The results obtained with the MDFPP (Fig.7.13.) correlated well with the results found with the smaller scale units, namely the MJTA and the BSDFPP, thus confirming the beneficial impact of pre-ozonation on direct filtration performance.

Filter runs with BSDFPP and MDFPP were repeated several times under similar treatment conditions and with Biesbosch water characterised by variable quality. In total more than 10 series of filter runs were performed. Powerful beneficial effect of ozone on particle and turbidity removal in direct filtration was consistently observed in all filter runs conducted. It is interesting to note that the particle concentration in the produced filtrate was consistently comparable or even lower in comparison with the particle concentration in demineralised water used for the flushing of the particle counter.

The filtration unit contributes substantially to the total cost of a direct filtration treatment plant. Furthermore, the applied filtration rate strongly influences the net water production (m³/m²/day) of a filtration plant and accordingly related investment costs (see chapter 2). Consequently, separate filter runs were performed with the BSDFPP to preliminary assess the effect of filtration rate on filtrate quality and specifically to test if higher filtration rates can be applied. Raw Biesbosch water (turbidity 0.60 FTU, 950 particles/ml, temperature 16

°C) was pre-ozonated with 1.8 mg O₃ consumed/l, coagulated with 1.5 mg Fe(III)/l and 0.6 mg cationic polymer, and filtered through the anthracite-sand-garnet filter bed, at filtration rates of 5, 10, 15 and 20 m/h. Filtration rate, within the range tasted, did not have pronounced effect on filtrate quality as measured by filtrate turbidity and particle count (Figs. 7.14 and 7.15). Filtrate of exceptionally low turbidity (< 0.1 FTU) and particle concentration (~5 particles/ml) was produced after ripening period irrespective of the filtration rate applied.

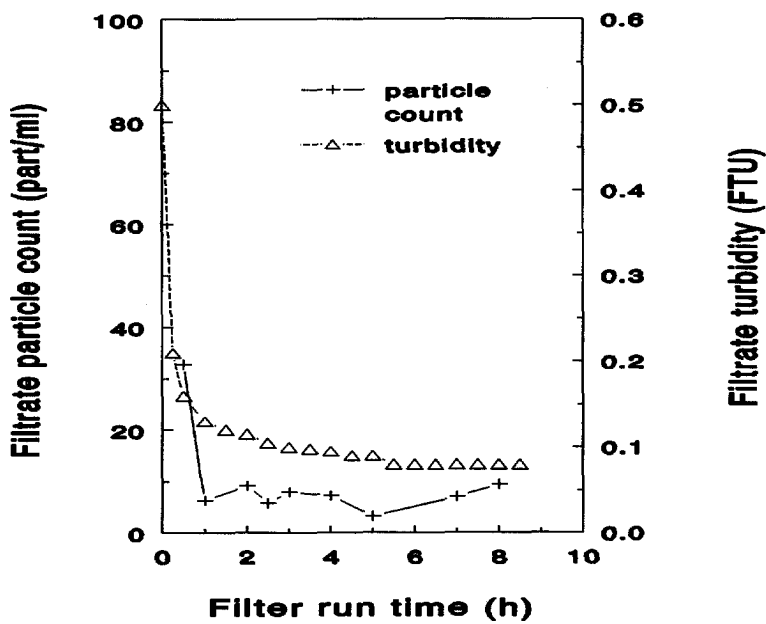


Fig.7.13. MDFPP filtrate turbidity and particle count. Pre-ozonation 1.8 mg O₃/L, coagulant: ferric sulphate 1.5 mg Fe(III)/L

It is known that filter transport efficiency deteriorates at higher filtration velocity and, as a consequence, the filtration efficiency may be reduced. Results obtained however, confirmed that under conditions investigated the filter transport mechanism is not critical process in particle capture in the filter. It appears that applied ozone pre-treatment and coagulation with iron and cationic polymer very efficiently destabilizes algae and other particles in alga-size range, alters their surface properties and provides favourable conditions for their agglomerations and attachment to the filter grains. In addition, cationic polymer presumably causes strong attachment of formed agglomerates to filter grains and improves shear strength of the deposits that specifically reduces detachment of the deposits.

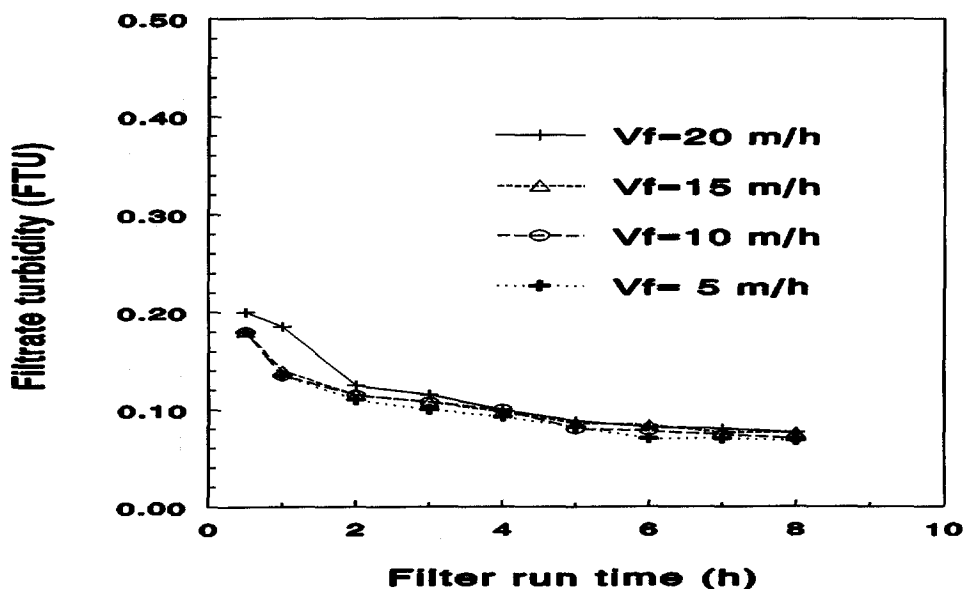


Fig.7.14. Effect of filtration rate on BSAFPP filtrate turbidity; 1.8 mg O_3 /l, 1.5 mg Fe(III)/l and 0.6 mg cat. polymer/l; anthracite-sand-garnet media; raw water turbidity 0.60 FTU.

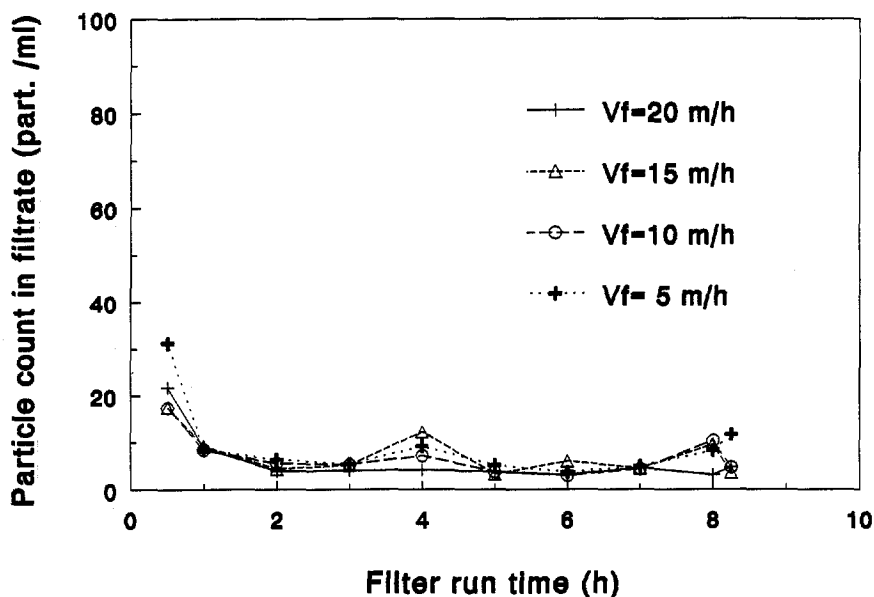


Fig.7.15. Effect of filtration rate on particle count in BSAFPP filtrate; 1.8 mg O_3 /l, 1.5 mg Fe(III)/l and 0.6 mg cat. polymer/l; anthracite-sand-garnet media; raw water particle count 950 part./ml.

Filter resistance in the filter bed positively correlated with the applied filtration rate (Fig. 7.16). Unfortunately, the BSDFPF limited the maximum length of filter runs to approximately 8 h, and, in addition, the system of piezometers used for resistance measurement limited the maximum resistance that can be measured to approximately 1.50 meters. Consequently, the filter bed resistances that correspond to longer filter runs were extrapolated (linear correlation between filter bed resistance and run time, with the correlation coefficient $r=0.99$, was established). Higher filtration rates of 15 m/h and 20 m/h, characterised by higher initial resistance and faster resistance development, limit the maximal length of filter runs to approximately 10 hours and 16 hours, respectively (assumed maximal filter resistance of 3.0 m). However, even this relatively short filter run time may be economically attractive in view of the considerably reduced required filter area (chapter 2).

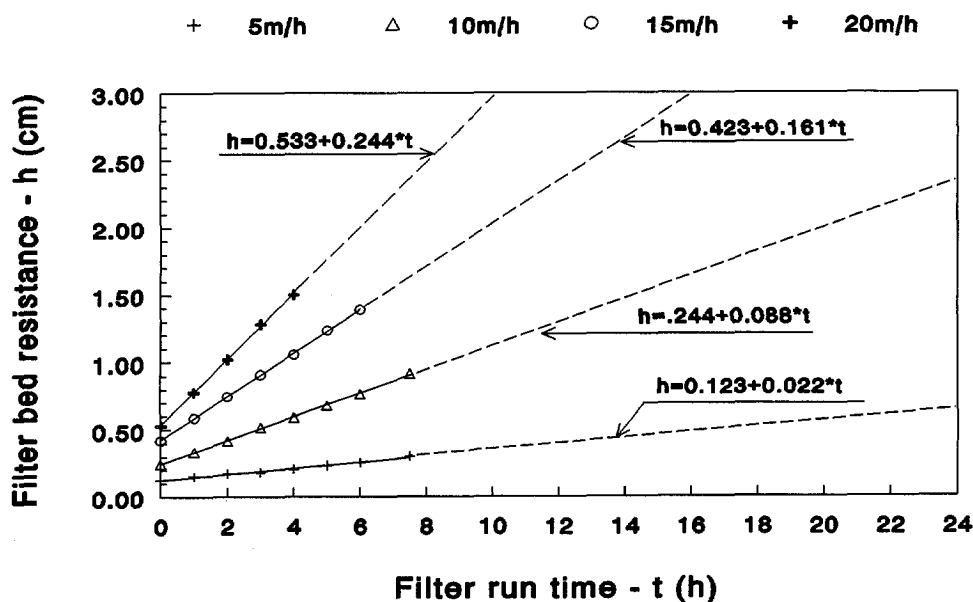


Fig. 7.16. Effect of filtration rate and run time on filter resistance; markers on solid lines measured values, broken line - extrapolated values.

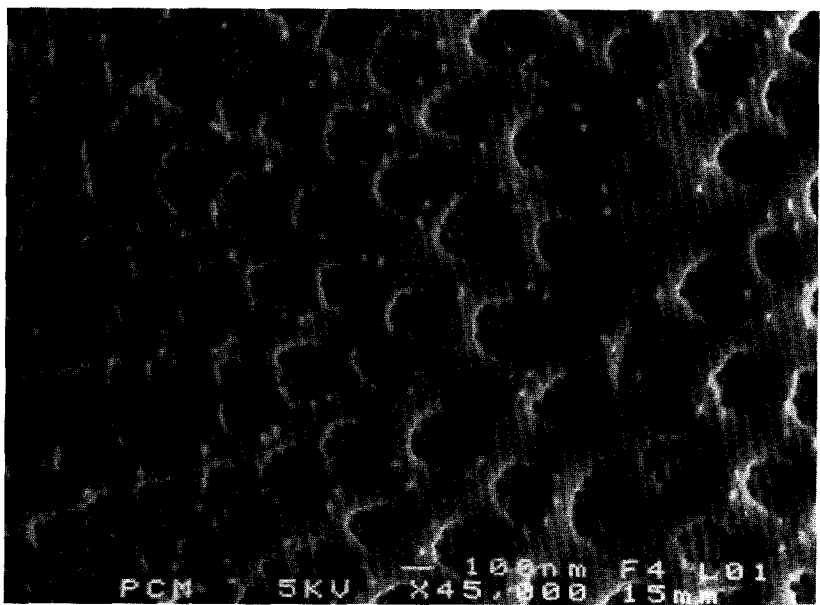
The available direct filtration pilot plants did not allow testing of filtration rates higher than 20 m/h. Nevertheless, results obtained indicate that direct filtration supported by pre-ozonation and coagulation with ferric sulfate and cationic polymer can likely be operated at much higher filtration rates than currently applied at the full-scale conventional treatment plants that treat Biesbosch water. Appropriately, the economic attractiveness of direct filtration applied in the treatment of Biesbosch water may possibly be even further advanced by maximizing the applied filtration rate and consequently reducing the size of the required filtration unit. However, further and more detailed optimisation pilot plant experiments are required to examine a wider range of process conditions (e.g. filtration rate, filter media composition, depth of supernatant water). Pilot plant experiments should be carried out

continuously through the year, thus covering various seasons. Such pilot plant experiments should be supported by the economic optimization of a filter unit that will lead to a least-cost design.

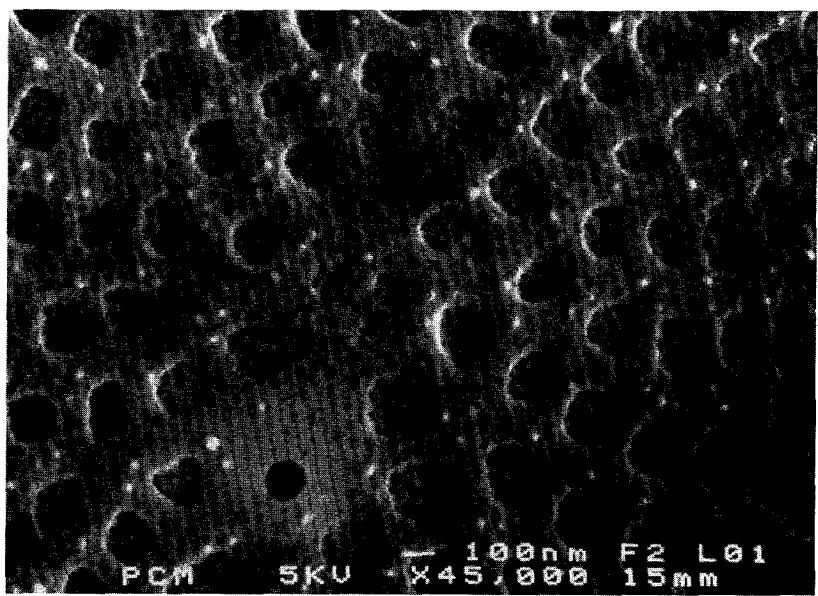
7.3.6. Process mechanisms

In addition to conventional water quality parameters that demonstrated enhanced algae removal following pre-ozonation, supplementary techniques like SEM and a video system for in-situ observation were employed to reveal the underlying mechanisms and propose a model that illustrates particle and algae removal. Ozone induced enhanced particle and algae removal can be attributed to a number of mechanisms that take place simultaneously. The SEM micrographs verified the commonly cited mechanism: reduced particle stability through a reaction of ozone with the organic coating on the particle surface (Jekel 1983, Singer 1990). Ozone attacks and partly removes organic coating on the valve elements of cylindrical diatoms, thus roughening the algal surface (Fig.7.18) improving attachment of metal coagulant precipitates on algal surface, and destabilizing algal cells. In addition, ozone attacked sites on algal cell walls, modifying algal surface properties. An ozone dosage of 1.8 mg/l seriously damaged the girdle element that linked two valves of cylindrical diatoms and protects their cytoplasm (Fig.7.17). The algal cells treated with ozone look like they lost their turgor. Even more serious damage was observed on other algal species. An ozone dosage of 1.8 mg/l is sufficient to cause a complete collapse of *M. aeruginosa* cells. Consequently, ozone reduces algal stability and enhances their possibility for agglomeration, in agreement with the mechanism proposed earlier by Sukenik *et al.* 1987. SEM micrographs also confirmed that algae under stress conditions, like oxidation, secrete and diffuse biopolymers into the surrounding media. Bernhardt and Clasen (1991) found that algae derived extracellular organic matter (EOM) from green algae, blue-green algae and diatoms cultures behave like anionic or non-ionic polyelectrolyte. They reported that the EOM from the green alga *Dictyosphaerium* proved to have very strong impact on coagulation and filtration, equivalent to that of a weak anionic polymer. These algal products can assist in the coagulation of other particulate matter present in water.

In-situ observation with the video system have demonstrated that ozone dosage ≥ 1.0 mg O₃/l completely immobilize or significantly reduce active locomotion of motile algal species like the characteristic motility of algal flagellates (like *R. minuta*, *Cryptomonas* sp., *Chlamydomonas*) as well as gliding locomotion in motile pennate diatoms (like *Navicula* sp. and *Nitzschia* sp.). Our earlier observation with a video system has shown that algal motility plays an important inhibitory role during algal coagulation with ferric sulfate. Through active coordinated locomotion motile algae try to avoid collisions with metal coagulant precipitates or release themselves from flocs once being entrapped thus significantly reducing their agglomeration kinetics and removal efficiency (Petruševski *et al.* 1993, chapter 3). Observation with the microscope and the video system has also shown that the interaction of ozone and algae is species dependent. Diatoms appear to be less resistant than other species.

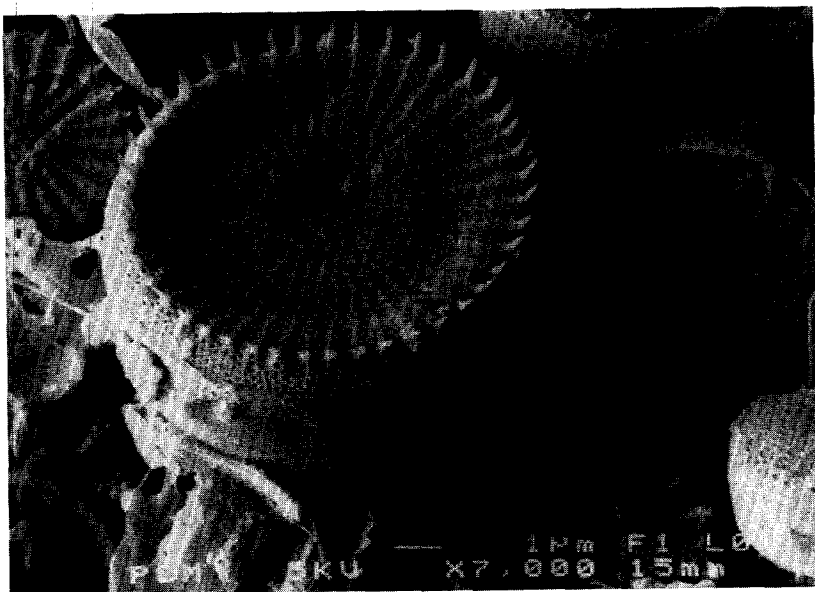


a.

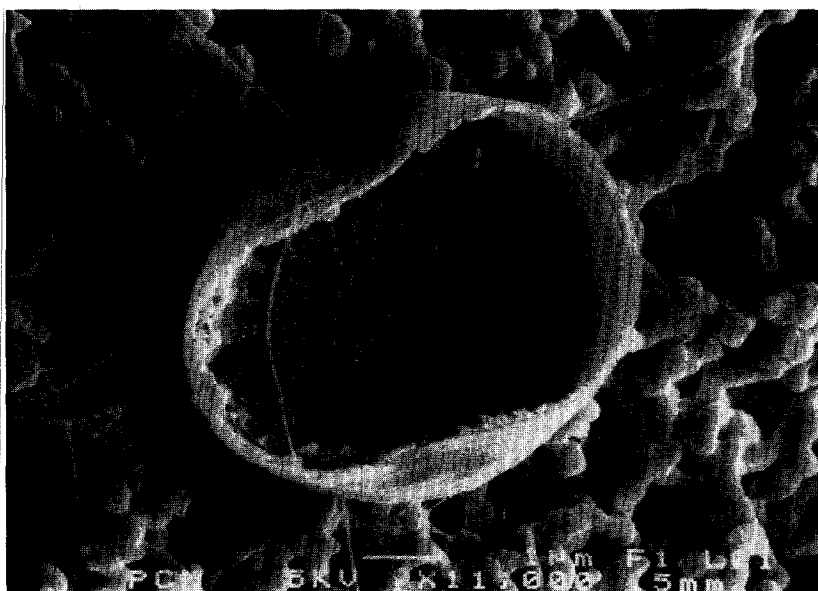


b.

Fig.7.17. SEM micrographs of *S. hantzschii* valve element before (a) and after (b) treatment with 1.8 mg O₃/L; scale bar 100 nm.



a.



b.

Fig.7.18. SEM micrographs of *S. hantzschii*, before (a) and after (b) treatment with 1.8 O₃/L; scale bar 1 µm.

S.hantzschii, *Navicula* sp., *Nitzschia* sp. started partly losing their colour at ozone dosage of 1.0 mg /l. Diatoms completely lost green colour at ozone dosages above 5 mg/l. μ -algae appeared to be the most ozone resistant algal species: even at ozone dosage of 10 mg/l these algae preserved their green colour.

Application of a cationic polymer as secondary coagulant reduced their surface charge thus increasing their agglomeration efficiency. In addition, video observations showed that polymers enhanced flocculation efficiency through sweep coagulation. The polymer added to water introduces a net-like structures that improve agglomeration kinetics, by entrapping more efficiently algae and other raw water particles as well as iron precipitates.

7.4. CONCLUSIONS

The results from semi-batch tests with MJTA as well as pilot plant experiments with BSDFPP and MDFPP demonstrated that pre-ozonation of Biesbosch reservoir water is essential to increase particle and algae removal from 1.0-log removal, commonly achieved in straightforward direct filtration, to ≥ 2.0 -log removal units (SWTR requirements, also in agreement with the interim standard of the German association of drinking water reservoirs regarding the chlorophyll- α concentration in produced water). Direct filtration applied to pre-ozonated Biesbosch reservoir water achieved approximately 3.0-log removal of particles and algae in the size range 3.0-150.0 μm and produce a filtrate of very low turbidity (< 0.1 FTU), and residual iron < 0.05 mg/l. The coagulating effect of ozone is dosage related. A positive correlation between the optimal ozone dosage and algal concentration was established with MJTA. Inspection of the filtrate under the microscope indicated that application of cationic polymer as a secondary coagulant improves removal of very small algae and particles < 3.0 μm . Filtration rates up to 20 m/h did not have any adverse effect on filtrate quality as measured by particle count and turbidity.

Very efficient removal of algae is a consequence of a number of process mechanisms involved. Pre-ozonation alters algal surface properties and immobilizes motile algae thus reducing their stability. In addition, oxidation provokes algae to release biopolymers that act as a coagulant aid that improves agglomeration of other particles. The coagulation of algal cell with iron salts, under the conditions applied, takes place exclusively through sweep coagulation. Application of cationic polymer as a secondary coagulant enhances the coagulation process by reducing algal negative surface potential. In addition, the polymer added to water introduces net-like structures that improve agglomeration kinetics. This further accelerates algal agglomeration kinetics. Algal-coagulant agglomerates formed in such a way are efficiently removed in anthracite-sand-garnet filter beds.

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Chapter 8

EFFECT OF PERMANGANATE PRE-TREATMENT AND COAGULATION WITH DUAL COAGULANTS ON PARTICLE AND ALGAE REMOVAL IN DIRECT FILTRATION*

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*B. Petruševski, A.N. van Breemen and G.J. Alaerts (1995). Proceedings IAWQ-IWSA Workshop on Removal of Microorganisms from Water and Wastewater, Amsterdam, October 1995. Submitted to *J Water SRT-Aqua*.

ABSTRACT - Potassium permanganate as an alternative pre-oxidant for the direct filtration of impounded surface water has been investigated. The experiments with the modified jar test apparatus and pilot plants showed that permanganate pre-treatment followed by coagulation with dual coagulants (ferric sulphate and cationic polymer) distinctly improved particle and algae removal commonly achieved in direct filtration. Additionally, this treatment completely eliminated increased filtrate turbidity and residual manganese. Efficient removal of algae and other particulate matter is suggested to be a consequence of several process mechanisms. Permanganate inactivates motile microorganisms, induces *in situ* production of natural, algae derived coagulant aid, enhances the coagulation process by oxidising and adsorbing organic molecules that otherwise may hinder coagulation, and accelerates the flocculation kinetics by increasing particle concentration. The subsequent application of dual coagulant results in further coagulation through enmeshment in a precipitate, and adsorption coagulation and charge neutralisation.

8.1. INTRODUCTION

Direct filtration is an economically and environmentally attractive process for producing drinking water from oligotrophic and, to a certain extent, mesotrophic impounded surface water, because of the comparatively simple treatment scheme and lower chemicals requirement. The production of drinking water from these water bodies is associated with algae-related problems, notably the algal penetration through the treatment system causing several inconveniences (Petruševski *et al.* 1993a, Chapter 2). Particles, and particle types such as algae, are not subject to specific regulation in existing drinking water quality regulations. In drinking water treatment practice, turbidity has been used for decades as a basic, lumping parameter to represent aesthetic and organoleptic values of drinking water, but it has also been used to indicate the presence of possibly harmful colloidal and particulate matter. The maximum admissible and guide turbidity levels have been continuously reduced as a consequence of general scientific and technical development, and more pronounced health concerns. Today, drinking water produced in the Netherlands does not generally exceed turbidity levels of 0.1 FTU (the official guide level proposed by VEWIN, The Association of Dutch Waterworks is 0.2 FTU, assuming that disinfection is included). In USA, guideline level of 0.1 FTU has been established for drinking water turbidity (Premazzi *et al.* 1989). However, at such low turbidity levels, this parameter is not a reliable indicator of particle concentration (Petruševski *et al.* 1995b, Chapter 6). In addition to common algae-associated inconveniences, several recent large-scale water-borne outbreaks of cryptosporidiosis in the USA and in the United Kingdom (Anon. 1990, Pontius 1993) have called into question current drinking water treatment standards by showing that water that fulfils existing regulations may still be hazardous to health. Specifically, a problem was caused by *Cryptosporidium* oocysts that had passed the treatment system but had been not identified by the turbidity or other standard water quality measurements. Conventional disinfectants like chlorine and ozone, at the levels commonly used in water treatment, are ineffective in eliminating oocyst infectivity (Parker *et al.* 1993, Pontius 1993). *C. parvum* oocysts are also reported to occur in Dutch surface water and in the large Biesbosch reservoirs in the Netherlands (Ketelaars *et al.* 1995). The outbreaks also argue in favour of

very efficient elimination of particles in the oocyst size range (4-12 μm). In addition, these developments stress the need for a more detailed method of particle counting to supplement turbidity measurement in assessing treatment performance. Particle counting supported by particle size measurement can be very useful in indicating plant's real capacity to remove particles in a specific size range, and consequently to fulfil the requirements established in the Surface Water Treatment Rule - SWTR (Von Huben 1991) for removal or inactivation of particles like *Giardia* cysts (3-log removal for raw water with < 1 cyst per 100 l, 4-log removal for raw water with 1-10 cysts per 100 l, 5-log removal for raw water with 10-100 cysts per 100 l). Ketelaars *et al.* (1995) reported that the concentration of *Giardia* cysts in Biesbosch water varies between 0.05 and 0.75 cysts per 100 litres, with an average value of 0.04 cysts per 100 litres. This indicates that 3-log removal of *Giardia* cysts is adequate for Biesbosch water to comply with the removal requirements established in the SWTR.

Pre-treatment with oxidants such as chlorine, chlorine dioxide and ozone may enhance the coagulation process and also assist to better remove particulate matter, and specifically algae in subsequent treatment (Hodges *et al.* 1979, Janssens *et al.* 1987, Langlais *et al.* 1991, Petruševski *et al.* 1993a, Chapter 5). However, after the hazardous properties of some chlorine and chlorine dioxide by-products (e.g. chloroform and likely chlorite) were recognised, the use of these chemicals as pre-oxidants became unpopular, or was even banned in some countries (e.g. Germany). Pre-chlorination appears to contribute most significantly to the formation of chlorination by-products, particularly trihalomethanes (THMs). In the last decade, ozone has been investigated and applied as an effective replacement for chlorine. Laboratory and pilot plant investigations and full-scale applications have confirmed that properly applied pre-ozonation under favourable conditions can strongly enhance subsequent treatment efficiency, and reduce the number of particles in filtrate by more than one order of magnitude (Reckhow *et al.* 1986, Janssens *et al.* 1987, Hubel *et al.* 1992, Petruševski *et al.* 1994, Chapter 7).

However, in addition to the inability of ozone to show such coagulating effect with particular raw water types (Reckhow *et al.* 1986, Chang and Singer 1991, Langlais *et al.* 1991, Tobiason *et al.* 1992) a recent investigation also revealed that the ozonation of water containing bromide (e.g. the rivers Meuse and Rhine) may lead to bromate formation to a level suspected of being hazardous to health (Kruithof *et al.* 1993). Another negative consequence of pre-ozonation is the considerable production of assimilable organic carbon (AOC) in the oxidised water and sometimes even in drinking water causing after-growth of bacteria and higher organisms in the distribution system (Van der Kooij 1990). These aspects are of particular concern in the Netherlands where chlorination is no longer used routinely to safeguard the quality of drinking water in the distribution system.

Therefore, potassium permanganate has been considered as an alternative pre-oxidant for the direct filtration of impounded surface water from the Biesbosch storage reservoir. The results from preliminary experiments designed to assess the effect of ozone, hydrogen peroxide, the combination of ozone and hydrogen peroxide, and potassium permanganate, suggested that,

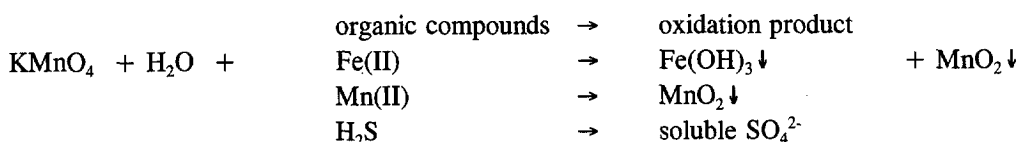
besides pre-ozonation, pre-treatment with potassium permanganate enhances the removal of particulate matter and algae in direct filtration. However, drawbacks, notably increased manganese and turbidity levels in the filtrate were also experienced (Petruševski *et al.* 1993b, Chapter 5).

The objectives of this chapter are:

- (a) to review the literature on potassium permanganate use in water treatment practice focusing on its application as pre-treatment aimed at improving particle and algae removal in direct filtration,
- (b) to present the results of batch and continuous pilot plant experiments designed to study treatment strategies improving treatment performance whilst resolving potassium permanganate related inconveniences,
- (c) to quantify and to detail the effect of pre-treatment with potassium permanganate on direct filtration performance, and
- (d) to describe the involved process mechanisms.

8.2. POTASSIUM PERMANGANATE CHEMISTRY

Manganese has several valencies and therefore a large number of reaction pathways. Consequently, permanganate, the highest (7+) oxidation state of manganese, is one of the most versatile oxidation agents. Oxidation reactions that take place under weakly acid, neutral, and weakly alkaline conditions (pH = 6-9), however, are the most interesting in drinking water treatment practice. Under these conditions the permanganate is reduced by the dissolved iron and manganese, hydrogen sulfide and organic compounds in the raw water into stable insoluble manganese dioxide, a hydrous product of indefinite stoichiometric composition:



This oxidation product may be represented more correctly as MnO_(1+x), where the x ranges from about 0.1 to 0.95, depending on the particular conditions of formation (Poselt *et al.* 1968). For the sake of convenience, this compound is further designated as MnO₂. This compound when initially precipitated is of colloidal size (0.3-0.4 μm) and has a needle-like shape. MnO₂ changes colour from dark brown to yellow with increasing pH. Presence of MnO₂ in water can be easily observed even at very low concentrations (Poselt *et al.* 1968). Figure 8.1 schematically represents arrangements of MnO₂ surface atoms that assume a well-ordered crystal and exchangeable hydrogen and hydroxide ions bound to the compound surface. The hydrous manganese dioxide is amphoteric in terms of net surface charge. However, within the pH range normally encountered in drinking water treatment practice (5

to 9) this compound exhibits a net negative surface charge (Posselt *et al.* 1968). Because of size and negative surface charge of the MnO_2 particles, the colloidal dispersions are very stable at neutral and alkaline pH and in absence of multi-valent cations (Morgan and Stumm 1964). As a consequence of its colloidal size and its large surface area in the order of $300 \text{ m}^2/\text{g}$, MnO_2 is a very strong adsorbent. Rapid rates of sorption of metals (Ag^+ , Ba^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Nd^{3+} , Sr^{2+}) in less than 5-10 minutes, and of cationic organics (*p*-dodecylbenzyltrimethylammonium chloride) in approximately 10 minutes, have been reported. In contrast, neither the anionic (dodecylbenzene sulfonate, humic acids) nor nonionic (nonylphenoxynonylethoxyethanol) organic solute adsorb onto MnO_2 surface to any significant extent (Posselt *et al.* 1968, Colthurst and Singer 1982). On the other hand, presence of divalent cations such as Ca^{2+} facilitates the adsorption of anionic molecules such as humic acids on the negatively charged MnO_2 surface (Colthurst and Singer 1982). Ion-exchange sorption and direct ionic attraction were proposed to be the principle mechanisms involved in these reactions (Posselt *et al.*, 1968). In addition, it was found that the Langmuir sorption equation was adequate to describe sorption equilibria between metal ions or organic cations and hydrous MnO_2 , with equilibrium capacities from 0.1 to 0.31 mole/mole of MnO_2 . Sorption of Mn(II) was found to be strongly pH dependent with equilibrium capacity increasing with an increase of solution pH.

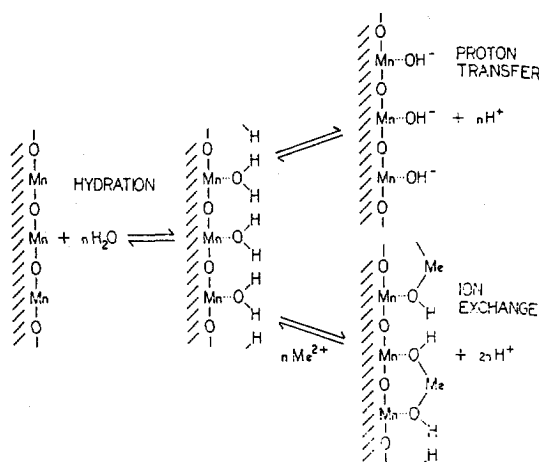


Fig.8.1. Schematic representation of the surface structure and surface reactions of MnO_2 (Posselt *et al.* 1968).

8.3. PERMANGANATE IN WATER TREATMENT

The beneficial effect of potassium permanganate in water treatment may be essentially related to partial or complete oxidation of noxious compounds present in raw water, and to manganese dioxide hydrate which is formed in these oxidation reactions, given its sorptive properties and increased flocculation kinetics.

Generally, under standard water treatment conditions, these processes occur simultaneously.

Effectiveness of potassium permanganate in controlling taste and odour, in particular of algal origin, is well documented in literature (Rauch 1964, Ficek 1978, Ficek and Boll 1980, Middlemas and Ficek 1986, Hubel *et al.* 1992). Low potassium permanganate doses alone, or in combination with the activated carbon, achieved excellent reduction of odour caused by *Aphanizomenon* sp., *Anabaena* sp., *Microcystis* sp., *Oscillatoria* sp., *Melosira* sp., etc., as well as those from actinomycetes. Hubel *et al.* (1992) reported that in bench tests potassium permanganate reduced the concentration of 115 µg/l geosmin that was spiked in raw water, by 86 to 98 percent. Permanganate also easily reacts with other odour causing organics such as phenol, aldehydes, amines and acroleins. Different oxidation products such as humic acid, formic acid, oxalic acids, tartaric acid, carbon dioxide, acetic acid, propionic acid, etc., can be formed in these reactions in function of the permanganate dosage and the organics type and level in the water.

Permanganate oxidation of dissolved Fe(II) and in particular of Mn(II) in ground and surface water has been used for more than forty years to convert them into colloidal form. This permits their more effective elimination by subsequent treatment (Adams 1960, Willey and Jennings 1963, Ficek 1978). Though oxidation is a governing process mechanism in these applications, the sorption of dissolved Mn(II) to MnO₂ also contributes substantially in overall removal. The rate of Mn(II) oxidation depends on pH, and at pH 7-8 the reaction is very fast (Ficek and Boll 1980). Hubel *et al.* (1992) reported that the addition of potassium permanganate in the conventional surface water treatment schemes with ozone as a pre-oxidant significantly enhanced removal of manganese.

The application of potassium permanganate as an algicide for algal growth control in surface water reservoirs and water cooling towers has been studied elsewhere (Kemp *et al.* 1966, Fitzgerald 1964 and 1966). The effective dose of potassium permanganate was alga dependent. Comparative toxicity tests have shown that potassium permanganate doses between 1 and 16 mg/l were algicidal for most filter-clogging and taste and odour producing algae such as diatoms, *Microcystis aeruginosa*, *Anabaena circianalis*, *Oscillatoria rubescens*, etc. (Fitzgerald 1964 and 1966, Kemp *et al.* 1966). The wide range of potassium permanganate levels required to achieve the algicidal effect might also be correlated to differences in the composition of the algal growth medium and its content of potassium permanganate reducing agents. Fitzgerald (1964) reported that variation in the pH between 6-8.5 did not have any effect on the algicidal properties. The algicidal activity was attributed to its strong oxidizing activity (Kemp *et al.* 1964).

Bernhardt and Lusse (1989) reported that the inactivation of zooplankton by potassium permanganate (0.5-1.0 mg/l and 15-20 min contact time) resulted in significantly increased zooplankton removal efficiency in a flocculation filtration system. They found that permanganate oxidation increased the elimination rate of *Notholca caudata* from a mean of 9% to 60-90%.

The application of potassium permanganate could prevent the formation of a slime layer and the attachment of zebra mussels (*Dreissena polymorpha*) in raw water transportation mains (Ficek and Boll 1980, Klerks and Fraleigh 1991). This specific permanganate application may be of particular interest for several Dutch water supply companies (e.g. Water storage corporation Brabantse Biesbosch, Waterworks South Holland) that currently use chlorine to prevent attachment of zebra mussels in long, raw water transportation mains.

The use of potassium permanganate with the aim to reduce THM formation in a treatment scheme with post-chlorination was investigated in several studies (Ficek and Boll 1980, Colthurst and Singer 1982). Pre-oxidation with potassium permanganate changed the organic molecules but resulted in little reduction in THM formation. KMnO_4 alone could not sufficiently control THM formation because the required permanganate dosages were high and THM reduction modest. In addition, permanganate oxidation of phenols that might be present in the raw water may, at permanganate : phenol ratio of 4:1 favour the formation of humic substances, and thus increases THM formation potential (Ficek and Boll 1980). However, potassium permanganate may effectively replace chlorine as a pre-oxidant thus avoiding the THM formation associated with pre-chlorination, by reducing THM formation during chlorine disinfection through prior oxidation and adsorption of THM precursors and by improving the efficiency of the coagulation-separation step.

A few recent studies indicated that potassium permanganate may behave as a coagulant aid. Jun Ma and Guibai Li (1993) found that pre-treatment with potassium permanganate resulted in an enhanced coagulation-flocculation process reducing the coagulant dosages and improving turbidity removal. Petruševski *et al.* (1993a) (chapter 5) reported that pre-oxidation with potassium permanganate clearly enhanced algal removal efficiency in direct filtration. Typically, pre-treatment with potassium permanganate halved the algal concentration in filtrate. The effect of potassium permanganate as a coagulant aid was related to the colloidal MnO_2 formed in the pH range used in water treatment. Colloidal MnO_2 seemed to enhance flocculation kinetics and act as adsorbent. The drawbacks frequently precluding permanganate use in water treatment, however, are violet coloration of the water and elevated manganese levels in the water.

There is currently no suggestion in literature that oxidation with potassium permanganate results in the formation of hazardous by-products.

8.4. EXPERIMENTAL PROCEDURE

The modified jar test apparatus (MJTA), the bench scale direct filtration pilot plant (BSDFPP) and the mobile automated direct filtration plant (MDFPP) experimental set-ups developed and used in the experiments have been described elsewhere (Petruševski *et al.* 1993a, 1994, 1995a, 1995b, Chapter 3). A large number of experiments with the MJTA were performed to scan the effect of a variety of process conditions on the reduction of permanganate related drawbacks (Chapter 5) and possible further improvement of direct filtration performance (i.e. flocculation G^*t , coagulation pH, use of a cationic polymer as sole coagulant and in combination with ferric sulfate). Favourable process conditions that were first identified in the MJTA experiments, (such as pre-treatment with potassium permanganate in combination with coagulation with dual coagulants) were further tested with the BSDFPP and MDFPP.

In the experiments with MJTA pre-concentrated Biesbosch water was used, with algal concentration that corresponds to that during spring blooms (3000-5000 particles/ml). The concentration procedure applied, based on use of tangential flow micro membrane filtration is described elsewhere (Chapter 4, Petruševski *et al.* 1995). The pilot plants used Biesbosch water, conveyed over a distance of 30 km, to the site of water treatment plant Kralingen (Rotterdam). Particle count in the raw Biesbosch water used for the filter runs with BSDFPP and MDFPP reported here was approx. 1250 particles/ml.

The ferric sulphate solution, used in the experiments with the MJTA, was prepared from analytical grade $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$. Ferric sulphate, used in the pilot plant experiments, was prepared at the water treatment plant Kralingen-Rotterdam, by the oxidation of ferrous sulphate by oxygen. In addition to ferric sulphate synthetic cationic polymer Superfloc C-573 (Cytec Industries BV, Rotterdam, the Netherlands) was used as a sole or secondary coagulant.

The particle counter and the turbidity meter used to assess direct filtration performance are described in Chapter 3.

The total residual iron and manganese were determined by atomic absorption spectrometry at the wavelength of 248.3 nm for iron (NEN 6460, Schuit 1993) and 279.5 nm for manganese (NEN 6466).

Electrophoretic mobility (EM) of algae and other particles was measured by using a zeta potential meter (Tom Lindstrom AB) under 90 volt potential difference and equivalent cell length of 6.56 cm. An average of 10 measurements in each direction was taken.

Conventional analytical techniques like turbidity, particle counting etc. were not sufficient to delineate the effect of different treatment steps on algae and other particles and perceive the governing process mechanisms. Appropriately, supplementary analytical techniques were

employed, namely the video system, the high resolution scanning electron microscopy (SEM) and the measurements of electrophoretic mobility. These techniques provided an important additional information that were essential to reveal the underlying process mechanisms and propose a conceptual model that describes coagulation and removal of particulate matter in the developed direct filtration treatment scheme. The techniques used are described in Chapter 3 and Chapter 7)

The results from MJTA experiments are the averages of duplicates. Results from pilot plant experiments reported here are the results from single filter runs. However, filter runs were conducted throughout the year (in total more than 20 filter runs) thus covering different algal species. Trends reported here were found to be highly reproducible.

8.5. RESULTS AND DISCUSSION

8.5.1. Preliminary experiments

The results of the preliminary experiments, designed to test the effect of pre-oxidation by various oxidants, inclusive potassium permanganate, on particle and algae removal, were reported elsewhere (Petruševski *et al.* 1993a, 1993b, Chapter 5). These experiments demonstrated that pre-treatment with potassium permanganate distinctly improved particle and algae removal at all dosages tested (0.5 to 5 mg KMnO_4/l). Typically, concentrations of algae and other particles in algal size range in filtrate were reduced by 50 percent in comparison to direct filtration treatment that operates under identical process conditions, without permanganate pre-treatment. Unfortunately, filtrate turbidity and residual Mn concentration were higher in pre-oxidised samples. Permanganate dosage and residual Mn were positively correlated. Permanganate dosages of ≥ 1 mg KMnO_4/l elevated the manganese level in the filtrate significantly above the maximum admissible concentration (50 $\mu\text{g Mn/l}$ according to the EEC drinking water directives, 20 $\mu\text{g/l}$ VEWIN recommendation); Oxidation with 0.5 mg KMnO_4/l produced filtrate with residual Mn below the maximum admissible concentration established in the EEC drinking water directives (approx. 20 $\mu\text{g/l}$) but nevertheless still at operationally unacceptable level in a view of possible problems in a distribution network. Most of the residual Mn in the filtrate was present in the form of MnO_2 precipitates. Accordingly, the elevated turbidity was also linked with MnO_2 . Light violet colour in the filtrate was observed only at dosages > 2 mg KMnO_4/l .

The experiments described below aimed at minimising filtrate turbidity and residual manganese whilst at least maintaining the achieved particle and algae removal efficiency. In view of the problems that may be associated with presence of manganese in drinking water even at concentrations below 20 $\mu\text{g/l}$, (formation of coatings on piping which may slough off as a black precipitate, growth of certain nuisance organisms that may induce taste, odour and turbidity problems etc., Premazzi *et al.* 1989) elimination of residual Mn below ≤ 10 $\mu\text{g/l}$ was set as an operational objective.

The Mn in the filtrate may be caused by dissolved MnO_4^- or by colloidal MnO_2 precipitates. The presence of MnO_4^- would be caused by either overdosing of potassium permanganate or too short contact time preventing the oxidation from being completed before or within the filters. Mn present in this form cannot be removed by filtration. On the other hand, removal of MnO_2 is expected to take place according to the same mechanisms governing removal of inert aquatic colloids.

8.5.2. Determination of raw water permanganate demand

First, a procedure was established to determine the raw water's permanganate demand, defined as the maximum amount of potassium permanganate that is reduced to MnO_2 within the operationally acceptable time. A contact time of 30 minutes was assumed to be feasible for in-line direct filtration (contact filtration). Different concentrations of potassium permanganate (0.1-1.5 mg KMnO_4/l) were added to 0.5 l jars filled with raw water, water was stirred and permanganate concentration was continuously monitored. The permanganate concentration was measured spectrophotometrically as optical absorbency at 525 nm; very good correlation ($r=0.998$) with MnO_4^- concentration was found in the range 0.05-1.50 mg KMnO_4/l (Fig. 8.2).

The procedure allows fast determination of the raw water permanganate demand and helps avoiding permanganate overdosing. The permanganate demand of pre-concentrated raw Biesbosch water (method based on tangential flow filtration system is described in Chapter 3) with an algal concentration that corresponds to an average spring bloom (chlorophyll-a $\approx 10 \mu\text{g/l}$) was 0.7 mg KMnO_4/l . Accordingly, the permanganate dosages up to 0.7 mg KMnO_4/l will be reduced to MnO_2 within 30 minutes. On the other hand, if higher permanganate dosages are required to serve treatment objectives, the additionally added permanganate should be reduced before the filtration step. Bernhardt and Lusse (1990) reported that application of sodium sulphite as a reductive agent accelerated the precipitation rate of potassium permanganate and reduced the residual manganese concentration in the full scale direct filtration plant effluent.

However, the preliminary MJTA experiments showed that pre-treatment with 0.7 mg KMnO_4/l halved the particle concentration in filtrate, thus increasing the particle removal efficiency from 75 % to above 87 %.

Algae present in the raw water exerted their own permanganate demand. However, most of the permanganate was consumed by dissolved compounds in the raw water. Parallel experiments with Biesbosch reservoir water with and without particles and algae (with size $> 0.45 \mu\text{m}$), showed that algae consumed only approximately 0.1 mg KMnO_4/l , or 15 percent of the total permanganate demand of the raw water.

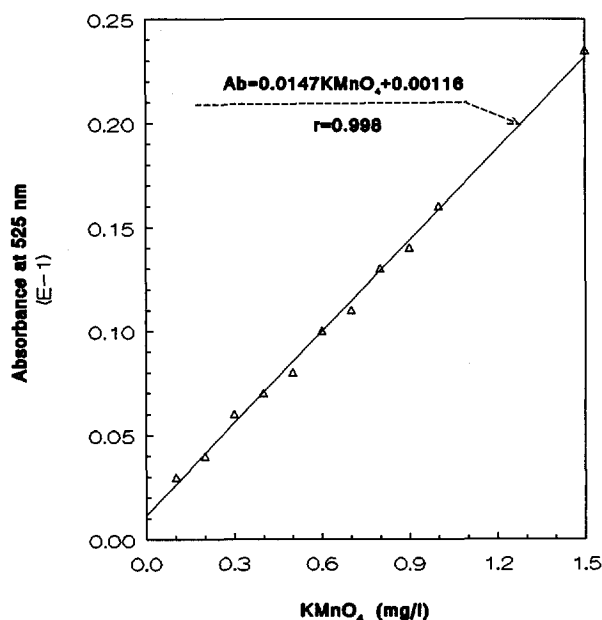


Fig.8.2. Calibration curve for spectrophotometrical determination of MnO_4^- concentration.

8.5.3. Removal of MnO_2 in direct filtration

Application of potassium permanganate at concentrations in the range of the raw water permanganate demand, or at higher dosages with a provision for control of excess permanganate by a reductive agent, is likely to avoid occurrence of permanganate-related residual Mn. On the other hand the particular portion of the residual Mn requires removal of the MnO_2 precipitates. The colloidal, sub-micron size of the MnO_2 precipitates was considered the reason for penetration through filters. Therefore, it was hypothesized that removal depends on optimized coagulation-flocculation; different treatment strategies to enhance agglomeration and subsequent removal were tested: optimisation of coagulation conditions (type and dosage of coagulant, coagulation pH, coagulant aids), separate flocculation and three layer filter media.

Separate flocculation

MJTA experiments showed that a separate flocculation unit improved particle and turbidity removal and reduced the residual Mn concentration. The higher the G^*t during flocculation, the lower residual manganese levels were. The beneficial effect of higher G^*t was more pronounced at higher flocculation G , while the results obtained with lowest tested $G=20\text{ s}^{-1}$ were erratic. However, residual Mn concentrations in the filtrate remained above $80\text{ }\mu\text{g/l}$. The flocculation apparently increased the number of contact opportunities between the MnO_2 colloids and coagulant precipitates, however, it did not enhance sufficiently the growth of the

MnO₂ colloids into the agglomerates that could be efficiently removed by filtration.

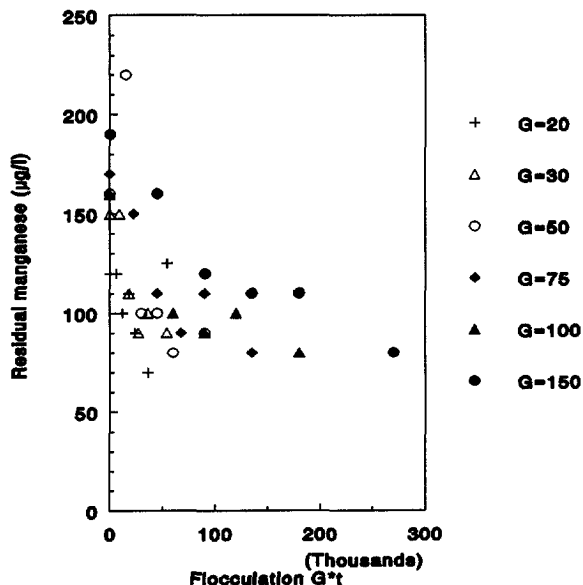


Fig.8.3. Effect of flocculation G*t on residual Mn in the MJTA filtrate; KMnO₄ dosage 0.7 mg/l, coagulant: 1.5 mg Fe(III)/l.

Three layer filtration

The anthracite-sand-garnet filter strongly favoured performance with respect to turbidity and residual iron in common direct filtration (Petruševski *et al.* 1993a, Chapter 3). The bench scale direct filtration pilot plant (BSDFP) experiments demonstrated the capacity of the three-layer filter to produce filtrate with approximately 30% lower residual Mn in comparison with a filter equipped with the anthracite-sand media (Fig.8.4). Residual Mn was consistently below the maximum admissible concentration defined by the EEC directives (50 µg/l), but remained considerable (25–40 µg/l) and above the VEWIN recommendation and the objective established in this study. The increase in residual Mn during initial filter run hours, which was observed with both filter media, may be attributed to the dilution effect of filter backwash water present in the filter at the beginning of the filter run. Given the overall good performance of the anthracite-sand-garnet filter media on filtrate quality (residual Mn and Fe, filtrate turbidity and particle concentration) this filter was retained for further optimisation.

Optimisation of the coagulation conditions for MnO₂ removal

Filter runs with the three-layer filter showed that the MnO₂ precipitates could not be completely removed even by a fine garnet layer due to their colloidal size. The separate flocculation even at prolonged flocculation time and high flocculation G*t values could not

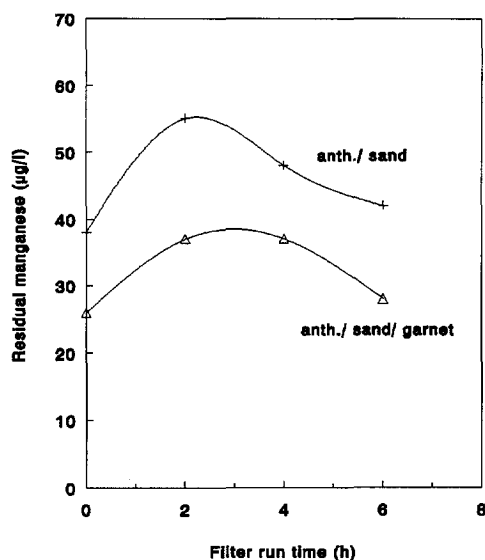


Fig.8.4. Residual Mn in the BSDFPF filtrate as a function of filter media; pre-treatment with 0.7 mg KMnO_4/l , coagulant 1.5 mg $\text{Fe(III)}/\text{l}$, filtration rate 2.8×10^{-3} m/s.

provide for adequate agglomeration of these colloids, presumably because their negative surface charge prevented complete coagulation. Therefore, efficient coagulation was considered to be the prerequisite to further improve agglomeration of the MnO_2 colloids and their subsequent removal. Under the treatment conditions common for direct filtration of Biesbosch water (high coagulation pH of approx. 8.0 and iron-based coagulant), coagulation is almost exclusively achieved through sweep coagulation (Petruševski *et al.* 1995b, Chapter 6). Two different approaches can be considered to improve MnO_2 coagulation:

- to further enhance sweep coagulation, and
- to alter the coagulation condition so that adsorption coagulation becomes the governing coagulation mechanisms.

Sweep coagulation can be enhanced by increasing the applied dosage of ferric sulphate, thus increasing overall particle concentration in the coagulated suspension and improving agglomeration kinetics. However, the coagulant dosages that were considered maximally acceptable for direct filtration in order to keep head loss low (≤ 2 mg $\text{Fe(III)}/\text{l}$) could not sufficiently reduce residual Mn (Chapter 6).

The colloidal size and negative surface charge of the MnO_2 precipitates, suggests that charge neutralisation by adsorption coagulation is necessary, either by using metal coagulants at low coagulation pH at which positively charged iron hydrolysis species prevail or by applying a cationic polymer as main coagulant.

Coagulation pH

MJTA experiments showed that decreasing coagulation pH improved MnO_2 and particle removal (Fig. 8.5). Experimental conditions comprised pre-oxidation with 0.7 mg/l KMnO_4 , coagulation at variable pH (6-9) with 1.0 mg Fe(III)/l, followed by pH correction to 8.0 ± 0.1 and filtration through the small scale sand filters at filtration rate of $1.8 \cdot 10^{-3}$ m/s. The pH was increased before filtration to avoid the reported negative effects of low pH on the performance of in-line direct filtration (Petruševski *et al.* 1995b, Chapter 6). However, the required manganese removal could not be achieved by lowering the coagulation pH only. The coagulation pH range examined was still above the isoelectric point (IEP) for the iron hydroxo-complexes; in the experiments with Biesbosch reservoir water we found that the IEP lies between pH 5 and 6 (Petruševski *et al.* 1995b, Chapter 6). It is surmised that further reduction of coagulation pH close to IEP would enhance adsorption-coagulation; however, such low coagulation pH values were not considered feasible for the Biesbosch water characterised by high pH and high buffering capacity.

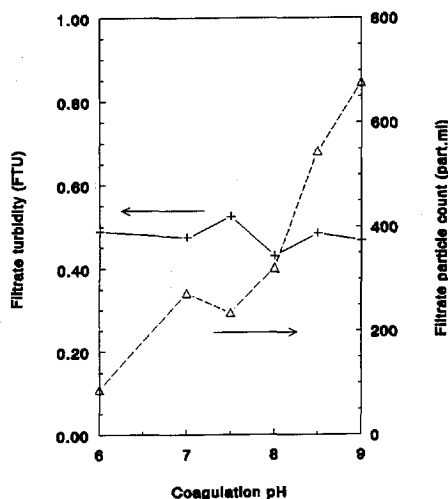


Fig.8.5. Effect of coagulation pH on MJTA filtrate turbidity and particle count.

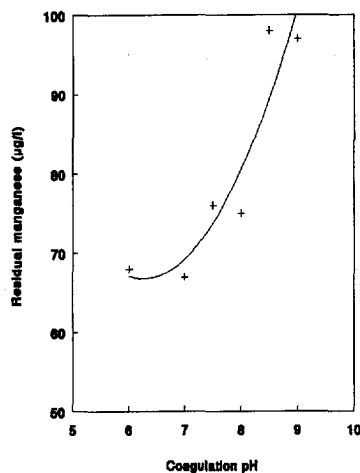


Fig.8.6. Effect of coagulation pH on residual Mn in the MJTA filtrate.

Cationic polymer as coagulant

Coagulation through adsorption and charge neutralisation can be achieved irrespective of coagulation pH by replacing metal coagulants with cationic polymers. After a comparative examination the synthetic cationic polymer Superfloc C573 was selected for further experiments. The MJTA experiments comprised pre-oxidation with 0.7 mg KMnO_4 /l, coagulation with the variable cationic polymer dosage ($G=200\text{s}^{-1}$, $t=30$ s, coagulation pH = 8.3) and filtration through small-scale filters at constant filtration rate ($1.8 \cdot 10^{-3}$ m/s). The

polymer dosing was beneficial to MnO_2 and particle removal (Figs.8.7 and 8.8). A polymer dosage of ≤ 3 mg/l resulted in significantly reduced residual manganese and particle concentration. A further increase in the polymer dosage up to 5 mg/l did not improve significantly filtrate quality. Polymer dosages > 5 mg/l resulted in deterioration of filtrate quality in terms of residual Mn and particle count, which was due to charge reversal and particle restabilisation (see paragraph 8.6, Fig.8.18).

Coagulation with polymer dosages ≥ 3 mg/l produced filtrate with residual Mn < 50 $\mu\text{g/l}$.

Unfortunately, the filtrate had an unacceptably high turbidity, presumably due to polymer penetration through the filter. In general, the high polymer dosages required to achieve efficient Mn removal caused poor filtrate turbidity which precluded the use of a cationic polymer as a coagulant in full-scale direct filtration. The application of synthetic cationic polymers as main coagulant also does not conform to the current drinking water treatment philosophy in the Netherlands that endorses only the use of metal coagulants, primarily iron salts.

The experiments confirmed that coagulation through adsorption and charge neutralisation is required to achieve efficient agglomeration and removal of MnO_2 colloids.

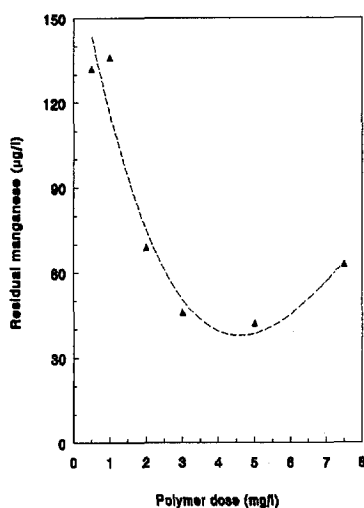


Fig.8.7. Effect of coagulation with cationic polymer on residual Mn in the MJTA filtrate.

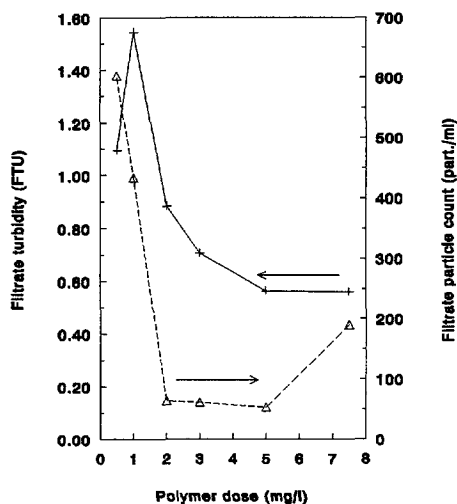


Fig. 8.8. MJTA filtrate turbidity and particle count as a function of cationic polymer dosage.

Cationic polymer as coagulant aid

To achieve good Mn and turbidity removal simultaneously, a series of the MJTA experiments was designed to assess the capability of coagulation with two coagulants: ferric sulfate and cationic polymer. Pre-treatment with 0.7 mg KMnO_4/l was followed by coagulation with 1.5 mg $\text{Fe(III)}/\text{l}$ at coagulation $\text{pH}=8.2$ and subsequent addition of different dosages of the cationic polymer ($G=200 \text{ s}^{-1}$, $t=30\text{s}$), and finally filtration through small scale filters at constant filtration rate of $1.8 \times 10^{-3} \text{ m/s}$.

Coagulation with dual coagulants, at cationic polymer dosages $> 0.35 \text{ mg/l}$, significantly reduced residual manganese ($< 20 \mu\text{g Mn/l}$). Also residual iron, filtrate turbidity and particle count were reduced (Figs.8.9 and 8.10). Though the MJTA is a very simple experimental batch set-up, that features a shallow non-ripened mono-layer filter bed, it produced filtrate of very high quality: turbidity approx. 0.2 FTU, low particle count that correspond to particle removal efficiency of 99%, residual Mn $< 20 \mu\text{g/l}$ and residual Fe approx. 0.1 mg/l. These results seemed to confirm earlier assumptions; they showed that direct filtration supported by pre-oxidation with KMnO_4 and coagulation with ferric sulphate and a cationic polymer, produces filtrate of very high quality, while eliminating the drawbacks related to KMnO_4 (Fig. 8.11).

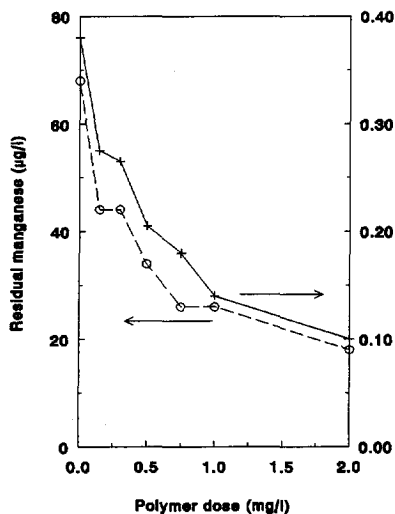


Fig.8.9. Residual Mn and Fe in the MJTA filtrate as a function of dosage of cationic polymer.

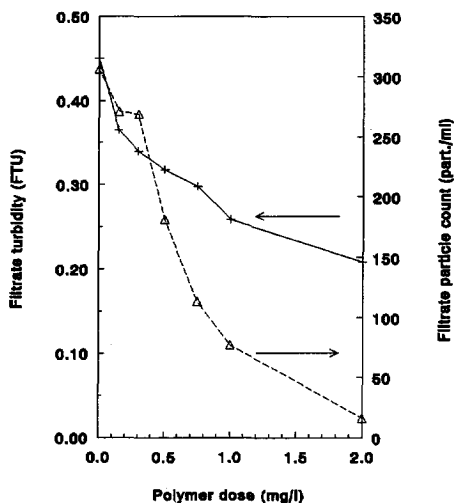


Fig.8.10. The MJTA filtrate turbidity as a function of cationic polymer dosage.

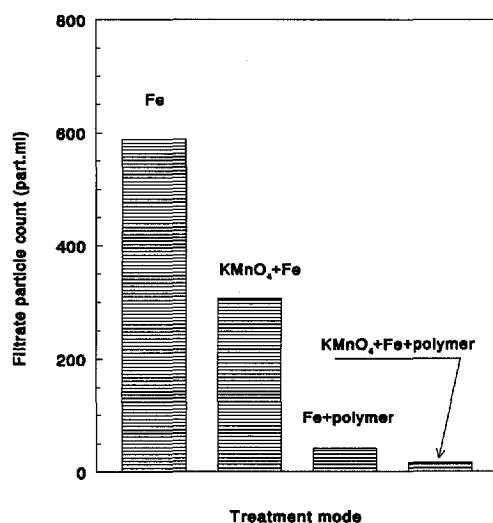


Fig.8.11. Effect of treatment mode on particle count in MJTA filtrate; 0.7 mg/l KMnO₄, 1.5 mg Fe(III)/l, 1.0 mg C-573/l; concentrated raw water: 4150 part./ml.

8.5.4. Pilot - plant experiments

Experiments were conducted with the larger scale pilot plants (BSDFPP and MDFPP) to verify the results obtained with MJTA. The BSDFPP was able to establish, in parallel, four different direct filtration treatment schemes (Fig.8.12) and to assess the effect of pre-treatment with potassium permanganate and the use of dual coagulants. Performance evaluation was based on particle removal capacity, filtrate turbidity and residual manganese. The target established was ≥ 2.0 -log removal of particles (SWTR requirements that also results in chlorophyll- $\alpha \leq 0.1$ mg/l), turbidity below 0.10 FTU and residual manganese below 10 $\mu\text{g/l}$. Dosages of KMnO₄, ferric sulphate and cationic polymer (C573) were 0.7 KMnO₄ mg/l, 1.5 mg Fe(III)/l and 1.0 mg/l, respectively. The coagulated suspension was filtered through anthracite-sand-garnet media at the filtration rate of 2.8×10^{-3} m/s.

Direct filtration treatment, which included pre-treatment with KMnO₄, coagulation with ferric sulfate and a cationic polymer, produced filtrate of superior quality: turbidity < 0.1 FTU, residual Mn < 5 $\mu\text{g/l}$, particle count approx. 10 part/ml or > 99% particle removal efficiency (particle count in raw Biesbosch water was 1250 particles per ml) and, residual Fe < 0.05 mg/l (Figs. 8.13, 8.14, 8.15 and 8.16). In addition, the filter ripening period was shorter in comparison to straightforward direct filtration and direct filtration supported by ozone treatment. The separate flocculation unit ($G=80 \text{ s}^{-1}$, $t=15$ min) did not yield additional filtrate quality improvement. However, it significantly reduced head loss development in the filter bed (Fig. 8.16).

Similar particle removal patterns were obtained with BSDFPP (Fig. 8.14) and MJTA

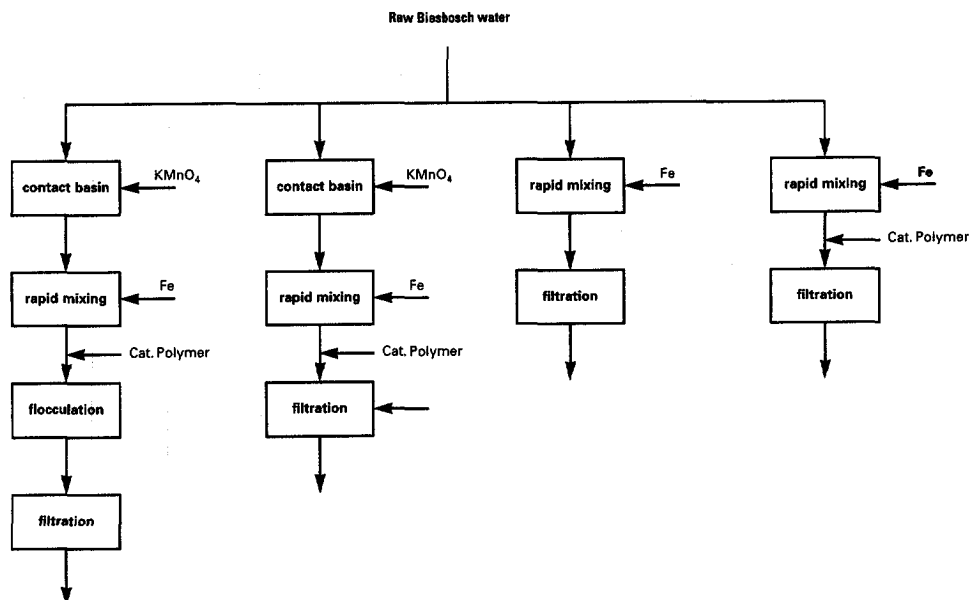


Fig.8.12. Treatment alternatives examined with the BSDFPP.

(Fig. 8.11) in response to a variety of pre-treatment conditions. This indicates that MJTA can be a very useful device for rapid scanning of the effect of different process conditions on direct filtration performance. Consequently, MJTA can reduce the number of time consuming pilot plant experiments.

Supplementary filter runs were performed with the MDFPP. It was considered that this set-up reflects more closely full-scale filter installations, because of its larger capacity and ability to operate continuously, and consequently to model complete filter run. In these experiments raw Biesbosch water was pre-oxidised with 0.7 mg KMnO_4/l , coagulated with 1.5 mg $\text{Fe(III)}/\text{l}$ and 1.0 mg cationic polymer (Superfloc C-573) and filtered through the three-layer, anthracite-sand-garnet filter media. The results obtained (Fig. 8.17) correlated well with the results obtained with the BSDFPP, confirming at larger scale the role of pre-oxidation with KMnO_4 in combination with ferric sulphate and cationic polymer coagulation.

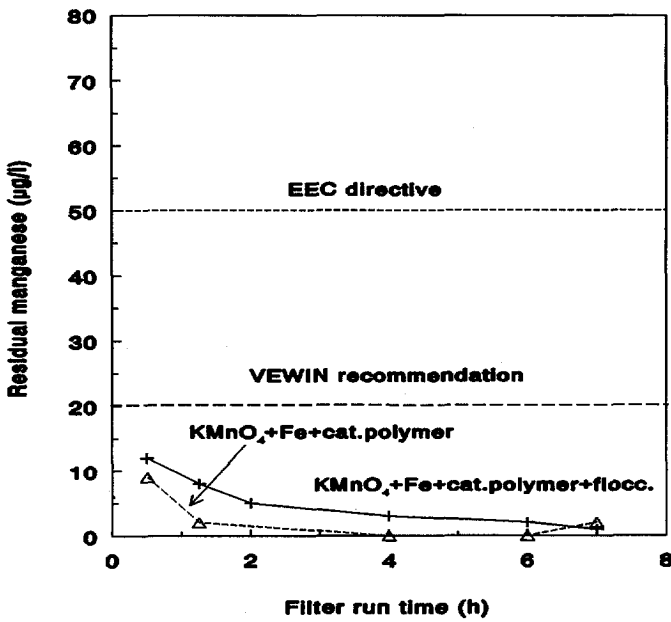


Fig.8.13. The residual Mn in the BSDFPF filtrate; 0.7 mg KMnO₄/l, coagulation: 1.5 mg Fe(III)/l and 1.0 mg C-573/l, filtration rate $2.8 \cdot 10^{-3}$ m/s.

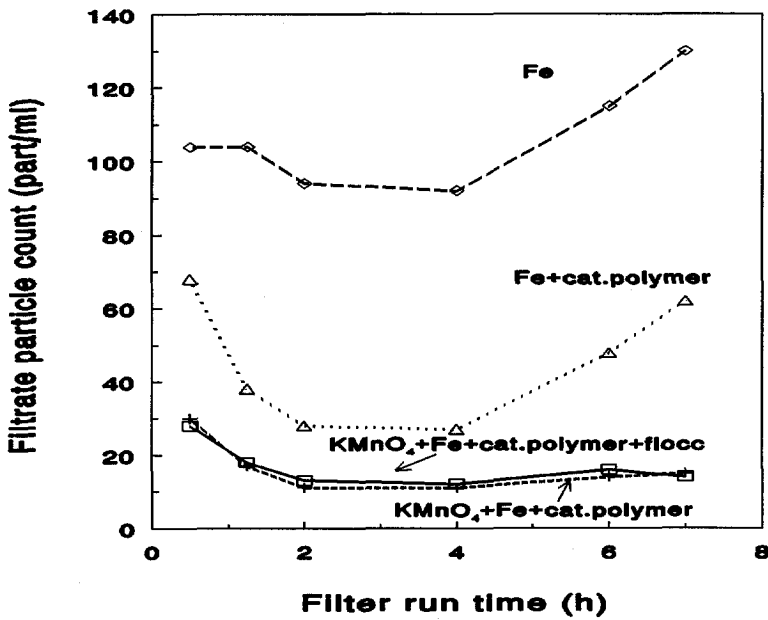


Fig.8.14. Particle count in the BSDFPF filtrate as a function of treatment mode.

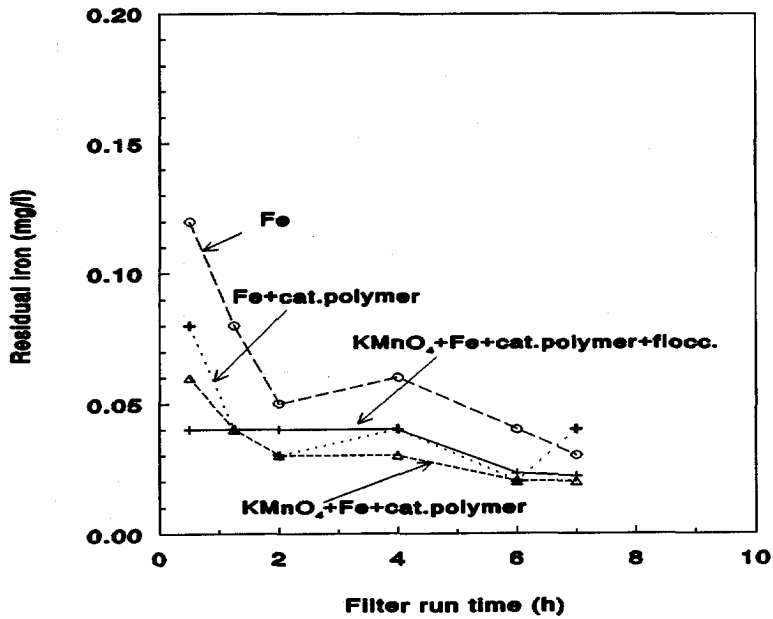


Fig.8.15. The residual Fe in the BSDFPP filtrate as a function of treatment mode.

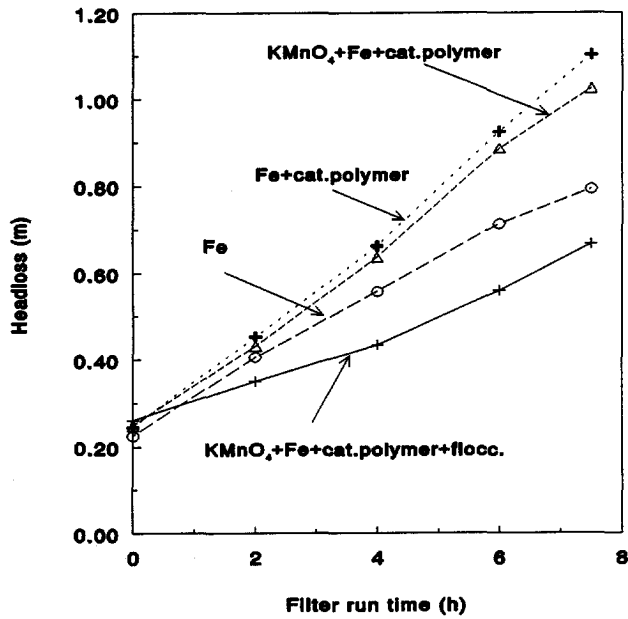


Fig.8.16. Headloss in the BSDFPP as a function of treatment mode.

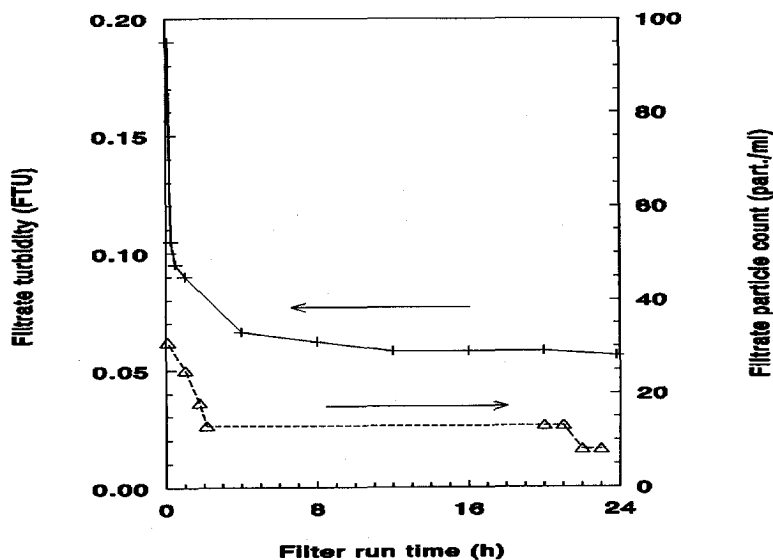


Fig.8.17. Filtrate turbidity and particle count in the MDFPP three-layer pilot filter.

8.6. Process mechanisms

In-situ observations with the help of video system of pre-concentrated Biesbosch reservoir water treated with different dosages of KMnO_4 showed that the permanganate pre-treatment had a pronounced effect on locomotion of motile algal species. Potassium permanganate dosages ≥ 0.5 mg/l, after 30 min retention time, completely arrested not only active locomotion of flagellated algae (*Rhodomonas minuta*, *Cryptomonas* sp., *Euglena* sp., etc.), but also the gliding motility of diatoms such as *Navicula* sp. and *Nitzschia* sp. The oxidation also strongly hindered or completely immobilized zooplankton like some motile species of ciliata, crustacea and copepoda. As suggested earlier, immobilisation of motile microorganisms is prerequisite in facilitating their coagulation and subsequent removal in filtration (Petruševski *et al.* 1993a). The algal cells remain integral after the oxidation and algae preserve their fresh green colour. It is not clear if the loss of motility is permanent, or if the microorganisms can recover their active locomotion after prolonged resting time. However, within one hour after addition of permanganate algae and zooplankton remained immobilised. Whether microorganisms regain their motility after a longer resting time was considered as irrelevant given the common detention times associated with direct filtration or conventional surface water treatment never surpass one hour.

Video observations demonstrated that dosages of $\text{KMnO}_4 > 2$ mg/l, can break-up large algal colonies. Most of these algal agglomerates are easily removable by filtration; by contrast their single cells are very difficult to remove due to their minute size. This problem was experienced specifically with colonies of *M. aeruginosa*. KMnO_4 dosages > 2 mg/l broke

up these colonies, presumably by oxidising the mucilage material that keeps algal cells together.

Negative algal surface charge also hinders algal agglomeration. In addition, it inhibits algal adherence onto the filtering material by the electrostatic repulsive forces as quartz sand used as standard filtering material at the pH that prevails in drinking water treatment has a negative charge as well. The negative algal surface charge was not affected by the KMnO_4 pre-treatment and coagulation with ferric sulfate (coagulation pH ~ 8). Actually, the negative surface potential, measured as electrophoretic mobility, further slightly increased, presumably due to precipitation of the negatively charged MnO_2 colloids onto the natural particles. The cationic polymer used as a secondary coagulant, on the other hand, strongly reduced the negative surface charge. This reduction was proportional to the applied polymer dosage (Fig. 8.18). Cationic polymer dosages > 3 mg/l reversed the charge of natural particulate matter from negative to positive. It was also observed that negative surface charge on average increases slightly at low, initial polymer dosages (~ 0.25 - 0.5 mg/l). This phenomenon was presumably caused by agglomeration of very small particulate organic matter and of initially precipitated MnO_2 colloids that were too small to be detected with the instrument used for measurements of electrophoretic mobility. These particles however, might have higher negative surface charge than algae and other, larger particulate matter (e.g. inorganic debris, oocysts and cysts). The dosages of cationic polymer in the filter runs with the pilot plant installations (Figs. 8.13-8.17) were insufficient to neutralise completely the negative charge of the algae and other natural particulate matter. Nevertheless, charge reductions accomplished with these polymer levels were sufficient to promote agglomeration and subsequent removal of the algae and other natural particulate matter, and in particular of the inorganic MnO_2 colloids.

High resolution scanning electron microscopy, that was able to examine fully hydrated material, was used to investigate in detail the effect of the different treatment steps on the algal cell architecture. The KMnO_4 pre-oxidation induced a number of clearly discernable effects on algal behaviour and cell architecture. The treatment caused an excessive release of algal biopolymers into the surrounding media. On SEM micrographs (Fig. 8.19) it can be observed that *Stephanodiscus hantzschii* when exposed to 0.7 mg KMnO_4 /l intensively secreted biopolymers through furtoportules, algal organelles positioned around the valve element. It is unclear whether this secretion is to be considered a common algal response to stress conditions or whether permanganate oxidation damaged the algal furtoportules and caused leakage of algal intra-cellular material. Herth (1978, 1979) and Herth and Bartholtz (1979) suggested that the furtoportules in several *Cyclotella* and *Thalassiosira* species secrete almost pure and crystalline β -chitin fibrils. The glue-like appearance of the released biopolymers through the furtoportules (Fig. 8.19 and Fig. 8.20 - right and up-left corner) suggests that this material very probably also contains chitin fibrils. The functioning of this algal organella has not yet been fully elucidated and is still a point of discussion (Round *et al.* 1992). Besides chitin, algae may release other compounds, that are species- and growth phase-specific. Bernhardt and Clasen (1991) reported that extra-cellular organic matter

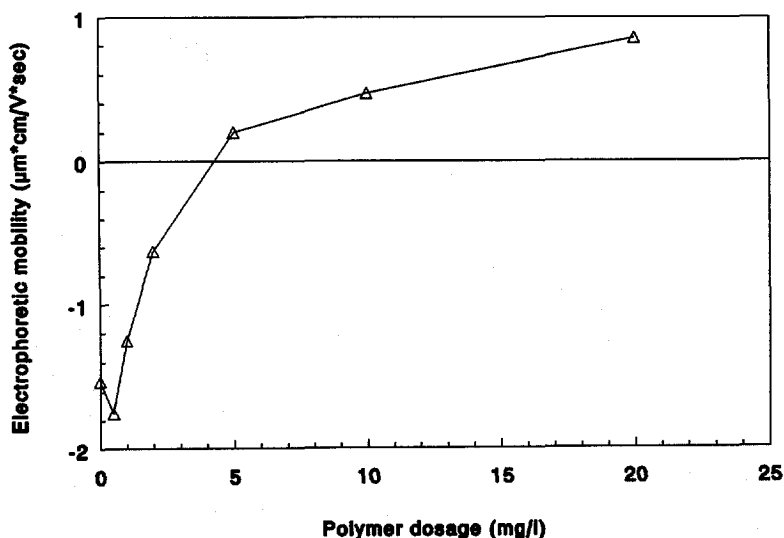


Fig.8.18. Electrophoretic mobility as a function of cationic polymer dosage.

(EOM) from cultures of green and blue-green algae and diatoms behaves like anionic and non-ionic polymer. They found that in particular the EOM from the green alga *Dictyosphaerium* assists in flocculation and filtration, comparable to the functions of a weak anionic polymer. Their results together with the likely presence of chitin strongly suggest that the algal biopolymers secreted in response to permanganate oxidation behave as a coagulant aid. KMnO_4 pre-treatment of algae laden raw waters contributes, among the other effects, to *in situ* production of natural coagulant aid.

The SEM micrographs also demonstrate that the pre-oxidation with 0.7 mg KMnO_4/l degrades algal cells. Serious damage on the girdle elements that link the valves of cylindrical diatoms were easily visible (Fig.8.22). It should be noted that KMnO_4 dosage ≤ 1.0 mg KMnO_4/l damages algae less than ozone at dosages ≤ 2.0 mg O_3 consumed/l, which is an alternative oxidant also used to enhance algal removal in direct filtration (Petruševski *et al.* 1994, Chapter 7).

Specific for KMnO_4 pre-oxidation is the formation of MnO_2 colloids. Comparison of the SEM micrographs of the valve and girdle elements of cylindrical diatoms before (Fig.8.21) and after permanganate treatment (Figs 8.22, 8.23 and 8.24) shows colloidal precipitates on the algal surface. Such precipitates are absent on algal cells after treatment with ozone (Petruševski *et al.* 1994, Chapter 7); they have a white colour on SEM micrographs which is typically associated with very dense and compact surfaces, primarily metals. It can be concluded therefore, that these precipitates are MnO_2 colloids precipitated onto the algal surface. These precipitates alter algal surface properties, but the influence on algal coagulation and removal is unclear. As mentioned earlier, permanganate pre-oxidation had a negligible effect on the particles' negative surface charge. On the other hand, the MnO_2

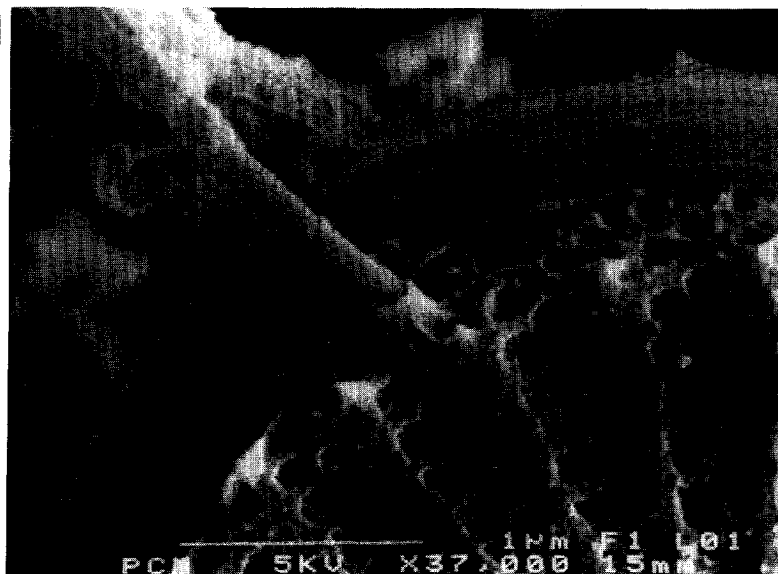


Fig.8.19. SEM micrograph of *S. hantzschii furtoportula* that releases biopolymer in response to permanganate treatment; scale bar = 1 μm .

precipitates may influence algal coagulation and removal through other mechanisms. Once attached to the algal surface, these precipitates increase the algal specific weight and thus improve their settling properties. Also pre-oxidation may improve the algal coagulation with ferric sulfate by reducing the amount of natural organic matter that can react with and bind iron into insoluble and highly dispersed colloidal complexes. These colloids do not contribute to coagulation of particulate matter and are also difficult to remove by filtration. Permanganate reduces the amount of reactive natural organic matter through direct oxidation, physical coverage of algae surface and other organic particulate matter with MnO_2 precipitates, and through sorption of organic molecules onto the MnO_2 colloidal surface. Given the high concentration of Ca^{2+} cations in Biesbosch water it may be expected that in addition to cationic organic molecules the anionic ones are also adsorbed onto the MnO_2 surface. Similarly, algal cells covered with inert MnO_2 offer more favourable conditions for the adherence of ferric hydroxide. In addition to these direct effects, the MnO_2 colloids also increase the particle concentration in raw reservoir water that is generally low, even in coagulated suspensions, given the low coagulant dosages. This is of particular importance for the in-line direct filtration as it does not include a separate flocculation unit and provides only limited particle collision opportunities.

Furthermore the pre-oxidation induces direct, *in-situ* particle agglomeration, even before coagulant addition (Figs. 8.22 and 8.25). Filella *et al.* (1993), with the help of high-resolution high-contrast Transmission Electron Microscopy (TEM), recently revealed the presence and significance of the fine organic matrices or meshes of filaments in natural surface waters. These fine organic meshes embed very small inorganic and organic colloids

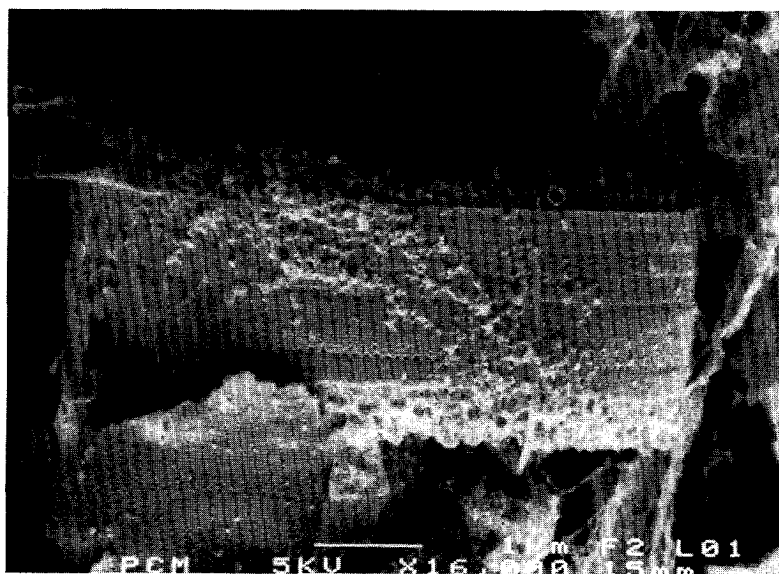


Fig.8.20. SEM micrograph of *S. hantzschii* after permanganate treatment with MnO₂ deposits on the girdle element and released biopolymer around alga; scale bar=1 μm.

and thus control their sedimentation and coagulation in surface waters. The fine mesh of organic fibres could also be observed here on the high resolution SEM micrograph (Fig. 8.25). In the case of KMnO₄ treatment of reservoir water it emerges that these fine organic matrices serve as nuclei for MnO₂ precipitation. They also embed other MnO₂ colloids formed elsewhere in water as well as secreted algal biopolymers, algae and other natural colloidal and fine particulate matter. This obviously improves particle coagulation, and agglomeration by bridging. The sole pre-oxidation with 0.7 mg KMnO₄/l was found to agglomerate algae by binding three cells of *S. hantzschii* with MnO₂ precipitates and possibly by secreted algal biopolymers (Fig. 8.22).

Coagulation with ferric sulfate at high coagulation pH (pH ~ 8), resulted in rapid formation of amorphous ferric hydroxide. This precipitated and partly covered algal cells (Fig. 8.26). This mechanism compares to the coverage of mineral particles to occur by aluminium hydroxide precipitates (Alaerts and Van Haute 1981). The subsequently added cationic polymer is strongly attracted to the negatively charged algal surface or precipitated ferric hydroxide. Polymer dosages ≥ 1.0 mg/l were sufficient to cover almost completely algal cells (Fig. 8.27). Adsorption of cationic polymer on algal surface reduced or completely neutralised its negative surface charge and thus facilitated the algal agglomeration and attachment on filtering material (Fig. 8.18). Short polymer chains (<1 μm) could be seen attached to the surface of μ-algae. The length of the chains and the relatively low particle concentration in the coagulated water strongly suggest that coagulation through direct polymer bridging under the conditions applied is not feasible and does not play a significant role.

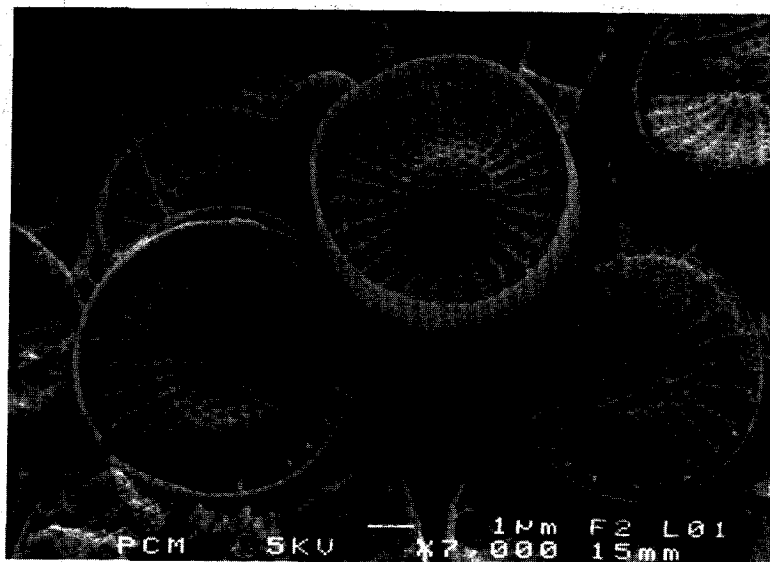


Fig.8.21. SEM micrograph of *S. hantzschii* cells before permanganate treatment; scale bar 1 μm .

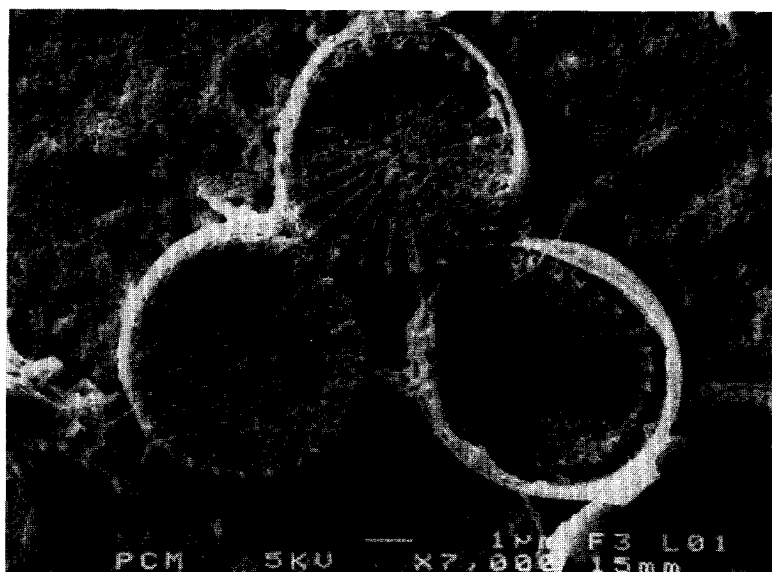
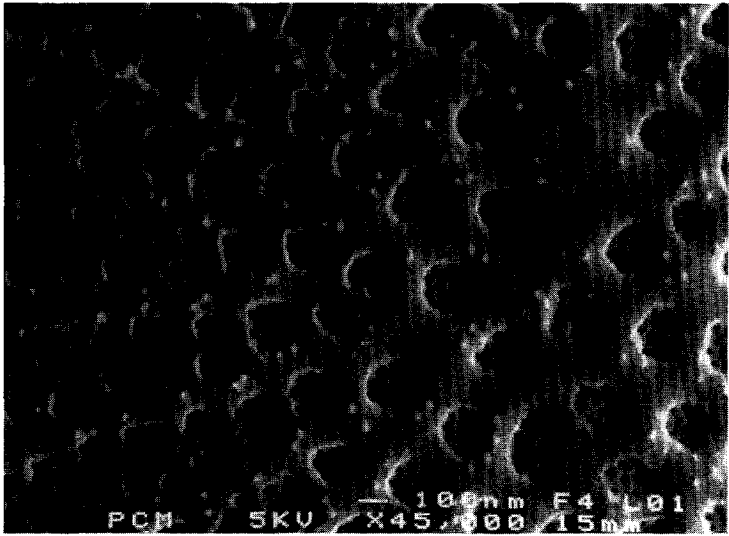
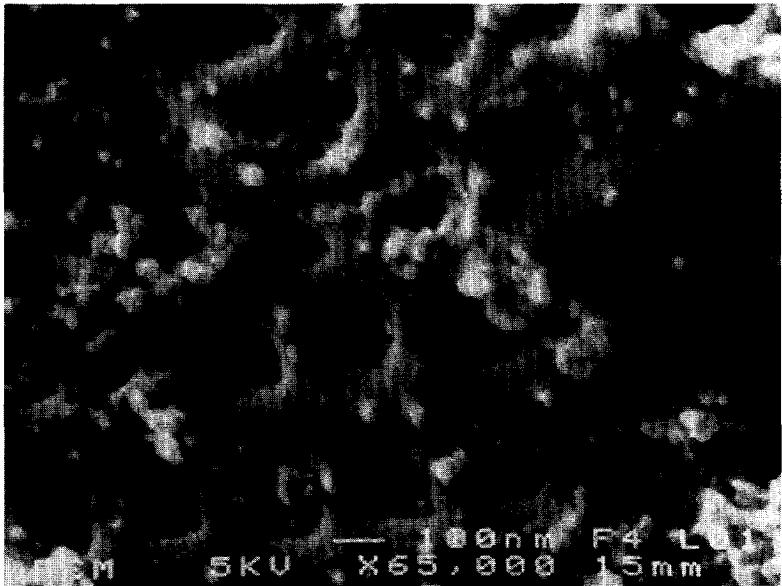


Fig.8.22. SEM micrograph of agglomerated *S. hantzschii* cells after permanganate treatment, with MnO_2 deposits on the valve elements and MnO_2 and biopolymer bonds.



a.



b.

Fig.8.23. SEM micrograph of *S. hantzschii* valve elements before (a) and after (b) permanganate treatment with MnO_2 deposits; scale bar = 100 nm.

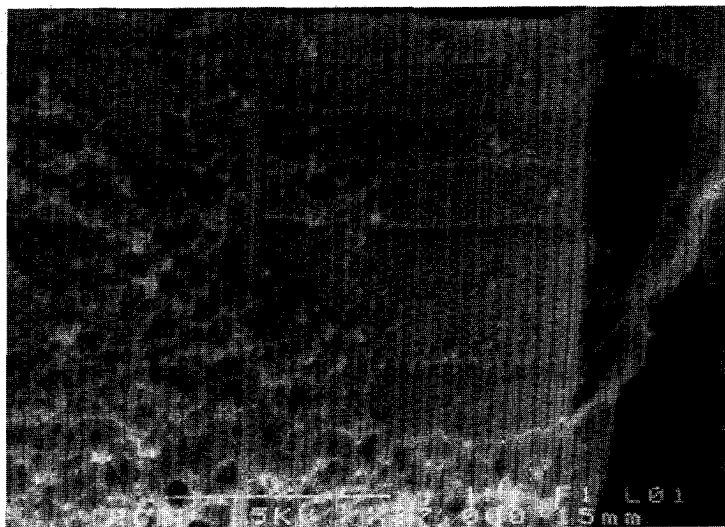


Fig.8.24. SEM micrograph of *S. hantzschii* girdle element with MnO_2 precipitates due to permanganate treatment; scale bar 1 μm .

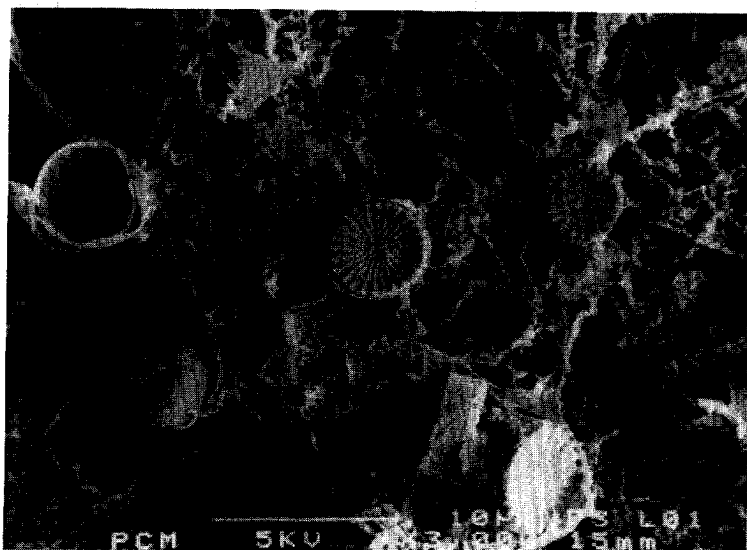


Fig.8.25. SEM micrograph of algal cells, MnO_2 precipitates and algal biopolymers trapped in fine organic meshes; scale bar=10 μm .

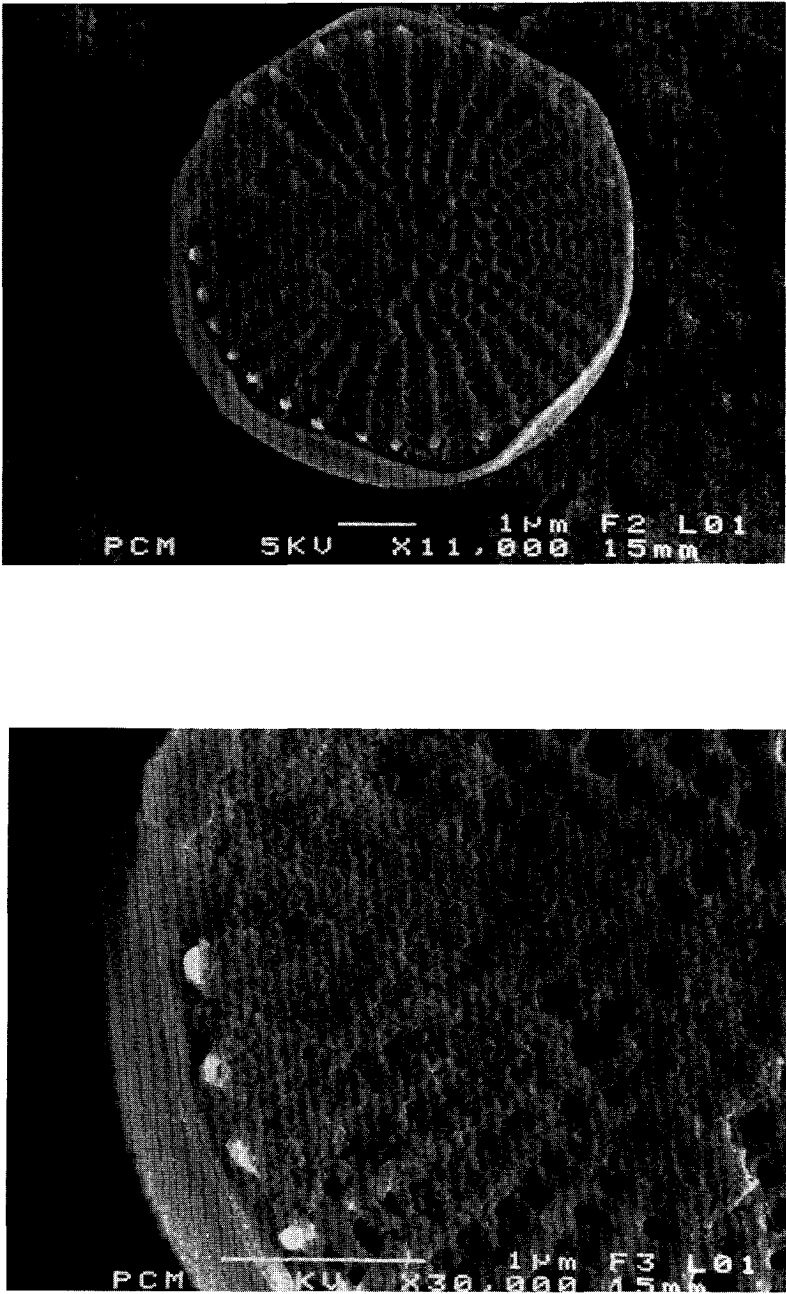


Fig.8.26. SEM micrograph of *S. hantzschii* after coagulation with ferric sulfate, with ferric hydroxide precipitates on the valve elements; scale bar=1 μm.

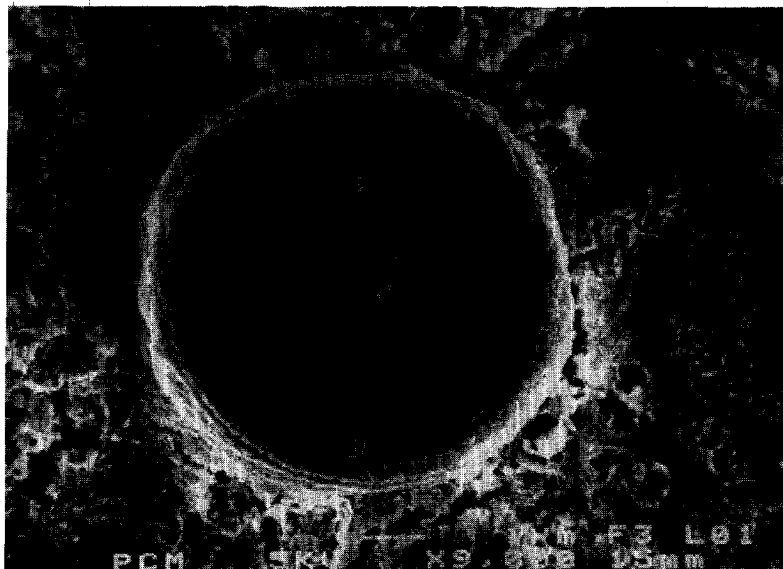


Fig.8.27. SEM micrograph of algal cell completely covered with cationic polymer; scale bar=1 μm .

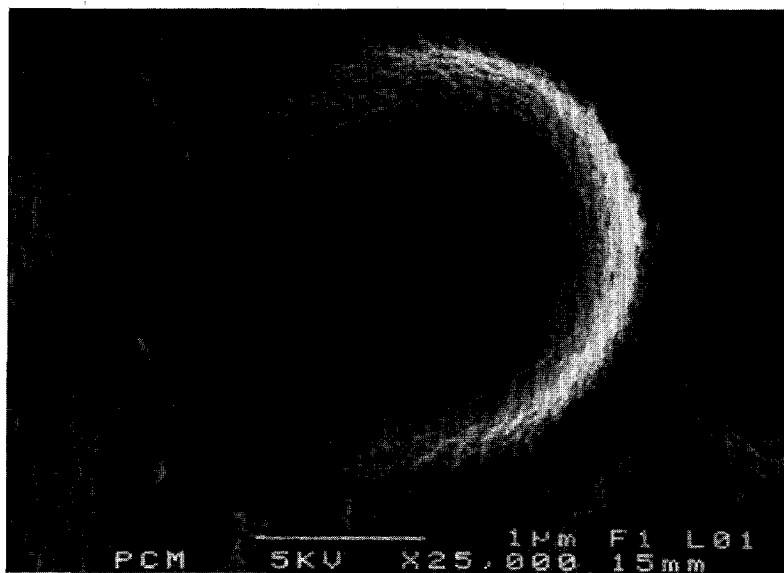


Fig.8.28. SEM micrograph of μ -algae after coagulation with ferric sulfate and cationic polymer with short polymer chains attached on algal surface; scale bar=1 μm .

8.7. CONCLUSIONS

A direct filtration treatment process was developed. It comprises pre-oxidation with KMnO_4 , coagulation with ferric sulphate and a cationic polymer, and filtration through a three layer filter, . The experiments with the batch and pilot plant set-ups showed that this treatment improved particle and algae removal in comparison to efficiencies commonly achieved in direct filtration, by more than a 1.0-log removal unit (1-log removal in direct filtration without oxidative pre-treatment, ≥ 2 -log removal units in direct filtration supported by permanganate pre-treatment and coagulation with dual coagulant). Furthermore, the application of cationic polymer completely eliminates the KMnO_4 related drawbacks, namely increased filtrate turbidity and residual Mn concentrations. The filtrate is of exceptionally high quality: turbidity < 0.06 FTU, residual Mn $< 5 \mu\text{g/l}$, residual Fe $< 0.05 \text{ mg/l}$, particle concentrations ~ 10 part/ml. In addition, this treatment requires shorter filter ripening period in comparison with direct filtration without oxidative pre-treatment and direct filtration supported by pre-ozonation. The treatment established is simple and does not require high investment costs.

Efficient removal of algae and other particulate matter (removal efficiency $> 99\%$) in direct filtration supported by KMnO_4 pre-oxidation and coagulation with ferric sulfate and a cationic polymer is suggested to be a consequence of several process mechanisms. Permanganate inactivates motile microorganisms, induces *in situ* production of natural, algae derived coagulant aid, enhances the coagulation process by oxidising and adsorbing organic molecules that otherwise may hinder coagulation, and accelerates the flocculation kinetics by increasing particle concentration. In other words, permanganate pre-oxidation enhances coagulation and agglomerate formation before coagulant addition. The subsequent application of a dual coagulant results in further coagulation through enmeshment in a precipitate, adsorption and charge neutralisation. These agglomerates are very efficiently removed in anthracite-sand garnet filter beds.

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Chapter 9

CONCLUSIONS

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9.1. Direct filtration for treatment of impounded water

Surface water is important source of fresh water in Western Europe. To ensure adequate provision capacity, during low river discharge episodes and during pollution events, and to improve on generally poor quality of river water, river water is often stored in impoundments. Impoundments overall improve the water quality, however, they may favour massive growth of algae. Consequently, the production of drinking water from impounded surface water cannot be dissociated from algae related treatment and distribution problems. Algae in drinking water may introduce several problems (formation of hazardous by-products, adverse effect on taste and odour, after-growth in the distribution network etc.). Presence of algae in drinking water also indicates that other, possibly pathogenic, microorganisms in the algal size range may penetrate treatment as well (e.g. *Cryptosporidium* oocysts and *Giardia* cysts).

Direct filtration is a simple and relatively inexpensive alternative to conventional treatment for impounded surface water provided that the water is of appropriate quality (low in turbidity, particulate matter, colour and DOC). Direct filtration can achieve on its own a maximal algae removal of 90 to 95%, thus still producing water with considerable algae concentration. The problem of algae penetrating through the treatment system may therefore question the reliability and feasibility of one-stage direct filtration. The problem of ineffective algae and particle removal is less pronounced in the case of conventional treatment given the presence of an additional particle removal barrier, available data on particle removal efficiency and the higher removal capabilities assumed in the Surface Water Treatment Rule-SWTR (2.5-log and 2.0-log removal of *Giardia* cysts for conventional treatment and direct filtration).

Although algae related problems are ubiquitous and of high significance, current knowledge and understanding of behavioral response of phytoplankton to different treatment techniques, are poorly developed. Similarly, little experience has been gained with experimental facilities and methodologies.

The Biesbosch water storage reservoirs, located in the central part of the Netherlands, account for more than half of the total amount of surface water used in the Netherlands for drinking water supply. Water delivered from these reservoirs is of an exceptionally high quality, and is in principle suitable for straightforward direct filtration (direct filtration without oxidative pre-treatment with ferric sulfate as sole coagulant), with an exception of short algal blooms in spring. The possible penetration of algae and other particles, particularly during short algal blooms in spring and late summer when the algal concentration exceeds several times the yearly average levels, together with the short filter runs during occasional intervals with very high concentration of zooplankton and filamentous algae, makes the application of direct filtration questionable. Currently, all the waterworks that use Biesbosch water for drinking water production apply conventional treatment, i.e. coagulation

and flocculation, followed by sedimentation or flotation and rapid sand filtration. Conventional treatment is regularly supported by granular activated carbon filtration and in some water treatment plants by ozone disinfection.

The aim of this study was to investigate the applicability of direct filtration as a single-stage process, or in combination with pre-treatment process(es) as an alternative to conventional treatment of Biesbosch water. The study attempts to increase the understanding of algal coagulation, flocculation and removal in direct filtration in order to allow significant improvement in the elimination efficiency of these micro-organisms in deep bed filtration.

9.2. Methodology and characterisation

Investigation presented in Chapter 3 indicate that extrapolation of the results from model studies applying algal cultures to natural conditions is highly questionable. A demonstrably better and feasible approach would be to use natural algae, from water bodies intended to be used as water source. The experimental difficulty due to their very low concentration for long periods of the year limits the opportunity to conduct experiments to short and unpredictable algae bloom periods. This can be solved by concentrating the algae in the water for the purpose of the experiments. The tangential flow filtration system equipped with a $0.45\ \mu\text{m}$ pore-size membrane efficiently recovers freshwater phytoplankton from large volumes of water. The procedure did not affect the algal properties that influence algal behaviour in water treatment processes. The tangential flow filtration system appear to be a useful laboratory tool for preparation of model waters which eliminates the problems associated with the use of cultured algae.

A batch set-up (a modified jar test apparatus) and a pilot plant set-ups (a bench scale direct filtration pilot plant and mobile automated direct filtration pilot plant) were developed and used for direct filtration modelling. It was found that those experimental set-ups are providing reliable and reproducible results of direct filtration performance, as well as good correlation with a larger scale unit (the automated mobile direct filtration pilot plant. In addition, a semi-batch and a continuous flow ozone reactor were developed for the pre-oxidation studies. These reactors are versatile, easy to use, allow a very precise determination of consumed ozone dosages, and also allow application of a combined chemical oxidation process (ozone + hydrogen peroxide).

Video technology (a video camera attached to an inverted microscope) can overcome shortcomings of conventional analytical techniques which are often lumping, physical and morphological characteristics, and provide greater and more detailed insight into the physical phytoplankton response to treatment conditions.

High resolution scanning electron microscopy that is able to examine fully hydrated material,

and consequently preclude preparation and observation artifacts, can be very useful to investigate in detail the effect of the different treatment steps on the algal cell architecture.

High particle concentrations (several hundreds of particles per ml) in the size range of cysts and oocysts of pathogenic microorganisms (3–20 μm) can be present in the filtrate of very low turbidity (≤ 0.10 FTU). In addition correlation between turbidity and particle count is poor at low turbidity levels (≤ 0.2 FTU). Therefore, in addition to turbidity, the particle concentration and size distribution measurement are more reliable indicators to establish the optimal treatment conditions and to assess treatment performance in a view of particle (*Giardia* cysts) removal requirements established in the SWTR. "Optimal" thus becomes a better defined and more focused concept. However, in many instances it appears that quality and treatment standards and norms are insufficiently developed when compared with the possibilities offered by the analytical methods. On the other hand, the proliferation of effluent characterisation parameters poses new problem to translate desired quality levels into more practical and operational guidelines

9.3. Agglomeration and optimization of direct filtration

Algal removal efficiency in straightforward direct filtration with Fe(III) as coagulant strongly varied with different algal species. An average overall algal biomass removal of 90% was achieved in this study. The most troublesome algal species to be eliminated were found to be the very small (e.g. μ -algae) and motile algae (like *R. minuta*). Although contribution of these algae to total algal biomass in raw water is small, they represent almost half of the algal biomass in the filtrate. The main cause of inefficient algae removal was poor agglomeration. The motility of numerous algal species (such as *R. minuta*, *Navicula* sp., *Cryptomonas* sp., *Chlamydomonas* sp., *Pandorina* sp., *Nitzschia*, etc.) was of decisive importance for their poor agglomeration and removal.

The three layer anthracite-sand-garnet filter media consistently produced filtrate of superior turbidity and residual iron in comparison with conventional anthracite-sand filter media. Anthracite-sand-garnet media only slightly improved particle removal during filter ripening period, and the beneficial effect diminished with the progress of filter run. In general anthracite-sand-garnet media ripened more rapidly than the dual media filter. Beneficial effect of three-layer media can be attributed to polishing effect of the fine garnet layer.

The optimal coagulant dosage and pH were closely correlated with the pre-treatment that precedes coagulation and the selected solid-liquid separation step. The optimal coagulation dosage for in-line direct filtration supported by oxidative pre-treatment (ozone or potassium permanganate) was considerably lower (4–6 times) than the coagulation dosage required for conventional treatment of the same water. The performance of direct filtration under the conditions investigated (coagulation with low dosage of Fe(III) coagulant, raw water with low

colloid and particle concentration) improved with an increase of pH. The optimum treatment performance in terms of filtrate turbidity, residual iron and particle concentration was achieved at $\text{pH} \geq 8.0$.

Straightforward direct filtration of Biesbosch water without additional pre- and/or post-treatment produces filtrate with higher turbidity, particle and algae concentration in comparison to conventional treatment. Consequently, it is questionable to promote this treatment as a viable alternative to conventional treatment for drinking water production from mesotrophic water. In order to be considered as a viable treatment option particle removal efficiency should be increased to at least 2-log removal units, in accordance with the direct filtration removal capacity assumed in the SWTR and corresponding to chlorophyll- α level in filtrate $\leq 0.1 \mu\text{g/l}$ (interim standard of the German Association of Drinking Water Reservoirs).

Plankton related problems could only be reduced if an appropriate pre-treatment precedes direct filtration:

- microstrainers applied as an initial treatment step extended short filter runs caused by zooplankton and large or filamentous algae;
- pre-oxidation with ozone or potassium permanganate enhanced particle and algae removal in direct filtration.

Pre-treatment with potassium permanganate, however, is associated with elevated residual manganese levels in the filtrate.

Pre-ozonation improved particle and algae removal in direct filtration by more than 1-log removal unit (from 90% to $>99\%$). An optimal ozone dosage exists that is correlated with algal concentration in raw water. A very short time interval between ozonation and coagulant addition (≤ 2 minutes) appeared to be of utmost importance to achieve high process performance. Pre-ozonation followed by direct filtration based on coagulation with Fe(III) coagulant and a small amount of cationic polymer ($\leq 1.0 \text{ mg Superfloc C573/l}$) provided practically complete particle and algae elimination. Filtration rates considerably higher than used in conventional plants (filtration rates up to 20 m/h tested) could be applied without adverse effect on filtrate quality.

Here, an alternative direct filtration process was developed that comprises pre-treatment with potassium permanganate, coagulation with ferric sulfate and Superfloc C573 as cationic polymer, and filtration through anthracite-sand-garnet filter media. The treatment distinctly improved particle and algae removal in comparison to efficiencies commonly achieved in direct filtration. Algae and particle removal efficiency $> 99\%$ is consistently achieved. The established procedure for determination of raw water permanganate demand and application of cationic polymer as a secondary coagulant, completely eliminated and the permanganate related drawbacks (MnO_2 passing the filter and pink colour of the water). This process is simple and does not require major investment costs.

9.4. Removal mechanisms

An overview of process mechanisms associated with the proposed direct filtration treatment scheme (direct filtration supported by microstraining and pre-oxidation), with possible negative effects is given in Fig. 9.1.

Very efficient removal of algae in direct filtration supported by pre-ozonation is a consequence of several process mechanisms. Pre-ozonation immobilizes motile algae, attacks and partly removes the organic coating on the algal surface, attacks sites on algal cell walls modifying their surface properties and provokes algae to secrete biopolymers. Subsequent addition of ferric sulfate and cationic polymers induce very efficient coagulation. This takes place simultaneously through sweep coagulation, and adsorption and charge neutralisation.

The efficient removal of algae and other particles, notably colloidal MnO_2 precipitates, in direct filtration supported by permanganate pre-oxidation and coagulation with ferric sulfate and cationic polymer, is suggested to be a consequence of several process mechanisms (Fig.9.2). Permanganate inactivates motile microorganisms, induces *in situ* production of natural, algae derived coagulant aid, oxidises organic matter and forms colloidal MnO_2 that adsorbs organic molecules that otherwise may hinder coagulation. MnO_2 precipitates accelerate the flocculation kinetics by increasing particle concentration. Furthermore, it induces direct, *in situ* particle agglomeration, even before coagulant addition. The fine organic meshes of filaments that are present in natural surface waters serve as nuclei for MnO_2 precipitation. They embed other MnO_2 colloids formed elsewhere in water as well as secreted algal biopolymers, algae and other natural colloidal and fine particulate matter. Subsequent coagulation at high pH with Fe(III) results in rapid formation of amorphous ferric hydroxide that partly covers algal cells. The cationic polymer induces adsorption and charge neutralisation-coagulation that further supports formation of agglomerates that are efficiently removed in anthracite-sand-garnet filter bed.

9.5. Direct filtration of Biesbosch reservoir water

Water from Petrusplaat, the last in the series of Biesbosch water storage reservoirs, meets most of water quality requirements that are suggested in the literature as required for successful of direct filtration. However, a high concentration of algae during the short spring blooms casts doubt on the process reliability. In addition the length of filter runs may be significantly reduced during occasional periods with high concentration of zooplankton and filamentous algae. From the previous conclusions, it can be derived that straightforward direct filtration without pre-treatment cannot be accepted as a reliable treatment alternative for drinking water production from Biesbosch water because of undesirable high concentration of algae in produced water and unacceptable particle removal efficiency.

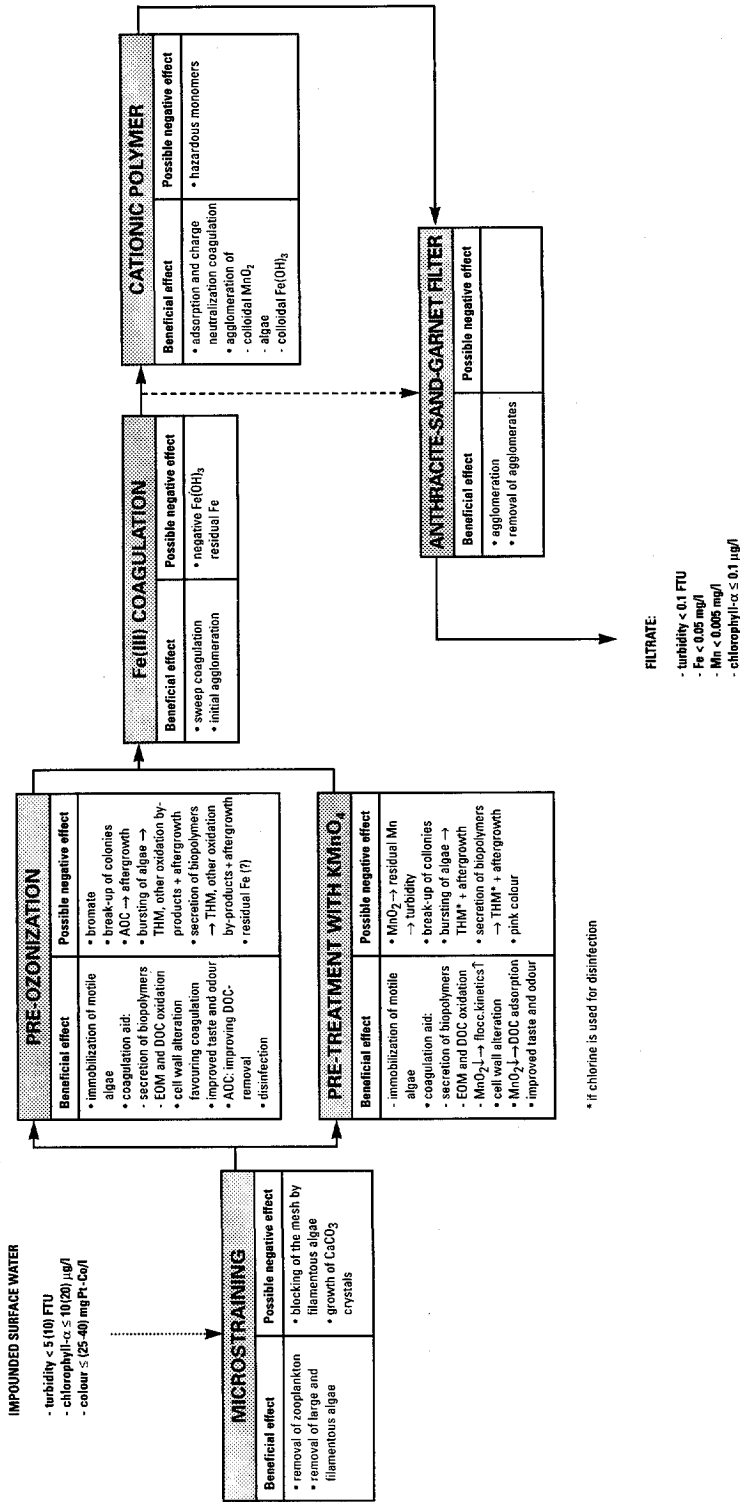


Fig. 9.1. Process mechanisms and possible side effects associated with direct filtration supported by microstraining, pre-oxidation and coagulation with ferric sulfate and cationic polymer.

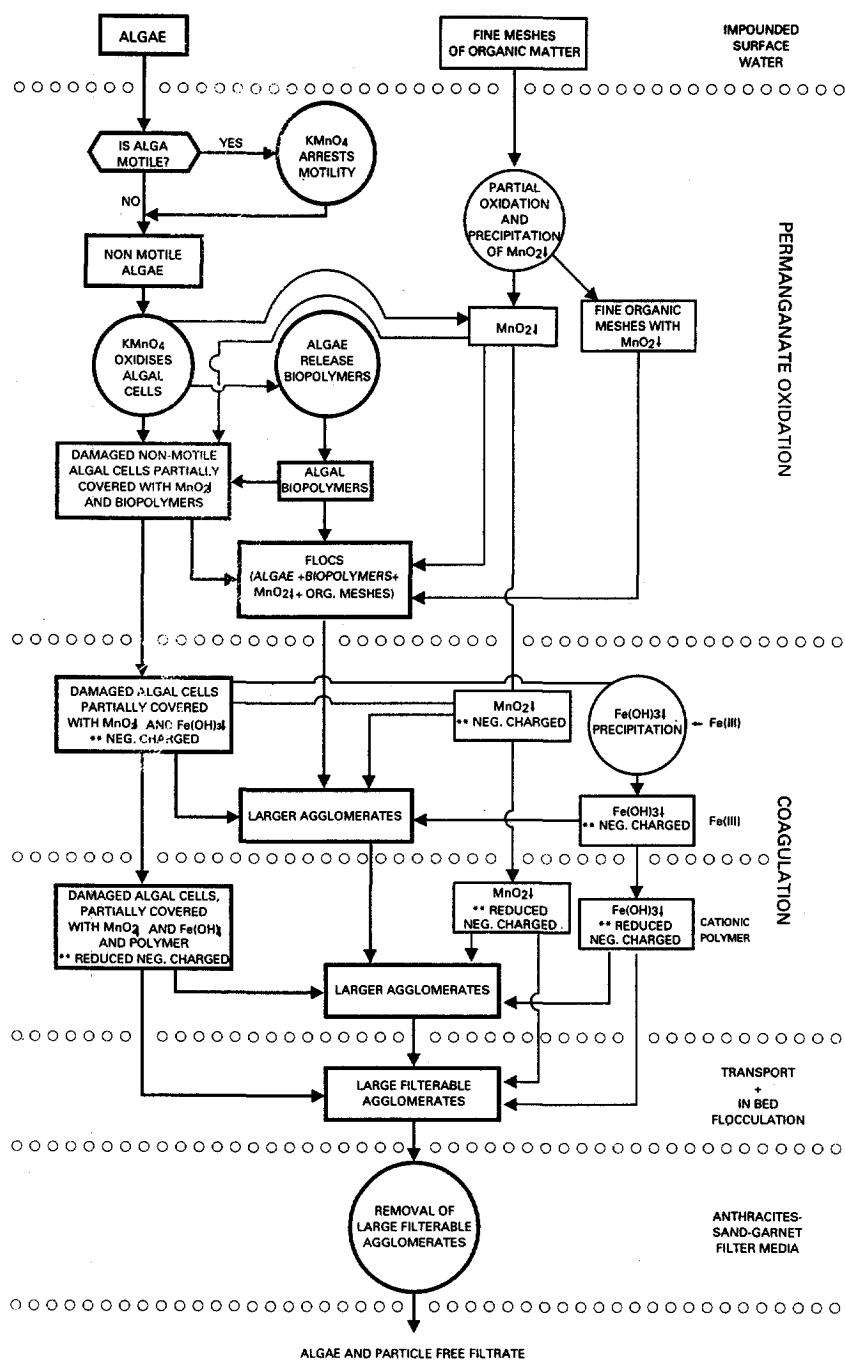


Fig.9.2. Diagram of the proposed conceptual model that describes algae removal in direct filtration supported by permanganate pre-treatment and coagulation with double coagulants.

However, in contrast to straightforward direct filtration, direct filtration of Biesbosch water supported by appropriate pre-treatment is very attractive alternative to conventional treatment of Biesbosch water. This would comprise microstraining, oxidation with ozone or potassium permanganate, and properly optimized coagulation and filtration through an anthracite-sand-garnet filter media.

The high concentration of zooplankton that commonly follows spring algal blooms, together with the common spring blooms of filamentous algae lead to the recommendation that the application of microstrainers as an initial treatment step is needed during certain periods of the year, and will substantially diminish problems of fast direct filter clogging.

Direct filtration that comprises pre-ozonation with $\leq 1.8 \text{ mgO}_3$ consumed/l, coagulation with 1.5 mg Fe(III)/l , and filtration through the anthracite-sand-garnet filter media (filtration rate of 10 m/h), produces filtrate of very high quality in reliable manner:

- turbidity $< 0.1 \text{ FTU}$,
- residual iron concentration $< 0.05 \text{ mg/l}$, and
- very low concentration (a few particles per ml) of particles $> 2.7 \mu\text{m}$.

In addition, very high particle ($> 2.7 \mu\text{m}$) removal was achieved, approximately 3-log removal, indicating that this treatment is likely also to be very efficient in removing *Giardia* cysts. Consequently, the capabilities of the established direct filtration treatment exceed the credits given to this treatment process in the SWTR (2-log removal), thus reducing the need for disinfection. Results obtained also indicate that the process can probably achieve equally high removal of *Cryptosporidium* oocysts.

The ozone dosage should be correlated with the algal concentration in Biesbosch water. In addition to chlorophyll- α , the particle count should be used as a indicator of algal concentration, to be routinely used to establish the required ozone dosage. The additional application of a cationic polymer (Superfloc C573) as a secondary coagulant in addition to ferric sulfate results in practically complete elimination of algae and other particles $> 1.0 \mu\text{m}$. In addition, filtration rates up to 20 m/h can be applied without adverse effect on filtrate quality.

Relatively low ozone dosages ($\leq 1.8 \text{ mgO}_3/\text{l}$) coupled with short contact time (2-3 minutes) were required to achieve ozone-related beneficial coagulation effects. This together with the results from the recent studies on bromate formation in Biesbosch water under different treatment conditions (Kruithof *et al.* 1995) indicate that bromate formed as a consequence of pre-ozonation will be below existing standards and probably below the detection limit ($2 \mu\text{g/l}$). Nevertheless, bromate issue as related to further direct filtration studies, should, in future, receive considerable attention, bearing in mind that much more rigorous bromate standards may be introduced (e.g. $0.5 \mu\text{g/l}$ proposed Dutch drinking water standard). In general two approaches may be followed to reduce or avoid bromate-related inconveniences: to introduce treatment conditions less favourable to bromate formation or to replace ozone with an other oxidant.

Potassium permanganate can be applied as an alternative pre-oxidant. The dosage should be defined by determining the actual Biesbosch water's permanganate demand. A dosage of 0.7 mg KMnO_4 , that corresponds to an average spring algal bloom (chlorophyll- $\alpha \approx 10 \mu\text{g/l}$), is sufficient to improve direct filtration efficiency (on average 50% reduction of algal concentration in filtrate). Application of cationic polymer ($\leq 1.0 \text{ mg/l}$) as a secondary coagulant in addition to 1.5 mg Fe(III)/l is required to eliminate permanganate related drawbacks, notably increased residual manganese and elevated filtrate turbidity, and to further improve treatment performance. Treatment consisting of pre-oxidation with 0.7 mg KMnO_4/l , coagulation with 1.5 mg Fe(III)/l and less than 1.0 mg/l of cationic polymer (C-573), and filtration through anthracite-sand-garnet filter media, produces filtrate of exceptionally high quality:

- turbidity $\leq 0.06 \text{ FTU}$,
- residual $\text{Fe} < 0.05 \text{ mg/l}$
- residual $\text{Mn} < 5 \mu\text{g/l}$, and
- very low particle and algae concentration ($< 10 \text{ particles/ml}$), corresponding to particle removal efficiency of more than 2-log removal unit.

In comparison to current full scale conventional treatment of Biesbosch water, direct filtration supported by ozone or permanganate pre-treatment achieves comparable or higher particle and turbidity removal with 4 to 6 times lower coagulant dosages, and with a higher degree of reliability (unaffected by algal blooms).

Expected removal efficiencies for turbidity, particle and algae in conventional treatment (coagulation, flocculation, sedimentation, dual-media filtration) and different direct filtration treatment schemes is given in Fig. 9.3.

Direct filtration should be considered only as a part of a treatment scheme for drinking water production. It should be typically followed by (biological) granular activated carbon filtration (to reduce concentration of pesticides, other micropollutants, assimilable organic carbon - AOC and dissolved organic matter). In addition, a certain level of disinfection may be needed as a function of raw water quality and actual plant elimination capacity. Slow sand filtration may be considered as the last polishing treatment step (if the site and financial considerations allow), that in addition to its disinfection capacity may introduce several other benefits like production of biologically stable water, providing an extra barrier for removal of oocyst and cyst pathogenic microorganisms like *Cryptosporidium* and *Giardia*, and an efficient additional barrier for zooplankton and other higher organisms that commonly grow in activated carbon filters and may enter drinking water etc.

Recent developments in the field of membrane filtration in addition suggest that this process may in (near) future become a very attractive alternative to current post-treatment. Direct filtration can in that case be considered as an appropriate process to precede membrane filtration.

| Optimized process conditions | | TREATMENT PROCESS | | | | |
|--------------------------------|---|-------------------|---------------------------------------|--|--|---|
| | | Conventional* | DIRECT FILTRATION | | | |
| | | | Fe(III) + Dual-layer filtration | Fe(III) + Three-layer filtration | Pre-oxidation + Fe(III) + Three-layer filtration | Pre-oxidation + Fe(III) + cat. polymer + Three-layer filtration |
| Fe(III) mg/l | | 6.0 - 8.0 | 1.0 - 1.5 | 1.0 - 1.5 | 1.0 - 1.5 | 1.0 - 1.5 |
| pH | | 7.0 - 7.5 | 8.0 - 8.3 | 8.0 - 8.3 | 8.0 - 8.3 | 8.0 - 8.3 |
| cationic polymer (mg/l) | | — | — | — | — | < 1.0 |
| O ₃ (mg/l) | | — | — | — | 1.0 - 1.8 | 1.0 - 1.8 |
| or KMnO ₄ (mg/l) | | — | — | — | — | < 0.7 |
| Flocculation: | | | | | | |
| G (s ⁻¹) | | 20 - 80 | — | — | — | — |
| T (min) | | 20 - 40 | — | — | — | — |
| Mineral particles | | | | | | |
| Turbidity | | | | | | |
| A L G A E | Motile | | | | | |
| | Very small non-motile algae (< 4.0 µm) | | | | | |
| | Non-motile algae (> 4.0 µm) | | | | | |
| Cryptosporidium oocysts* | | | | | | |
| Giardia cysts** | | | | | | |

REMOVAL EFFICIENCY

| | |
|--|---------------------------|
| | poor removal (<70%) |
| | moderate removal (70-95%) |
| | excellent removal (>95%) |

* assumption based on measured particle removal efficiencies
 ** for conventional treatment based on SWTR;
 for direct filtration assumption based on measured particle removal efficiencies

Fig. 9.3. Expected removal of turbidity, mineral particles, algae, oocysts and cysts in conventional treatment and different direct filtration treatment schemes.

Samenvatting

Petruševski B. (1996). *Algae and particle removal in direct filtration of Biesbosch water*. Doctoraatsthesis, International Institute for Infrastructural, Hydraulic & Environmental Engineering (IHE), Technische Universiteit Delft (TUD), 1996, Delft, Nederland, 214 pagina's.

Vlokkingsfiltratie is om economische redenen en vanuit milieutechnisch oogpunt een aantrekkelijk alternatief voor de conventionele behandelingswijze van voorbezonken oppervlaktewater, tenminste als de waterbron van geschikte kwaliteit is: Laag in troebelheid, zwevend stof gehalte, kleur en opgelost organische stofgehalte. Echter vlokkingsfiltratie heeft een beperkt verwijderingsrendement op zwevende deeltjes en algen. Algen aanwezig in het drinkwater kunnen aanleiding geven tot diverse problemen, zoals de vorming van gevaarlijke gechloreerde bijproducten, een negatieve beïnvloeding van smaak en reuk, nagroei in het leidingwerk etc. De aanwezigheid van algen in het drinkwater is ook een indicatie dat andere, mogelijk pathogene micro-organismen met afmetingen min of meer gelijk aan die van algen onvoldoende door het behandelingsproces verwijderd worden (zoals bijvoorbeeld *Cryptosporidium* oocysts en *Giardia* cyst). Door het doorslaan van algen en andere deeltjes wordt de haalbaarheid van vlokkingsfiltratie in twijfel getrokken.

Ofschoon de aan algen gerelateerde problemen alomtegenwoordig en van grote betekenis zijn, is de kennis van het gedrag van phytoplankton in de verschillende zuiveringstechnieken maar matig ontwikkeld. Bovendien is weinig informatie beschikbaar over de toe te passen onderzoeksmethoden en faciliteiten.

De Biesbosch-bekkens voorzien in meer dan helft in de totale hoeveelheid oppervlaktewater voor rechtstreeks drinkwaterproductie in Nederland. Het water afkomstig van de bekken is van uitzonderlijke hoge kwaliteit en is in principe geschikt voor vlokkingsfiltratie, met uitzondering van korte periodes van algenbloei. Het mogelijk doorbreken van algen en andere deeltje, met name tijdens de periodes van algenbloei, en de korte filterslooptijden tijdens periodes met zeer hoge concentraties van zooplankton en draadvormige algen, stellen vraagtekens bij de geschiktheid van vlokkingsfiltratie. Alle drinkwaterproductiebedrijven die Biesbosch water gebruiken, passen conventionele zuiveringstechnieken.

Het doel van deze studie was de toepasbaarheid van vlokkingsfiltratie als afzonderlijk of in combinatie met een voorbehandeling te onderzoeken als alternatief voor de conventionele behandeling van Biesbosch water. De studie poogt het inzicht te vergoten in coagulatie, flocculatie en verwijderingsredement van deze micro-organismen in vlokkings filtratie aanzienlijk te verbeteren.

Een batch opstelling, aangepaste apparatuur voor bekerproeven en een pilot plant opstelling zijn ontwikkeld en gebruikt voor vlokingsfiltratie. Verder zijn een semi-batch en een continue stroom ozon reactor ontwikkeld en ingezet in zgn. voor-oxidatie studies. Innovatieve procedures werden geïntroduceerd voor de bereiding van model water, gebaseerd op het concentratie van algen in een natuurlijke waterstroom met behulp van een membraan microfiltratie systeem met tangentele stroming. Om de tekortkomingen van de conventionele waterkwaliteits analyse te omzeilen en om meer inzicht te krijgen in het gedrag van phytoplankton tijdens de behandeling, is een video systeem gebruikt voor in situ observatie waarbij de videocamera gekoppeld werd aan een microscoop. Het effect van oxidatiemiddelen op de morfologie van algen is onderzocht met een hoge resolutie scanning elektronen microscoop.

Het algenverwijderingsredement in vlokingsfiltratie varieert sterk voor verschillende algen soorten tussen 5 en 100%). Gemiddeld is een verwijderingsredement van 90% bereikt tijdens deze studie. Onvoldoende uitvlokking wordt als hoofdoorzaak voor het slechte verwijderingsredement gezien. De slechte uitvlokking en verwijdering werd met name door beweeglijkheid van de talrijke algen soorten veroorzaakt.

Problemen die verband hielden met plankton konden allen verminderd worden indien een geschikte voorbehandeling werd ingezet. Korte filterlooptijd, veroorzaakt door zooplankton en grote draadvormige algen konden worden vermeden door het inzetten van microzeven. Voor-oxidatie met ozon of kaliumpermanganaat gaf een verbetering van deeltjes en algenverwijdering in de vlokingsfiltratie.

Voor-oxidatie verbeterde de verwijdering van deeltjes en algen in de vlokingsfiltratie met meer dan 1.0-log verwijderings eenheid (verbetering van 90% naar 99.7%). Een optimale ozondosering is gecorreleerd aan de algenconcentratie in het ruwe water. Relatief lage ozondosering ($\leq 1.8 \text{ mgO}_3/\text{l}$) in combinatie met een korte contacttijd (2-3 minuten) bleken voldoende voor een gunstige coagulatie van het Biesbosch water.

In deze studie werd een alternatief ontwikkeld bestaande uit voorbehandeling met kalium permanganaat, coagulatie met ijzersulfaat en kationisch polymeer Superfloc C573 en filtratie door een antraciet-zand-granaatzand filter medium. Deze behandeling verbeterde duidelijk de deeltjes en algen verwijdering in vergelijking tot gebruikelijke verwijderingsredement verkregen met vlokingsfiltratie. Algen- en deeltjesverwijderingsredementen van groter dan 99% werden bij voortdurend bereikt. De nadelen van het gebruik van permanganaat namelijk doorbreken van MnO_2 colloïden en roze kleuring van het effluent worden compleet geëlimineerd. Ontwikkeld proces is eenvoudig en vereist geen hoge investeringskosten.

Het hoge verwijderingsredement van algen is een gevolg van verschillen procesmechanismen waaronder de immobilisatie van beweeglijke algen, de verwijdering van de organische coating op de algen, het loskomen van biopolymeren van de algen en gelijktijdige coagulatie door sweep coagulatie and adsorptie en ladingneutralisatie.

Vlokingsfiltratie ondersteund met een voorbehandeling met ozone of kaliumpermanganate, coagulatie met ijzersulfaat en kationisch polymer en filtratie over een antraciet-zand-granaatzand filter bed is een levensvatbaar en economisch aantrekkelijk alternatief voor de conventionele behandeling van Biesbosch water.

Curriculum Vitae

Branislav Petruševski was born in Skopje, Yugoslavia on August 19, 1956. After primary school and gymnasium in Beograd, Yugoslavia, he received a B. Sc. degree in Civil Engineering in 1981 from University of Beograd.

After graduation he joined Energoprojekt, the largest Yugoslav consulting and contracting company where he worked till 1990. There he started his career as an assistant design engineer and advanced to a position of a project manager with full responsibility for overall realisation of different sanitary engineering projects. While there, he was involved in excess of twenty international and national projects of great variety: water treatment plants, conveyance systems, regional and rural water supply and environmental management projects.

In 1985 he came to the Netherlands to the International Institute for Infrastructural, Hydraulic and Environmental Engineering (IHE), Delft, where he obtained the post-graduate diploma in sanitary engineering with distinction in 1986. After six months research work in the field of water treatment at KIWA Research and Consultancy, the Netherlands he obtained M. Sc. degree with distinction in Environmental Engineering from IHE Delft.

From November 1990 till March 1995 he worked at the Delft University of Technology, Faculty of Civil Engineering, Laboratory for Sanitary Engineering, and the IHE Delft on the joint research project "Direct filtration of impounded surface water".

In April 1995 he joined the engineering and consulting company Stork Comprimo, Amsterdam where he is currently working as a water treatment consultant.



The aim of the International Institute for Infrastructural, Hydraulic and Environmental Engineering, IHE, is to transfer scientific knowledge and technological know-how related to transport, water and the environment to professionals, especially from developing countries.

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